Reply to "Comment on '$Pb_{1-x}Ca_xTiO_3$ solid solution ($x=0.0$, 0.25, 0.50, and 0.75): A theoretical and experimental approach'"

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Chandra [Phys. Rev. B **77**, 017101 (2008)] disagrees with the coexistence of a pseudocubic structure with a long-range tendency for cubic symmetry and tetragonal in a short-range order for the $Pb_{1-x}Ca_xTiO_3$ (PCT) system obtained by the polymeric precursor method (PPM), as proposed in our original paper [Phys. Rev. B **75**, 144111 (2007]. However, we did not show the Rietveld results for the samples in this paper. The Rietveld refinement results shown clearly the coexistence of the tetragonal-cubic phases for the PCT synthesized by PPM instead of the tetragonal-orthorhombic structures as suggested by Chandra [Phys. Rev. B **77**, 017101 (2008)].

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In his comment concerning our results published in Ref. 1, Chandra[2] claims that there are contradictions between the x-ray diffraction (XRD) and Raman data: "these self-contradictory conclusions deserve a careful consideration and necessitate another look at the analysis of XRD and Raman data." First, it is important to point out the differences between different techniques as Raman scattering and x-ray diffraction: while Raman scattering probes the short and medium-range order within distances of about few lattice parameters (hence sensitive to local structural disorder/distortions), XRD probes the medium and long-range order. Therefore, it is expected that each technique may lead to different results for the same analyzed sample, especially if there is a certain amount of structural disorder. Thus, only the correct interpretation of the results obtained by these different probes may lead to a complete understanding of the material behaviors.

The relationship of our Raman results from $Pb_{1-x}Ca_xTiO_3$

TABLE I. Refinement indexes for the $Pb_{1-x}Ca_xTiO_3$ ($x=0.0$, 0.25, 0.50, 0.75, and 1.0) powders. *T* indicates tetragonal, *C* cubic, and *O* orthorhombic.

Sample	System	Chi^2	R_B (%)	R_F (%)	R_{WP} (%)	R_P (%)
PT	Tetragonal	1.99	2.20	1.16	11.22	8.28
$PCT_{0.25}$	Cubic	6.96	8.12	3.95	20.91	15.68
	Tetragonal	1.76	2.29	1.34	10.49	7.80
	Tetragonal cubic	1.65	2.26	1.28 (*T*) 3.02 (*C*)	10.18	7.61
	Tetragonal orthorhombic	1.89	14.02	1.54 (*T*) - (*O*)	10.88	8.11
$PCT_{0.50}$	Cubic	3.73	5.04	2.57	16.30	12.96
	Tetragonal	1.90	4.82	2.54	11.61	8.94
	Tetragonal cubic	1.42	2.93	1.45 (*T*) 1.55 (*C*)	10.05	7.58
	Tetragonal orthorhombic	1.53	5.80	2.12 (*T*) - (*O*)	10.39	7.93
$PCT_{0.75}$	Cubic	3.87	5.26	2.62	16.80	13.06
	Tetragonal	2.30	3.11	1.66	12.95	9.92
	Tetragonal cubic	2.07	2.78	1.51 (*T*) 1.39 (*C*)	12.29	9.05
	Tetragonal orthorhombic	2.02	12.50	2.03 (*T*) - (*O*)	12.11	9.03
CT	Orthorhombic	1.28	3.88	4.64	14.57	9.48

(PCT) solid solutions is very well known; i.e., in a modified or solid solution of ABO_3-type perovskites in their cubic paraelectric phase, the local disorder leads to "defect-active Raman scattering." In many cases, the Raman spectra show intense broad bands that are characteristic of the ferroelectric phase while the XRD results stem from a completely cubic structure where the phonons should be inactive in Raman scattering.[3,4] In our work[1] the Raman results for $x=0.50$ and 0.75 show only broad bands that are characteristics of highly disordered material. Furthermore, the presence of the Raman peak corresponding to the E(1TO) soft mode up to $x=0.75$ can be interpreted as a "memory" of the tetragonal phase which are the only conclusions that can be tracked from Raman spectra within this range of Ca^{2+} concentration.

