

Comparison of the Cc and $R3c$ space groups for the superlattice phase of $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$

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Recent controversy about the space group of the low temperature superlattice phase of $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ is settled. It is shown that the $R3c$ space group for the superlattice phase cannot correctly account for the peak positions of the superlattice reflections present in the neutron diffraction patterns. The correct space group is reconfirmed to be Cc . A comparison of the atomic coordinates of Cc and Cm space groups is also presented to show that in the absence of superlattice reflections, as is the case with x-ray diffraction data, one would land up in the Cm space group. This superlattice phase is found to coexist with another monoclinic phase of the Cm space group.

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I. INTRODUCTION

Ever since its discovery, the perovskite lead zirconate titanate $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ (PZT) has remained by far the most widely used piezoelectric ceramic material for transducer and actuator applications.¹ Recently, Noheda *et al.*^{2,3} showed that the tetragonal compositions with $x=0.50, 0.51, \text{ and } 0.52$ transform to a monoclinic phase with Cm space group. In a subsequent comprehensive study of the temperature dependence of the piezoelectric resonance frequency, dielectric constant, and crystal structure using x-ray, electron, and neutron diffraction data, Ragini *et al.*⁴ and Ranjan *et al.*⁵ discovered yet another low temperature monoclinic phase, which is a superlattice of the Cm phase discovered earlier by Noheda *et al.*² It was also shown that this superlattice phase results from an antiferrodistortive phase transition involving antiphase tilting of oxygen octahedra in the Cm phase⁵ and its space group is Cc .⁶ The discovery of this superlattice phase has necessitated further modifications of the PZT phase diagram as given in Ref. 7. Recently, Frantti *et al.*,⁸ while confirming the reports by Ranjan *et al.*⁵ about the appearance of a superlattice phase of PZT using powder neutron diffraction data, have proposed $R3c$ space group for this phase in analogy with the $R3m$ to $R3c$ transition⁹ on the Zr-rich side of the morphotropic phase boundary (MPB) in PZT. These workers have also proposed that this $R3c$ superlattice phase coexists with the monoclinic Cm phase discovered earlier by Noheda *et al.*² On the other hand, Noheda *et al.*¹⁰ carried out a TEM study of the low temperature transitions in PZT with $x=0.520$ and confirmed the findings of Ragini *et al.*⁴ about the appearance of a superlattice phase and proposed the same space group (Cc), which was earlier established by Hatch *et al.*⁶ However, according to Noheda *et al.*,¹⁰ the superlattice phase with the Cc space group is a minority monoclinic phase, which coexists with the majority monoclinic phase with the Cm space group discovered earlier.² Noheda *et al.*¹⁰ have proposed that the superlattice phase of PZT results from local internal inhomogeneities or local stresses. There is thus a need to settle the existing controversy about the origin of the superlattice reflections observed in PZT with $x=0.520$ at low temperatures. In particular, it needs to be settled whether the superlattice reflections are due to a monoclinic phase with Cc space group as proposed by Hatch *et al.*,⁶ or due to a rhombohedral phase with $R3c$ space group as proposed by Frantti *et al.*⁸ The second issue to be settled is whether or not

there is another coexisting phase as proposed by Frantti *et al.*⁸ and Noheda *et al.*¹⁰ The third issue to be settled is that if there is a coexisting Cm phase with the superlattice phase, is it pseudo-rhombohedral type or pseudo-tetragonal type. Using Rietveld analysis of powder x-ray diffraction (XRD) data, Ragini *et al.*¹¹ have reported that the monoclinic Cm phase which coexists with the tetragonal $P4mm$ phase at room temperatures is of pseudo-rhombohedral type whereas Noheda *et al.*² have reported a pseudo-tetragonal-type monoclinic Cm phase at low temperatures.

