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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(Received 14 July 2007; published 4 January 2008)

The evolution of different phases in the important ferroelectric material $Pb_{1-x}Ca_xTiO_3$ for different values of x has recently been studied by de Lazaro *et al.* [Phys. Rev. B **75**, 144111 (2007)] using x-ray diffraction (XRD) and Raman techniques, arriving at self-contradictory results (pseudocubic from XRD and noncubic from Raman). A "tailing" of many Bragg peaks can be seen in the XRD data of de Lazaro *et al.*, similar to that observed by Chandra and Pandey [J. Mater. Res. **18**, 407 (2003)], but this has not been included in their analysis. Our detailed Rietveld analysis has shown that for $0.40 \leq x \leq 0.56$, the orthorhombic (*Pbnm*) and tetragonal (*P4mm*) phases coexist. We also present our Raman data, which differ with those of de Lazaro *et al.* but follow an expected sequential change in the entire compositional range.

$Pb_{1-x}Ca_xTiO_3$ (PCT) is fast becoming an important material as it shows promise for application in areas where large anisotropy is required.[1–5] Consequently, studies on the evolution of composition dependent crystal structures and phase transitions have also attracted great interest and are being pursued by using a wide variety of techniques such as x-ray diffraction (XRD), neutron diffraction, Raman, thermal, and dielectric measurements.[1,6–9] Composition dependence of structure in $Pb_{1-x}Ca_xTiO_3$ is likely to be complicated since the two end compositions ($x=0.0$ and $x=1.0$), i.e., $PbTiO_3$ and $CaTiO_3$, have widely different structures at room temperature. The former has a simple perovskite structure with tetragonal *P4mm* space group, while the latter possesses a tilted perovskite structure with orthorhombic *Pbnm* space group.[1] Therefore, a very careful analysis of the diffraction data is necessary, or else it may lead to conflicting conclusions regarding the structure of their solid solutions with intermediate compositions.

Recently, de Lazaro *et al.*[10] have proposed that the pseudocubic structure of PCT presents a long range tendency for cubic symmetry, while the short range displacements bring the solid solution to a tetragonal symmetry. These authors, while discussing XRD results on their sol-gel derived $Pb_{1-x}Ca_xTiO_3$ samples, state in Sec. III.A (p. 144114) that "…the experimental results indicate that, with increasing amount of calcium, the diffraction profiles shows a tendency to form a cubic symmetry." This means that $Pb_{1-x}Ca_xTiO_3$ is undergoing a composition dependent tetragonal to cubic phase change at $x \geq 0.40$. Contrary to this, while discussing their own Raman results in Sec. II.B (p. 144115), the authors conclude that "…the structure does not belong to a tetragonal-cubic transition…" These self-contradictory conclusions deserve a careful consideration and necessitate another look at the analysis of the XRD and Raman data, and another check of the corresponding theoretical calculations which have been done by them to explain the observed XRD data. It appears that there exists some other alternative structural phase transition route than suggested by de Lazaro *et al.*[10] In the following discussion, it is shown that in the intermediate compositional range, i.e., $x=0.40–0.56$, the orthorhombic and tetragonal phases coexist.