In relation to the XRD results presented in the manuscript by Lazaro *et al.*,[1] a decrease was observed in lattice parameters characterizing an intensification of the symmetry with increasing Ca^{2+} content from the tetragonal to the cubic phase in the PCT solid solution obtained by the polymeric precursor method (PPM). Chandra[2] argues about the absence of the "tailing" analysis of the Bragg peaks in our manuscript.[1] Thus, Chandra[2] asserted that in a composition range of $0.40 \leq x \leq 0.56$ for $Pb_{1-x}Ca_xTiO_3$ the tetragonal phase ($P4mm$) coexists with the orthorhombic phase ($Pbnm$), according to Chandra and Pandey.[5] Whereas in the Ref. 5 PPM to synthesize the PCT samples was not used, the synthesis method used in Refs. 2 and 5 is based on the physical method of synthesis, the solid state reaction. As reported by Kakihana[6] and Segal,[7] the solid state reaction presents built-in problems to obtain homogeneous solid solutions, mainly if compared to chemical methods.

Chandra[2] affirms that the property of the PCT system is intrinsic and independent of the sample preparation route based on Refs. 8 and 9. Rajan *et al.*[8] obtained a PCT sample by using a solid state reaction, since only the precursor used as Pb^{2+} and Ca^{2+} source $[(Pb_{1-x}Ca_x)CO_3]$ was obtained using the coprecipitation method, i.e., in Ref. 8 PCT compounds were synthesized by the same method employed by Chandra[2] and, as expected, produced a similar result. Kuo *et al.*[9] (also cited by Chandra) observed that the PCT obtained by the sol-gel technique is tetragonal for $x>0.65$, cubic in the region $0.35<x<0.65$, and orthorhombic for $x<0.35$. In addition, the authors also write in this paper: "the absence of the intermediate tetragonal phase between orthorhombic and cubic phases ($0<x<0.35$) may be mostly attributed to the very restricted region in the PCT system."

To analyze the tailing of Bragg peaks in our manuscript[1] as proposed by Chandra,[2] the XRD result was evaluated by Rietveld analysis for the PCT samples with $x=0.0$, 0.25, 0.50, 0.75, and 1.0 (heat treated at 700 °C for 2 h). X-ray diffraction data were collected using a Rigaku DMax 2500PC diffractometer applying 40 kV and 150 mA with Cu Kα radiation, graphite monochromator and rotary anode. In the analysis, the 2θ range from 10° up to 110° in a step-scanning mode was used with a step width of 0.02° s^{-1} and a fixed time of 3 s. The divergence slit used was fixed at 1°, and the receiving slit was fixed at 0.3 mm. Rietveld refinements for the samples with $x=0.0$, 0.25, 0.50, 0.75, and 1.0

