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

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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$_{MT}$) to low-temperature monoclinic (F$_{LT}$) 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$_{LT}$ phase. It is shown that for the model proposed by Ranjan et al., the correct space group of the F$_{LT}$ 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.

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Ranjan et al. proposed a simple model for visualizing the structure of the F$_{LT}$ phase. In this model, they considered the stacking of two monoclinic cells of the CMS type in the [001] direction. Then they introduced an R-point instability of the form $a^0a^0c^-$, doubling the c parameter. They argue, because of such an antiphase tilt about the [001] direction, the C centering and mirror planes of the CMS 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$_{MT}$ to F$_{LT}$ 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 $a_c = a_p + c_p$, $b_c = b_p$, $c_c = -a_p$, 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$_{MT}$ phase is different from the C centered unit cell of the F$_{LT}$ phase proposed by Noheda...
TABLE I. Refined structural parameters and R factors of Pb(Zr$_{0.52}$Ti$_{0.48}$)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, $\beta = 124.51(1)^\circ$. R factors: $R_h = 4.01$, $R_p = 6.78$, $R_{wp} = 8.64$, $R_e = 7.84$.

<table>
<thead>
<tr>
<th>Atoms</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>B(Å$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>0.00</td>
<td>0.75</td>
<td>0.00</td>
<td>1.0(1)</td>
</tr>
<tr>
<td>Zr/Ti</td>
<td>0.216(2)</td>
<td>0.25</td>
<td>0.197(4)</td>
<td>0.5(3)</td>
</tr>
<tr>
<td>O1</td>
<td>-0.044(1)</td>
<td>0.25</td>
<td>-0.092(3)</td>
<td>0.9(2)</td>
</tr>
<tr>
<td>O2</td>
<td>0.196(1)</td>
<td>0.483(1)</td>
<td>-0.093(2)</td>
<td>0.7(1)</td>
</tr>
<tr>
<td>O3</td>
<td>0.196(1)</td>
<td>0.017(1)</td>
<td>0.407(2)</td>
<td>0.7(1)</td>
</tr>
</tbody>
</table>

et al. Two of the axes of the monoclinic unit cells for both the space-groups are along (110) directions of the elementary ABO$_3$ perovskite cell. However, the third axis for the Cc case is along (112) of the elementary perovskite cell whereas it is parallel to (100) for the Cm.

For the Rietveld refinement of the $F^{LT}_M$ 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 $F^{LT}_M$ 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 $\frac{1}{2}$b, with respect to the origin of the Pm3m unit cell shown in Fig. 2 of Ranjan et al. The Cc space-group has only one Wyckoff site symmetry 4(a) 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 $\delta$’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 Pm3m 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 Pm3m as the components of the $\Gamma_4^+$ 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,a,0); Amm2, (a,a,a); 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($F^{LT}_M$) structure of PZT corresponds to the polarization direction (a,b,c) with components of equal magnitude along x and y and a different magnitude along z.

Antiphase tilting of oxygen octahedra transforms under Pm3m as the components of the $\Gamma_4^+$ IR.$^3,9,10$ Using ISOTROPY to couple the $\Gamma_4^+$ and $\Gamma_4^\pm$ IR’s, we obtain three possible antiphase tilt systems that can combine with the Cm ferroelectric structure: a’ a c’ 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’0 a0 c’ 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

FIG. 1. Observed (open circles), calculated (solid lines), and difference (lines at the bottom of the figure) powder neutron-diffraction patterns of Pb(Ti$_{0.52}$Zr$_{0.48}$)O$_3$ at 10 K. Inset depicts the observed and calculated profiles for the superlattice reflections (marked with arrows).
To summarize, we have revisited the space-group of the \( F_{MT} \) 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 \( Pm\tilde{3}m \) paraelectric phase. We have presented the results of Rietveld refinement of the \( F_{MT} \) phase for the correct space-group \( Cc \) using powder neutron-diffraction data.