Antiferrodistortive phase transition in Pb(Ti$_{0.48}$Zr$_{0.52}$)O$_3$: Space group of the lowest temperature monoclinic phase

D. M. Hatch and H. T. Stokes

Department of Physics and Astronomy, Brigham Young University, Provo, Utah 84602

Rajeev Ranjan, Ragini, S. K. Mishra, and Dhananjai Pandey

School of Materials Science and Technology, Institute of Technology, Banaras Hindu University, Varanasi 221005, India

Brendan J. Kennedy

School of Chemistry, The University of Sydney, Sydney, New South Wales 2006, Australia

Ranjan *et al.* [Phys. Rev. B **65**, 060102(R) (2002)] have recently presented results of a powder neutron-diffraction study of the high-temperature monoclinic (F_M^{HT}) to low-temperature monoclinic (F_M^{LT}) phase transition in Pb(Ti$_{1-x}$Zr$_x$)O$_3$ discovered by Ragini *et al.* [Phys. Rev. B **64**, 054101 (2001)]. They attribute the presence of superlattice reflections in the diffraction data to tilting of oxygen octahedra and propose a monoclinic space group Pc for the F_M^{LT} phase. It is shown that for the model proposed by Ranjan *et al.*, the correct space group of the F_M^{LT} phase should be Cc. This has also been corroborated by a group-theoretical approach to the problem. A different set of refined structural parameters for the Cc space group obtained from the Rietveld analysis of the powder neutron-diffraction data of Ranjan *et al.* is also presented.

Recently Noheda *et al.* studied the well-known solid solution Pb(Ti$_{1-x}$Zr$_x$)O$_3$ (PZT) piezoelectric ceramic using high-resolution synchrotron x-ray data.[1,2] They showed that the tetragonal phase (F_T) of PZT for $x=0.500$ and 0.520 transforms to a monoclinic Cm phase (F_M^{HT}) at 200 and 250 K, respectively. Ragini *et al.*[3] presented evidence based on electron-diffraction data for yet another low-temperature phase transition from the monoclinic Cm phase to another monoclinic phase (F_M^{LT}) in which the c parameter is doubled. Superlattice reflections characteristic of c parameter doubling are seen in the electron-diffraction data but were not discernible in the synchrotron x-ray diffraction data of Noheda *et al.* The presence of two transitions (i.e., from F_T to F_M^{HT} and F_M^{HT} to F_M^{LT}) were also confirmed in the physical properties measurements by Ragini *et al.* (dielectric and resonance frequency measurements) which showed anomalies at two different temperatures. Very recently, Ranjan *et al.*[4] presented powder neutron-diffraction data for $x=0.520$ in the temperature range 280 K–10 K and confirmed the appearance of superlattice reflections corresponding to the F_M^{HT} to F_M^{LT} phase transition below 210 K. These superlattice reflections cannot be accounted for by the Cm space-group proposed by Noheda *et al.* This caused Ranjan *et al.* to propose a different space-group symmetry.

Ranjan *et al.* motivated their selection of the F_M^{LT} structure based upon the experience with superlattice reflections in the ABO$_3$ perovskite family. Familiar perovskites such as SrTiO$_3$, LaAlO$_3$, and KMnF$_3$ undergo transitions in which the antiferrodistortive transitions involve octahedral tilts brought about by instabilities at the $R(q=\frac{1}{2},\frac{1}{2},\frac{1}{2})$ and $M(q=\frac{1}{2},\frac{1}{2},0)$ points of the cubic Brillouin zone.[5] From the specific superlattice reflections in their data, Ranjan *et al.* inferred that the F_M^{HT} to F_M^{LT} transition involved an antiphase tilting of octahedra driven by an R-point instability.