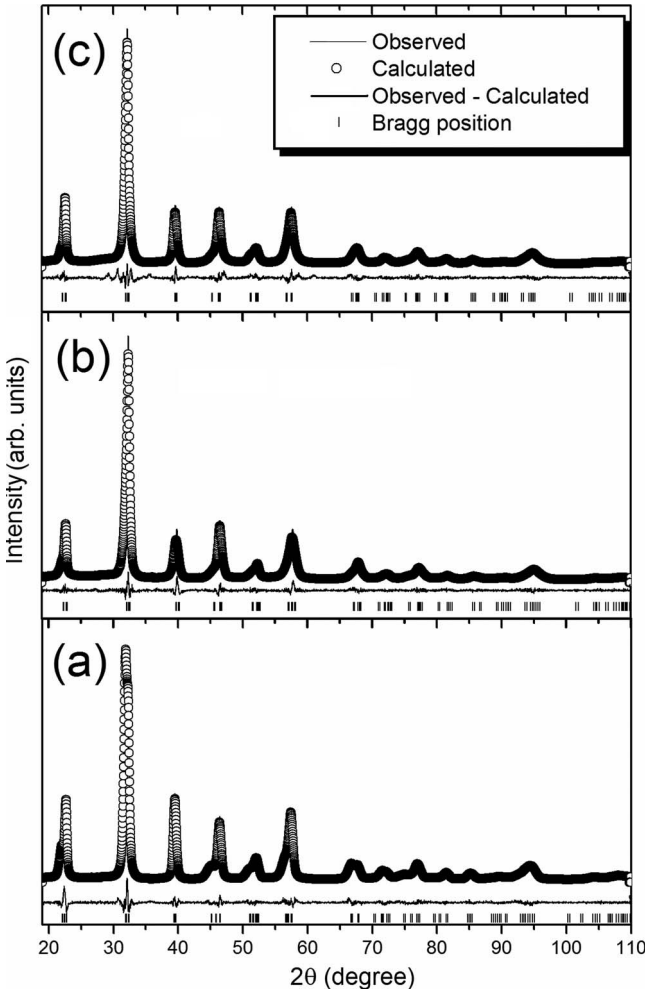

FIG. 1. Rietveld refinement considering the coexistence of the tetragonal and cubic systems performed for the $Pb_{1-x}Ca_xTiO_3$ obtained by the polymeric precursor method: (a) $PCT_{0.25}$, (b) $PCT_{0.50}$, and (c) $PCT_{0.75}$.

in $Pb_{1-x}Ca_xTiO_3$ were conducted by means of the general structure analysis system (GSAS) program of Larson and Von Dreele.[10,11] The peak profile function was modeled by using a convolution of the pseudo-Voigt[10] with the asymmetry function described by Finger *et al.*[12] To obtain the best fit, the CIF number 1610 for a tetragonal structure ($P4mm$),[13] 153406 for a cubic structure (Pm-$3m$) (Ref. 14) and 1000022 for an orthorhombic structure ($Pbnm$) (Ref. 15) were used.

In our Rietveld results were verified that the tailing process occurs in the PCT obtained by PPM, but it is due to the presence of a tetragonal phase. The absence of an orthorhombic phase in PCT compounds obtained by PPM is demonstrated in the Rietveld analysis. Table I depicts the correlation factors obtained from the Rietveld refinement for PCT samples. Patterns of the undoped samples $PbTiO_3$ (PT) and $CaTiO_3$ (CT) were analyzed by the Rietveld method to indicate the fit of the tetragonal and orthorhombic structure, respectively. Analyzing Table I, it can be observed that the best correlation factors (R values) were provided by the coexistence of tetragonal and cubic phases for all PCT samples. The