In order to settle these issues, we have reexamined the low temperature structure of PZT with $x=0.520$ using Rietveld analysis of neutron powder diffraction data, keeping in mind the above possibilities as structural solutions. We have used the same powder neutron diffraction data that was used earlier.^{5,6} It is shown that a pseudo-tetragonal superlattice Cc phase coexisting with a pseudo-rhombohedral Cm phase accounts most satisfactorily for the observed features in the powder neutron diffraction data. The $R3c$ space group proposed by Frantti *et al.*⁸ is shown to give incorrect peak positions for the superlattice reflections. Using appropriate coordinate transformations, it is also shown that the refined parameters of the Cm phase reported earlier by Noheda *et al.*² by using XRD data at 20 K are in agreement with those of the Cc phase obtained by us, except for the sense of displacements along the monoclinic [010] which is responsible for the intensity of the superlattice peaks present in the powder neutron diffraction data. This sense of displacements along the monoclinic [010] could not be captured in the XRD work of Noheda *et al.*² since the superlattice peaks are not discernible in the XRD data.

II. REFINEMENT DETAILS

Structure refinement was performed using Rietveld refinement program DBWS 9411.¹² The background was estimated by linear interpolation between fixed values. A pseudo-Voigt function was chosen to generate profile shape for the neutron diffraction peaks. The Cc space group has only one Wyckoff site symmetry $4(a)$ with asymmetric unit of the structure consisting of five atoms of which we fix, by convention, Pb at (0.00, 0.25, 0.00). The remaining atoms have coordinates as follows: Zr/Ti at $(0.25 + \delta x_{\text{Ti/Zr}}, 0.25 + \delta y_{\text{Ti/Zr}}, 0.75 + \delta z_{\text{Ti/Zr}})$ and three oxygen atoms, O1 at $(0.00 + \delta x_{\text{O1}}, 0.25$

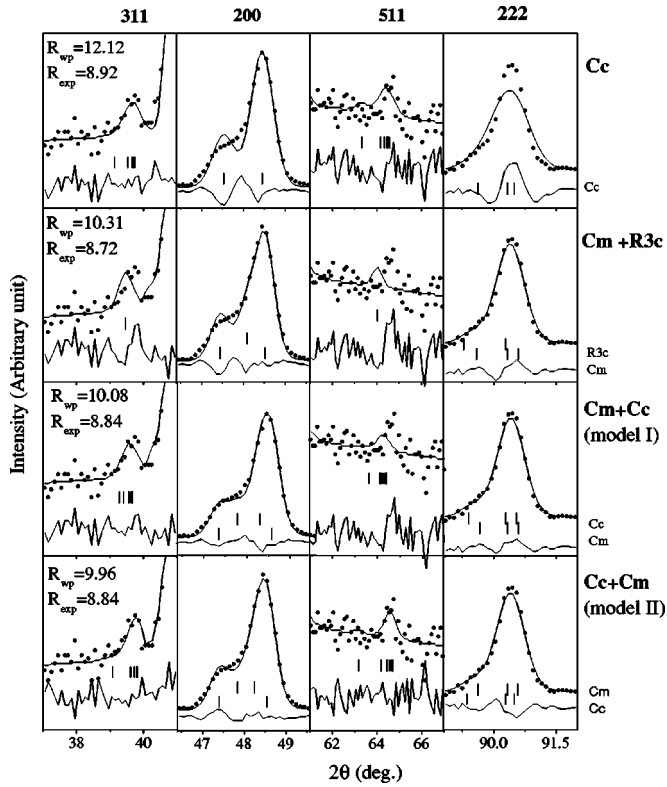


FIG. 1. Observed (dots), calculated (solid lines), and difference (bottom of the figures) profiles of the powder neutron diffraction pattern of $\text{Pb}(\text{Zr}_{0.520}\text{Ti}_{0.480})\text{O}_3$ at 10 K for the 311 and 511 superlattice reflections and 200 and 222 pseudocubic elementary perovskite reflections. The indices for superlattice reflections are with respect to a doubled pseudocubic cell. The short vertical bars represent the peak positions of the various phases.