Ranjan *et al.* proposed a simple model for visualizing the structure of the F_M^{LT} phase. In this model, they considered the stacking of two monoclinic cells of the Cm type in the [001] direction. Then they introduced an R-point instability of the form[5] $a^0 a^0 c^-$, doubling the c parameter. They argue, because of such an antiphase tilt about the [001] direction, the C centering and mirror planes of the Cm space-group are destroyed, resulting in the space-group symmetry Pc. The Pc space-group possesses 27 refinable positional coordinates and 10 refinable thermal parameters, but in keeping with the physically intuitive model for the F_M^{HT} to F_M^{LT} phase transition, Ranjan *et al.* carried out a constrained Rietveld refinement involving only six/seven (model-I/model-II of Ranjan *et al.*) independently refinable positional coordinates and four isotropic thermal parameters. While their Rietveld refinement with the Pc space-group yields a reasonable fit to their neutron-diffraction data, we show here that the correct space group corresponding to the model used for the constrained refinement is actually Cc and not Pc.

It is clear from both Fig. 2 and Table I of Ranjan *et al.* that the pairs of oxygen atoms O(3)-O(5$'$), O(4)-O(6$'$), O(5)-O(3$'$), O(6)-O(4$'$) are related through a translation of $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. Similarly there is a pair of oxygen atoms near the origin and the body-centered position of the Pc unit cell. Likewise is the case for the Zr/Ti and Pb atoms inside the unit-cell of the Pc space group. Hence the monoclinic cell chosen by Ranjan *et al.* is in fact a body-centered cell and not primitive. With a new choice of unit cell axes, the correct space-group becomes Cc. Taking the b axis as the unique axis, the unit cell axes of the Cc and Pc space-groups are related as $\mathbf{a}_C=\mathbf{a}_P+\mathbf{c}_P$, $\mathbf{b}_C=\mathbf{b}_P$, $\mathbf{c}_C=-\mathbf{a}_P$, where the subscripts P and C refer to the unit cells of the Pc and Cc space-groups, respectively. It is important to emphasize that the C centered unit cell of the F_M^{LT} phase is different from the C centered unit cell of the F_M^{HT} phase proposed by Noheda

TABLE I. Refined structural parameters and R factors of Pb($Zr_{0.48}Ti_{0.52}$)O_3 at 10 K with Cc space-group. Lattice parameters: $a = 9.9948(8)$ Å, $b = 5.7093(6)$ Å, $c = 5.7312(7)$ Å, $\beta = 124.51(1)°$. R factors: $R_B = 4.01$, $R_p = 6.78$, $R_{wp} = 8.64$, $R_e = 7.84$.

Atoms	x	y	z	$B(\text{Å}^2)$
Pb	0.00	0.75	0.00	1.0(1)
Zr/Ti	0.216(2)	0.25	0.197(4)	0.5(3)
O1	−0.044(1)	0.25	−0.092(3)	0.9(2)
O2	0.196(1)	0.483(1)	−0.093(2)	0.7(1)
O3	0.196(1)	0.017(1)	0.407(2)	0.7(1)

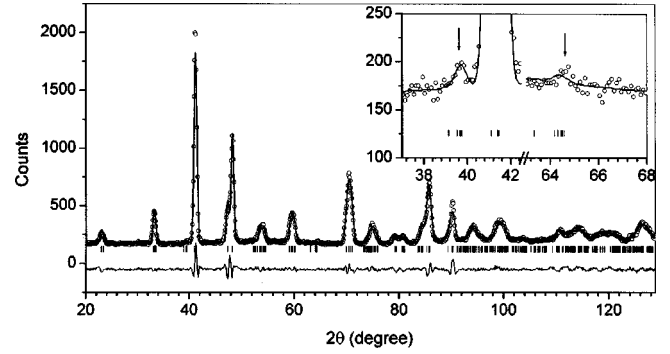

FIG. 1. Observed (open circles), calculated (solid lines), and difference (lines at the bottom of the figure) powder neutron-diffraction patterns of Pb($Ti_{0.48}Zr_{0.52}$)O_3 at 10 K. Inset depicts the observed and calculated profiles for the superlattice reflections (marked with arrows).