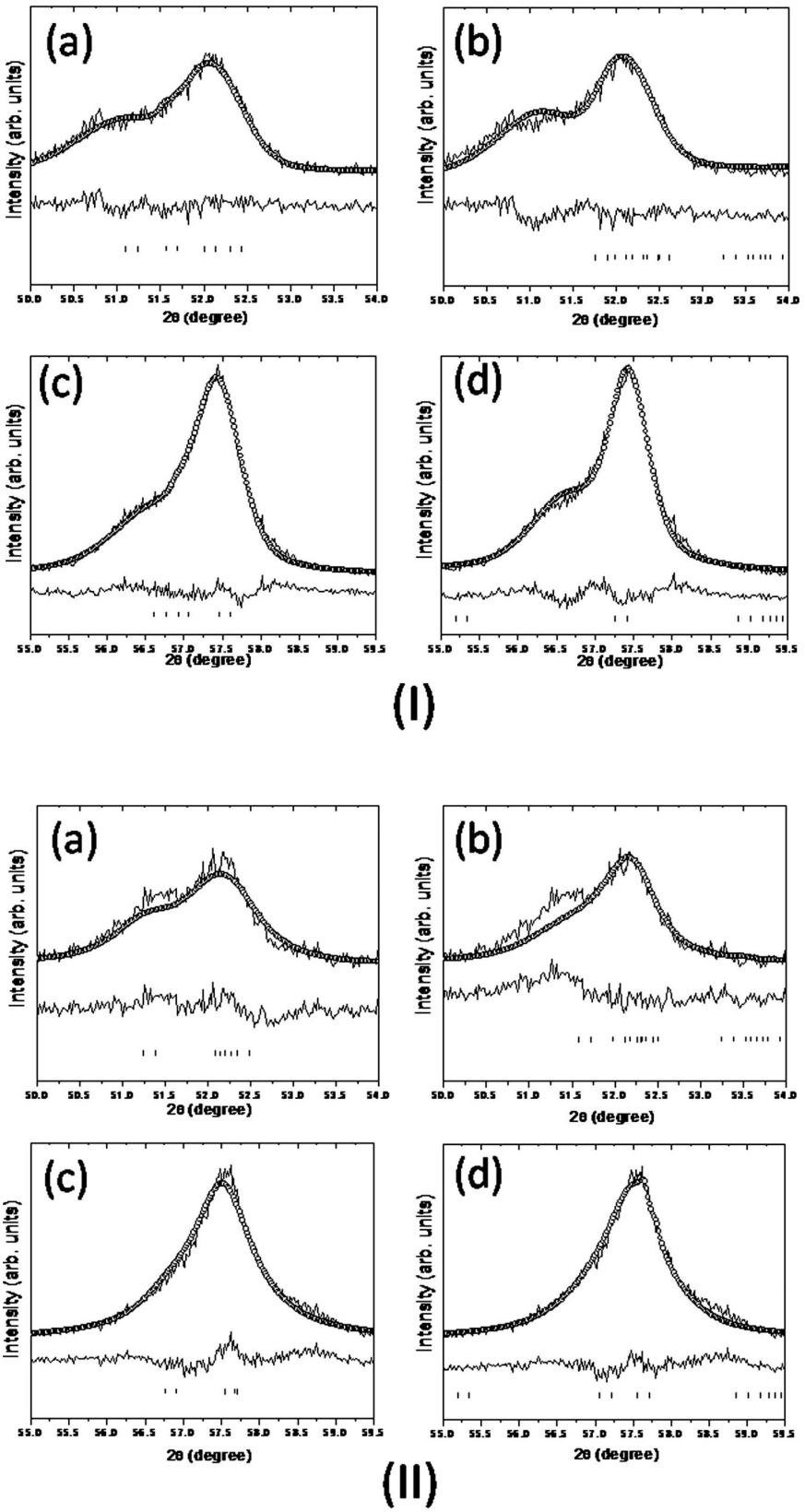

FIG. 2. Magnification of the fitting profiles in different 2θ ranges obtained by Rietveld refinement for the $Pb_{1-x}Ca_xTiO_3$ system. In (I) $x=0.25$, (II) $x=0.50$, and (III) $x=0.75$. For (I), (II), and (III): (a) and (c) indicate tetragonal-cubic and (b) and (d) tetragonal-orthorhombic systems.

refinement results for single tetragonal and cubic structures individually indicate a worse convergence if compared to a mixture of tetragonal-cubic phases. The convergence for a single orthorhombic structure was not found in the refinement for all PCT samples. Thus, Fig. 1 illustrates the refinements of the PCT powders with $x=0.25$, 0.50, and 0.75, which suggests the coexistence of the tetragonal and cubic structures.

To compare the refinement for tetragonal-cubic and tetragonal-orthorhombic arrangements, the regions of reflec-