$+\delta y_{O1}, 0.50 + \delta z_{O1}$), O2 at $(0.25 + \delta x_{O2}, 0.50 + \delta y_{O2}, 0.00 + \delta z_{O2})$ and O3 at $(0.25 + \delta x_{O3}, 0.00 + \delta y_{O3}, 0.00 + \delta z_{O3})$. The various δ 's represent the refinable parameters. There are four atoms in the asymmetric unit of the monoclinic phase with Cm space group. Pb is fixed at $(0.00, 0.00, 0.00)$, Zr/Ti at $(0.50 + \delta x_{\text{Ti/Zr}}, 0.00, 0.50 + \delta z_{\text{Ti/Zr}})$, O1 at $(0.50 + \delta x_{O1}, 0.00, 0.00 + \delta z_{O1})$ and O2 at $(0.25 + \delta x_{O2}, 0.25 + \delta y_{O2}, 0.50 + \delta z_{O2})$. Following Megaw and Darlington,¹³ the asymmetric unit of rhombohedral ($R3c$) structure with hexagonal axes consists of Pb at $(0.00, 0.00, 0.25 + \delta z_{\text{Pb}})$, Zr/Ti at $(0.00, 0.00, 0.00 + \delta z_{\text{Ti/Zr}})$, and O at $(1/6 + \delta x_{\text{O}}, 1/3 + \delta y_{\text{O}}, 1/12)$.

III. RESULTS AND DISCUSSION

A. Selection of the correct structural model for the superlattice phase

In order to make a choice among the various structural models for the superlattice phase, the Rietveld fits between observed and calculated profiles were compared for different models. Figure 1 shows the fits between observed and calculated profiles for the 200 and 222 pseudocubic elementary perovskite reflections, and 311 and 511 superlattice reflections, obtained after Rietveld refinements using the following

structural models: (i) pure Cc phase, (ii) coexistence of Cm and $R3c$ phases, (iii) coexistence of Cc and Cm phases (model I), and (iv) coexistence of Cc and Cm phases (model II). The main difference between the two $Cc+Cm$ coexistence models is that in model II, the Cc phase has a pseudo-tetragonal character while Cm has a pseudo-rhombohedral character while it is otherway round for model I. Hatch *et al.*⁶ have used the following constraints, $\delta y_{\text{Ti/Zr}} = \delta y_{O1} = 0$, $\delta x_{O2} = \delta x_{O3}$, $\delta y_{O2} = -\delta y_{O3}$ and $\delta z_{O2} = \delta z_{O3}$, for refining the structure of the superlattice phase using the Cc space group. In the present work, we realized that even without imposing these constraints, refinement converged smoothly with nearly identical parameters. As can be seen from Fig. 1, the pure Cc space group model accounts satisfactorily for the 311 and 511 superlattice reflections but considerable mismatch between the observed and calculated profiles is seen for the pseudocubic 200 and 222 profiles. Evidently, there is sufficient scope for improvement in the fits between the observed and calculated intensities for the 200 and 222 profiles and a two-phase structural model may be desirable. The $Cm+R3c$ phase coexistence model, proposed by Frantti *et al.*,⁸ gives better fit for the 200 and 222 pseudocubic profiles in comparison to that of pure Cc phase but distinct mismatch between the peak positions of the observed and calculated profiles for the 311 and 511 superlattice reflections is observed. The calculated peak positions of the superlattice reflections occur at lower 2θ angles as compared to the observed ones (see Fig. 1). The most marked difference can be seen at the 511 superlattice peak; the observed peak position of this superlattice reflection is at $2\theta = 64.65^\circ$ whereas the calculated peak is at $2\theta = 64.05^\circ$, a difference of 0.6° which can be easily noticed even on a medium resolution powder neutron diffractogram. A careful inspection of the inset to Fig. 3 of Frantti *et al.*⁸ also clearly reveals identical mismatch between the observed and calculated peak positions using $R3c$ space group. Attempts to force the match in the peak position of the superlattice reflections for the $R3c$ space group resulted in shifting of main perovskite reflections towards higher 2θ side, leading to large mismatch between the observed and calculated profiles. The peak position of the 511 superlattice reflection could be matched only when the 200 peak of the $R3c$ phase reaches the position of the 220 peak of the Cm phase in this model, but it leads to very large difference between the observed and calculated profiles for all the main perovskite peaks. Thus the $Cm+R3c$ phase coexistence model for the structure of PZT with $x=0.520$ at 10 K can be ruled out. This implies that the choice of the doubled rhombohedral cell proposed by Frantti *et al.*⁸ for indexing the superlattice reflections of the low temperature phase of PZT with $x=0.520$ is incorrect. The Cc space group used by Hatch *et al.*,⁶ on the other hand, does not lead to such a mismatch between the observed and calculated positions of the superlattice reflections, implying thereby that the unit cell corresponding to the Cc space group is the correct cell for exact indexing of the weak superlattice reflections in the powder neutron diffraction pattern. In the light of this subtle but very important fact, the doubt raised by Frantti *et al.*⁸ about the correctness of the Cc space group no longer holds valid.