As stated earlier, pure $CaTiO_3$ belongs to the orthorhombic *Pbnm* space group, while pure $PbTiO_3$ has tetragonal *P4mm* space group. Therefore, the intermediate compositions are expected to show a complex evolution or even a coexistence of structures of the two end members. In this type of suggested "morphotropic phase boundary" compositional range, separation of the phase fields of the two different ferroelectric crystallographic phases has been found to lead to a "peaking" in the piezoelectric response for many solid solution systems such as $(1-x)PbTiO_3+xPbZrO_3$,[11] $(1-x)[PbMg_{1/3}Nb_{1/3}O_3]+xPbTiO_3$,[12] etc. Similar behavior has also been observed in the PCT system.[1] In fact, for $x=0.40–0.50$ range in the PCT system, which is also the subject of study of de Lazaro *et al.*,[10] such morphotropic phase boundary has been found to be present in an earlier careful Rietveld analysis of XRD data reported by Chandra and Pandey,[1] who observed the occurrence of superlattice reflections and "tailing" of some Bragg reflections in PCT samples prepared by a solid state reaction route. These features such as the presence of superlattice reflections can also be seen in the results reported by Kuo *et al.*[8] in their samples prepared by the sol-gel route, by Ranjan *et al.*,[13] who prepared PCT samples using a novel semichemical route, and by Jimenez and Jimenez,[14] who prepared their samples using a reactive method. This clearly shows that the property of the PCT system is intrinsic and independent of the sample preparation route. This statement refers to the XRD analysis of the series of phase transitions occurring in the PCT system. The observation of superlattice peaks and tailing of some diffraction peaks in the composition range $0.40 \leq \times \leq 0.56$ could only be explained by considering the coexistence of orthorhombic (*Pbnm*) and tetragonal (*P4mm*) phases as shown by Chandra and Pandey.[1] It is interesting to note that the XRD data of de Lazaro *et al.*[10] also show tailing as in the data of Chandra and Pandey,[1] but no due consideration was given by de Lazaro *et al.*[10] Figure 1(a) shows the tailing of peaks (indicated by vertical arrows) present in the data of de Lazaro *et al.* for PCT50 along with my data given in Fig. 1(b). In Fig. 2, the tailing of two typical peaks, namely, (210) and (211), are shown in expanded form. It is obvious that an excellent fit has been obtained after a detailed Rietveld
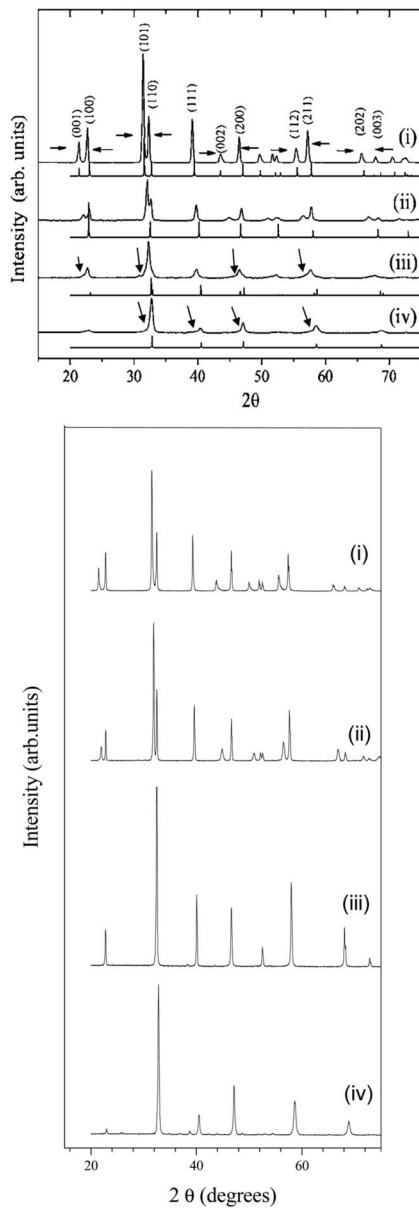
FIG. 1. (a) Scanned "Figure 2" from the paper of Lazaro *et al.* (Ref. 10). This shows the experimental (up) and theoretical (down) x-ray diffraction of $Pb_{1-x}Ca_xTiO_3$ solid solution treated at 700 °C: (i) $x=0.0$, (ii) $x=0.25$, (iii) $x=0.50$, and (iv) $x=0.75$. (b) My XRD data for $Pb_{1-x}Ca_xTiO_3$ solid solution: (i) $x=0.0$, (ii) $x=0.25$, (iii) $x=0.50$, and (iv) $x=0.70$.

FIG. 2. (a) and (b) respectively show the observed (…..) and calculated (__) fitting profiles, and also given below these is the difference profiles for 210 and 211 peaks of PCT50 obtained by just considering a tetragonal ($P4mm$) phase. (a1) and (b1) show the fitting profiles obtained by considering mixed tetragonal ($p4mm$)+orthorhombic ($Pbnm$) phases, which is obviously a better fitting of profiles.