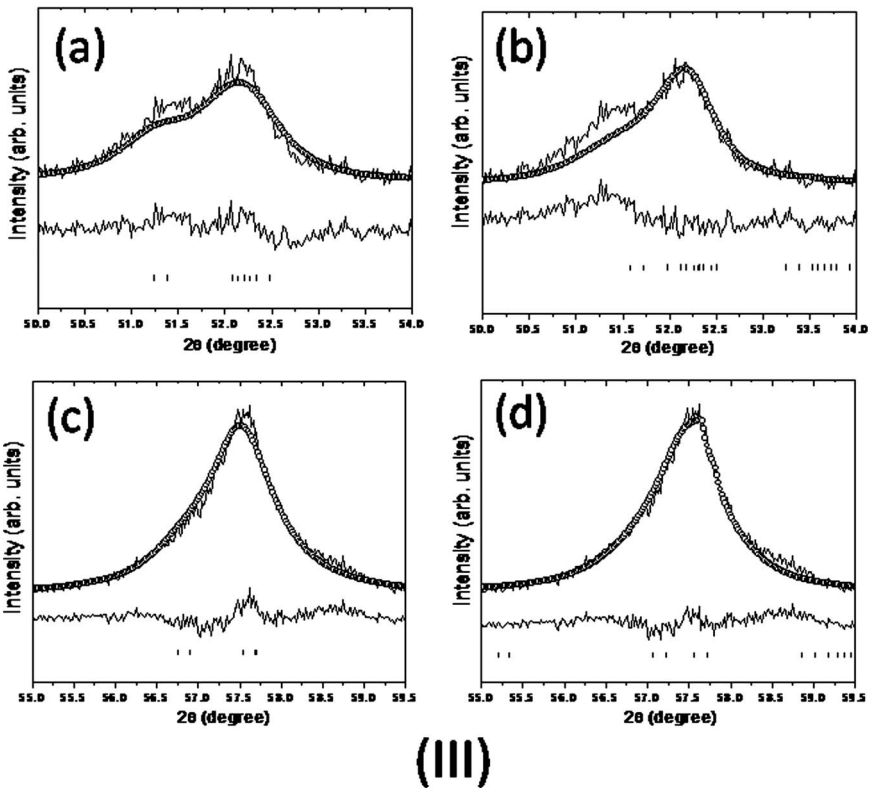

FIG. 2. (*Continued*).

tions considered by Chandra[2] are illustrated from Figs. 2I–III for both system types. Figures 2Ia–2Id illustrates the fitting of the PCT_{025} system, and it is observed that the best fit occurs for the tetragonal-cubic system. The same behavior is observed by Figs. 2IIa,b and 2IIIa,b for PCT_{050} and PCT_{075} samples, respectively. There is no significant difference for Figs. 2IIc,d and 2IIIc,d when comparing the shape behaviors of the calculated profiles for both systems in the diffraction regions selected by Chandra.[2] Thus, it can be observed that the adjustments do not improve by inserting the orthorhombic phase. Therefore, the analysis of the refinement index in Table I indicates the best fit. Analyzing this table, one can observe the discordance generated by the orthorhombic peak position in an R_B value for a tetragonal-orthorhombic system which passes from a higher to a smaller value if the tetragonal-cubic system is used for all PCT samples. On the other hand, the insertion of the cubic structure into the tetragonal system resulted in a diminishing of the refinement indexes, generating a best fit in the refinement.

Table II depicts the mass percentage of each structure (tetragonal and cubic) obtained from the refinement for a mixture of tetragonal and cubic phases which presented the best adjustment according to Table I. Analyses of Table II show that the cubic phase percentage increases markedly from $x=0.50$ which agrees with the increase expected in Ref. 1. As the GSAS program provides only the R_F values individually in the coexistence of phases, the R_F values were obtained for each phase analyzed. As expected, Table I verifies that the R_F values present a decrease if the mass percentage (see Table II) of the respective tetragonal or cubic phase is increased. For the orthorhombic phase, the GSAS program was unable to provide the R_F value, probably due to the absence of orthorhombic reflections in the XRD pattern. By analyses of the refinement index behavior for PCT samples obtained by PPM, it is clear that the best fit occurred with the tetragonal-cubic phase. In this way, according to XRD results the PPM method produce PCT samples with coexistence of the tetragonal-cubic phases in a long-range order, instead only cubic symmetry as proposed in our original paper.[1] These fact result in a tendency to cubic symmetry when the Ca^{2+} content is increased as suggested in our paper.[1] However, the orthorhombic symmetry was not found in this system as proposed by Chandra.[2]

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TABLE II. Mass percentage for the $Pb_{1-x}Ca_xTiO_3$ system with $x=0.25$, 0.50 and 0.75

	Mass (%)	
Sample	Tetragonal	Cubic
$PCT_{0.25}$	98.82	1.18
$PCT_{0.50}$	54.81	45.19
$PCT_{0.75}$	45.33	54.67

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