After ruling out the $Cm+R3c$ phase coexistence model, we considered the coexistence of the monoclinic Cm and

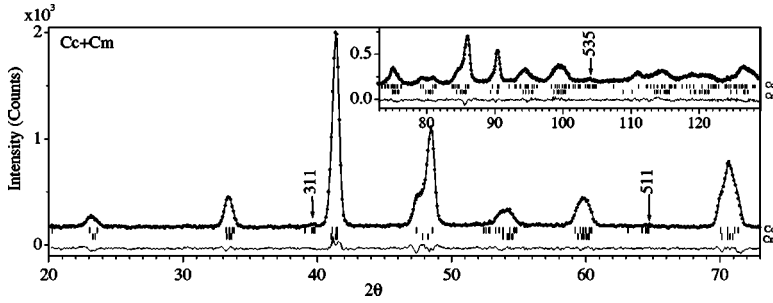


FIG. 2. Observed (dots), calculated (solid lines), and difference (bottom of the figures) profiles of powder neutron diffraction pattern of $\text{Pb}(\text{Zr}_{0.520}\text{Ti}_{0.480})\text{O}_3$ at 10 K in the 2θ range 20 to 130 deg using the coexisting $Cc+ Cm$ phases. The short vertical bars represent the peak positions of the two phases.

monoclinic Cc phases. It is evident from Fig. 1 that the fit for the 200 and 222 pseudocubic elementary perovskite reflections between the observed and calculated profiles is similar for models I and II of the coexistence of the Cm and Cc phases. For model I, when the Cc phase is considered to be pseudo-rhombohedral, which in turn requires the coexisting Cm phase to be pseudotetragonal to account for the splitting of the 200-type perovskite peaks, the calculated superlattice peak positions are seen to occur at lower 2θ angles as compared to the observed ones, similar to the $Cm+R3c$ phase coexistence model. However, for model II, where the Cc phase is considered to be pseudotetragonal (similar to that reported by Hatch *et al.*⁶), very good match between observed and calculated profiles is obtained for both the main perovskite reflections as well as the superlattice peaks. It is also clear that the consideration of pseudotetragonal or pseudorhombohedral type Cc phases does not make any difference as far as the fits for the main perovskite reflections are concerned. However, the match for the peak positions of the superlattice reflections are quite sensitive to the type of Cc phase chosen.