et al. Two of the axes of the monoclinic unit cells for both the space-groups are along $\langle 110 \rangle$ directions of the elementary ABO_3 perovskite cell. However, the third axis for the Cc case is along $\langle 112 \rangle$ of the elementary perovskite cell whereas it is parallel to $\langle 100 \rangle$ for the Cm

For the Rietveld refinement of the F_M^{LT} phase, Ranjan *et al.* have considered two slightly different models. In model I, the x,y components of the fractional displacements of the four oxygen atoms 3, 4, 5, 6 at $z = 1/4$ (Fig. 2 of Ranjan *et al.*) from their ideal perovskite positions were assumed to be identical. In model II, the x,y components of the fractional displacements were considered to be different. Refinement with model II led to nearly equal values of the positional coordinates as obtained by Noheda *et al.* for all the positional coordinates of atoms except the y coordinates of the planar oxygen atoms (3, 4, 5 and 6 of Fig. 2 of Ranjan *et al.*) In the present work, we have, therefore, refined the structure of the F_M^{LT} phase using model II of Ranjan *et al.* taking Cc as the correct space-group. The coordinates given in the *International Tables for Crystallography* for the $C1c1$ space group[6] correspond to the choice of origin in the c glide plane. This origin is shifted through $-\frac{1}{4}\mathbf{b}_P$ with respect to the origin of the Pc unit cell shown in Fig. 2 of Ranjan *et al.*

The Cc space-group has only one Wyckoff site symmetry 4(a) with general coordinates. The unit cell consists of four molecules of Pb($Zr_{0.52}Ti_{0.48}$)O_3, and the asymmetric unit of the structure consists of five atoms: one Pb at 0.00, 0.75, 0.00, one Zr/Ti at $0.25 + \delta x_{Ti}$, $0.25 + \delta y_{Ti}$, $0.25 + \delta z_{Ti}$, and three oxygen atoms, O1 at $0.00 + \delta x_{O1}$, $0.25 + \delta y_{O1}$, $0.00 + \delta z_{O1}$, O2 at $0.25 + \delta x_{O2}$, $0.50 + \delta y_{O2}$, $0.00 + \delta z_{O2}$, and O3 at $0.25 + \delta x_{O3}$, $0.00 + \delta y_{O3}$, $0.50 + \delta z_{O3}$. The various δ's represent the refinable parameters. In keeping with the structural model used by Ranjan *et al.*, Pb was fixed at 0.00, 0.75, 0.00, and $\delta y_{Ti} = \delta y_{O1} = 0$. Also, as per model II of Ranjan *et al.*, $\delta x_{O2} = \delta x_{O3}$, $\delta y_{O2} = -\delta y_{O3}$, and $\delta z_{O2} = \delta z_{O3}$. Thus out of the 15 positional coordinates for the asymmetric unit, only seven are independent and were considered for refinement. The refinement converged smoothly within a few cycles with reasonably good R factors. Subsequently, we removed the constraints and refined all 12 positional coordinates independently as allowed by the space-group Cc, but no significant improvement resulted. The weighted R factor decreased only marginally from 8.64 for the constrained model to a value of 8.55 for the unconstrained refinement.

Also the refined parameters were found to be identical within their respective estimated standard deviations. This indirectly validates the model proposed by Ranjan *et al.* Table I lists the various refined structural parameters along with the R factors for model II of Ranjan *et al.* It is worth mentioning that $\chi^2 = (1.21)$ for the Cc space-group is comparable to $\chi^2 = (1.20)$ for the Pc space group obtained from the same data in Ref. 4. The new set of values of the positional coordinates given in Table I matches very well (after using the coordinate transformation) with those obtained by Ranjan *et al.* Figure 1 depicts the observed, calculated and the difference plots after the completion of the refinement for model II.