FIG. 3. My present data for the room temperature Raman spectra of $Pb_{1-x}Ca_xTiO_3$ samples in the composition range $0 \leq x \leq 1.0$. The inset shows the data of de Lazaro *et al.* (Ref. 10).

analysis considering the coexistence of tetragonal and orthorhombic phases in the nominal composition range $0.40 \leq x \leq 0.56$ fits the XRD data. The explanation of data by the coexistence of the two (tetragonal+orthorhombic) phases also avoids the self-contradictory conclusions arrived at by de Lazaro *et al.*[10] from their XRD and Raman results.

The approach of de Lazaro *et al.*[10] in checking the nature of phase transition through Raman spectral studies is interesting, but their data and theoretical modeling needs another look. It essentially shows very little change (they only note a small change in the relative intensities of Raman peaks), and the data do not cover the full range starting from pure
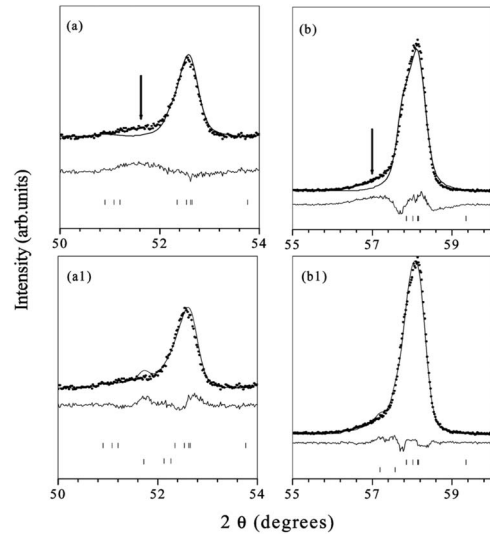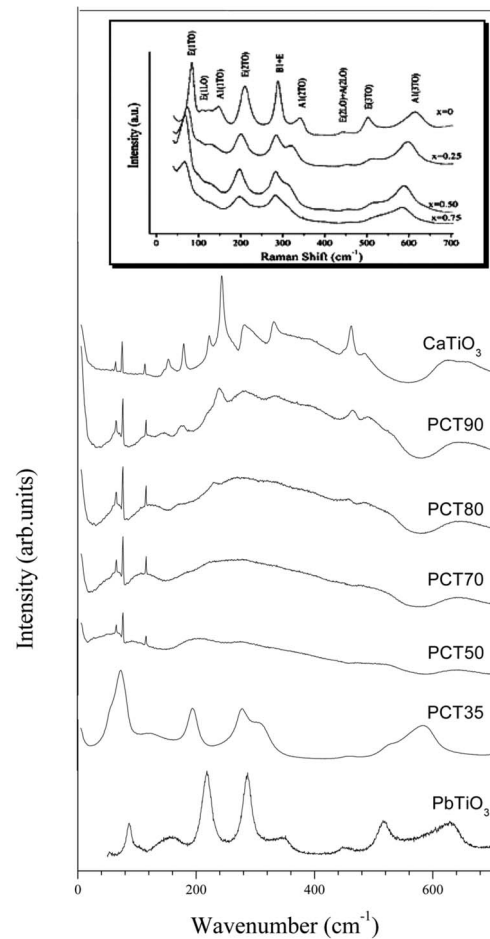
$CaTiO_3$ ($x=0.0$) to pure $PbTiO_3$ ($x=1.0$). The data in the region $x=0.40-0.60$ are very critical since a coexistence of two phases is expected in this composition range. Figure 2 shows our Raman data in a much wider composition range for the samples prepared using the solid state reaction route.[1] Similar results have been observed by Kuo *et al.*[8] in their PCT samples prepared using the sol-gel route. It is clear that the Raman spectra for our samples with $x=0.50$ and 0.70 are different from those of de Lazaro *et al.* taken in almost the same composition range. On the other hand, our data for lower values of x, viz. $x=0.35$ and 0.50, are similar to that reported by de Lazaro *et al.*[10] Therefore, the data of de Lazaro *et al.*[10] could be misleading beyond $x=0.35$ (i.e., the data for $x=0.50$ or $x=0.75$) as it widely differ with our data and the data of Ranjan *et al.*[13] or Kuo *et al.*[8] Our Raman data in Fig. 3 show expected sequential changes as we go from the tetragonal phase of pure $PbTiO_3$ to the orthorhombic phase of pure $CaTiO_3$.

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