Thus, we can conclude that PZT with $x=0.520$ at 10 K consists of a mixture of two phases with Cc and Cm space groups and not $R3c$ and Cm space groups proposed by Frantti *et al.*⁸ The elementary perovskite subcell parameters $a_p=c_m/\sqrt{2}=4.044$ Å, $b_p=b_m/\sqrt{2}=4.032$ Å, $c_p=1/2[a_m^2+c_m^2-2a_m c_m \cos(\pi-\beta)]^{1/2}=4.129$ Å of the Cc phase show pseudotetragonal relationship ($a_p \approx b_p \neq c_p$) while $a_p=a_m/\sqrt{2}=4.072$ Å, $b_p=b_m/\sqrt{2}=4.051$ Å, $c_p=c_m=4.093$ Å of the coexisting Cm phase are pseudorhombohedral ($a_p \approx b_p$

$\approx c_p$). This Cm phase is similar to that reported by Ragini *et al.*¹¹ in PZT ($x=0.520$) at room temperature, which coexists with the tetragonal phase. Figure 2 depicts the observed, calculated, and difference plots for $Cc+ Cm$ phase coexistence (model II) in the 2θ range 20 to 130 deg. As can be seen from this figure, the fit between the observed and calculated profiles is very good. The refined structural parameters for the Cc and Cm phases are given in Table I. The atomic coordinates of the Cc phase given in Table I and those reported by Hatch *et al.*⁶ are comparable. Further, the present refinement clearly reveals that the Cc phase is a majority phase (65%) while Cm is a minority phase (35%). Thus the present analysis of the bulk sample using neutron powder diffraction data does not support the minority character of the Cc phase, proposed by Noheda *et al.*,¹⁰ on the basis of TEM study of thin regions, for PZT with $x=0.520$.

B. Comparison of the refined structural parameters of the Cc phase with those obtained by Noheda *et al.*² using the Cm space group

It is worth comparing the refined coordinates of the Cc phase given in Table I with those obtained by Noheda *et al.*² for $x=0.520$ at 20 K using x-ray synchrotron data assuming the Cm space group. As pointed out earlier by Ragini *et al.*⁴ and Ranjan *et al.*,⁵ the superlattice reflections of PZT at this temperature are discernible on electron and neutron diffraction patterns only and not on the powder XRD patterns. In the absence of the superlattice peaks in the x-ray synchrotron data, the most plausible space group which can account for

TABLE I. Refined structural parameters and agreement factors for $\text{Pb}(\text{Zr}_{0.520}\text{Ti}_{0.480})\text{O}_3$ at 10 K using the coexistence of two monoclinic phases with Cc and Cm space groups.

Atoms	Space group: Cc				Space group: Cm				
	x	y	z	$B(\text{Å}^2)$	x	y	z	$B(\text{Å}^2)$	
Pb	0.00	0.25	0.00	0.84(6)	0.00	0.00	0.00	1.6(1)	
Ti/Zr	0.215(1)	0.24(1)	0.692(4)	0.1(2)	0.52(1)	0.00	0.44(1)	0.0(3)	
O1	-0.045(1)	0.238(4)	0.418(2)	0.3(1)	0.577(4)	0.00	-0.078(7)	0.5(7)	
O2	0.187(2)	0.486(3)	-0.078(4)	1.6(4)	0.290(7)	0.253(2)	0.415(6)	0.6(4)	
O3	0.196(1)	-0.013(2)	-0.103(3)	0.0(1)					
$a=10.004(7)(\text{Å})$, $b=5.701(5)(\text{Å})$, $c=5.719(6)(\text{Å})$					$a=5.758(1)(\text{Å})$, $b=5.729(1)(\text{Å})$, $c=4.0930(7)(\text{Å})$				
$\beta=124.36(5)^\circ$, % Molar=65.18(1), $R_B=5.22$					$\beta=90.59(1)^\circ$, % Molar=34.82(1), $R_B=4.19$				
$R_p=7.21$, $R_{WP}=9.96$, $R_{exp.}=8.81$, $\chi^2=1.34$									

TABLE II. Comparison of the coordinates and cell parameters of the Cc phase after appropriate transformation to equivalent Cm phase unit cell, with those given by Noheda *et al.* (Ref. 2) for the Cm phase.