The software package[7] ISOTROPY allows us to discuss the sequence of transitions included in the paper by Ranjan *et al.* in terms of irreducible displacement modes. The onset of ferroelectric polarization transforms under $Pm\bar{3}m$ as the components of the Γ_4^- irreducible representation (IR). (We use the IR notation of Miller and Love[8]). Depending upon the direction of the polarization, several phases can result. As can be seen from ISOTROPY, the subgroups and polarization directions allowed by just polarization onset are $P4mm,(a,0,0)$; $Amm2,(a,a,0)$; $R3m,(a,a,a)$; $Pm,(a,b,0)$; $Cm,(a,a,b)$; and $P1,(a,b,c)$. Some of these subgroup structures are the phases represented in Fig. 1 of Noheda *et al.*[2]. The $Cm(F_M^{LT})$ structure of PZT corresponds to the polarization direction (a,a,b) with components of equal magnitude along x and y and a different magnitude along z.

Antiphase tilting of oxygen octahedra transforms under $Pm\bar{3}m$ as the components of the R_4^+ IR.[5,9,10] Using ISOTROPY to couple the Γ_4^- and R_4^+ IR's, we obtain three possible antiphase tilt systems that can combine with the Cm ferroelectric structure: $a^-a^-c^0$, $a^-a^-c^-$, $a^-b^-c^-$, which result in space-groups Cm, Cc, $P1$, respectively. The tilt system we are seeking is thus $a^-a^-c^-$. A single antiphase tilt $a^0a^0c^-$ along the c direction of the Cm phase considered by Ranjan *et al.* is sufficient to reduce the symmetry to Cc, but the Cc symmetry also allows tilts in the ab plane to appear. From ISOTROPY we obtain for Cc the lattice vectors

$(-1,-1,-2)$, $(-1,1,0)$, $(1,1,0)$ and origin $(-\frac{1}{2},0,-\frac{1}{2})$, in terms of the cubic $Pm\overline{3}m$ coordinates.

To summarize, we have revisited the space-group of the F_M^{LT} phase of PZT as per the model proposed by Ranjan *et al.* The correct space-group for this model is Cc and not Pc.

This space-group is consistent with the group theoretical treatment for the antiphase tilting of oxygen octahedra in the $Pm\overline{3}m$ paraelectric phase. We have presented the results of Rietveld refinement of the F_M^{LT} phase for the correct space-group Cc using powder neutron-diffraction data.

[1] B. Noheda, D.E. Cox, G. Shirane, J.A. Gonzalo, L.E. Cross, and S.E. Park, Appl. Phys. Lett. **74**, 2059 (1997).

[2] B. Noheda, D.E. Cox, G. Shirane, R. Guo, B. Jones, and L.E. Cross, Phys. Rev. B **63**, 014103 (2000).

[3] Ragini, S.K. Mishra, D. Pandey, H. Lemmens, and G. VanTendeloo, Phys. Rev. B **64**, 054101 (2001).

[4] R. Ranjan, Ragini, S.K. Mishra, D. Pandey, and B.J. Kennedy, Phys. Rev. B **65**, 060102 (2002).

[5] A.M. Glazer, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. **B28**, 3384 (1972); Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr. **A31**, 756 (1975).

[6] *International Tables for Crystallography*, edited by T. Hahn (Kluwer Academic, Boston, 1992).

[7] H.T. Stokes and D. M. Hatch, computer code ISOTROPY (Brigham Young Univ., Provo, UT, 2000), software and documentation is available over the Internet at www.physics.byu.edu/~stokesh/isotropy.html

[8] S.C. Miller and W.F. Love, *Tables of Irreducible Representations of Space Groups and Co-Representations of Magnetic Space Groups* (Pruett, Boulder, 1967); A.P. Cracknell, B.L. Davis, S.C. Miller, and W.F. Love, *Kronecker Product Tables* (Plenum, New York, 1979), Vol. 1.

[9] D.M. Hatch and H.T. Stokes, Phys. Rev. B **35**, 8509 (1987); D.M. Hatch, H.T. Stokes, K.S. Aleksandrov, and S.V. Misyul, *ibid.* **39**, 9282 (1989).

[10] C.J. Howard and H.T. Stokes, Acta Crystallogr., Sect. A: Found. Crystallogr. **B54**, 782 (1998).