Atoms	Our results			Noheda <i>et al.</i> 's results		
	x	y	z	x	y	z
Pb	0.00	0.00	0.00	0.00	0.00	0.00
Ti/Zr	0.523(5)	-0.01(1)	0.430(2)	0.5230(6)	0.00	0.4492(4)
O1	0.537(3)	-0.012(4)	-0.090(2)	0.5515(23)	0.00	-0.0994(24)
O2	0.265(6)	0.236(3)	0.374(4)	0.2880(18)	0.2434(20)	0.3729(17)
O3	0.299(4)	0.737(2)	0.392(2)	0.2880(18)	0.7566(20)	0.3729(17)
$a=5.7190(\text{\AA}), b=5.7021(\text{\AA}),$ $c=4.129(\text{\AA}), \beta=90.51(^{\circ})$			$a=5.72204(\text{\AA}), b=5.70957(\text{\AA}),$ $c=4.13651(\text{\AA}), \beta=90.59(^{\circ})$			

the entire powder diffraction patterns was shown to be Cm by Noheda *et al.*² The atomic coordinates x_c, y_c, z_c given in Table I for the Cc space group can be transformed to x_m, y_m, z_m corresponding to the Cm space group via the following transformation equation: $x_m = x_c - z_c, y_m = y_c, z_m = 2x_c$. Since Pb is kept at origin in Noheda *et al.*'s² model, we need to shift the y_m coordinate through $-\mathbf{b}/4$. The equivalent x_m, y_m, z_m coordinates of the five atoms in the asymmetric unit of the Cc space group listed in Table I are given in Table II after incorporating this shift of origin. The same table also lists the coordinates obtained by Noheda *et al.*² using the XRD data. The asymmetric unit of the Cc space group has one additional O atom as compared to the asymmetric unit of the Cm space group. This is due to the fact that O2 and O3 atoms are related through a mirror at $y=1/2$ in the Cm space group but not in the Cc space group. As a result, the coordinates of O3 for the Cc space group given in Table II should be compared with the coordinates of the equivalent atom O2 in the Cm space group after adding (0, 0.5132, 0). A comparison can now be made between the coordinates for the Cc (proposed by us) and Cm (proposed by Noheda *et al.*²) space groups given in Table II. It follows that the refined x and z coordinates of all the atoms for the Cc space group are very close to those obtained by Noheda *et al.*² This shows that the structure of the low temperature monoclinic (F_M^{LT}) phase (Cc space group) retains the main structural framework of the higher temperature monoclinic (F_M^{HT}) phase with the Cm space group. The only difference is in terms of the sense of displacements in the y direction of all the atoms. The two sets of cell parameters listed at the bottom of Table II are

also quite close to each other, implying thereby that if one ignores the superlattice peaks in Fig. 2, as was the case with Noheda *et al.*² in their XRD studies, one would land up in the space group Cm .

IV. CONCLUSIONS

We have reconfirmed that the space group of the superlattice phase of the PZT with $x=0.520$, discovered by Ragini *et al.*⁴ and Ranjan *et al.*,⁵ is Cc . This superlattice phase can result from the monoclinic Cm phase discovered by Noheda *et al.*² by an antiferrodistortive phase transition.⁵ Further, this superlattice phase coexists with a secondary phase whose space group is also Cm but the equivalent perovskite cell parameters of this secondary phase bear pseudorhombic character¹¹ in contrast to the pseudotetragonal character of the equivalent perovskite cell parameters of the Cm phase discovered by Noheda *et al.*² The $R3c$ space group proposed by Frantti *et al.*⁸ for the superlattice phase cannot account for the peak positions of the superlattice reflections and is therefore discarded. If one ignores the superlattice peaks, as was the case with Noheda *et al.*² in their XRD studies, the most plausible space group of the low temperature phase becomes Cm .

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