

Pressure dependent phase transitions in (Pb,Ca)TiO₃: Determination of structure using high pressure synchrotron X-ray and Raman studies

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Received: 12 January 2010 / Accepted: 14 April 2011 / Published online: 3 May 2011
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Abstract Pressure dependent studies on technologically important ferroelectric material Pb_{0.70}Ca_{0.30}TiO₃ show the occurrence of a new hitherto unreported pressure dependent phase transition around 4 GPa. In the pressure range 4–14 GPa, the parent tetragonal (P4mm) phase of Pb_{0.70}Ca_{0.30}TiO₃ transforms in to a monoclinic (Cm) phase before attaining its paraelectric cubic (Pm3m) phase around 15 GPa. High pressure Raman studies reveal the presence of a critical pressure above which the ferroelectric phase starts to reappear in the paraelectric phase. This critical pressure is found to be much lower than the critical pressure observed in pure PbTiO₃. Possible reasons for this lowering of the critical pressure are presented.

Keywords XRD · Phase transition · Raman · Ferroelectric

1 Introduction

Phase transition studies in ferroelectric ceramics based on BaTiO₃ [1–6] and PbTiO₃ [7–10] continue to attract tremendous interest. Some of the important solid solutions based on PbTiO₃ with large technological applications are Pb(Zr_{1-x}Ti_x)O₃ [11–14], Pb_{1-x}Sr_xTiO₃ [15, 16], Pb_{1-x}Ca_xTiO₃(PCT) [17–23], etc. With increasing demand for smarter ceramics, pressure dependent studies in some of these PbTiO₃ based ceramics have attained significance [24–27]. These investigations have not only provided the fundamental insight towards the pressure dependent phase transitions but have also increased the applicability of such ceramics [28–31]. One of the above mentioned ceramics viz., Pb_{1-x}Ca_xTiO₃ has become subject for careful studies in recent times [17, 18, 21, 32]. Pb_{1-x}Ca_xTiO₃ shows interesting composition and temperature dependent phase transitions at ambient pressures [18, 33, 34] with potential for application in areas where ‘directionality’ or ‘anisotropy’ affects are important such as hydrophone, ultra-sonography, surface acoustic wave, etc. [18–20, 22, 35]. An added significant advantage reported for Pb_{1-x}Ca_xTiO₃ is that, for $x < 0.40$, these ceramics show high negative thermal expansion coefficient [32]. This also makes them a candidate in areas such as high precision optical mirrors, electronic industry, thermal switches, etc. [36–40]. But, pressure dependent studies in this important ferroelectric ceramic, Pb_{1-x}Ca_xTiO₃, still remains an unexplored area.

We present the results of pressure dependent Raman spectroscopy and synchrotron X-ray diffraction studies on Pb_{0.70}Ca_{0.30}TiO₃ ceramic which reveals the presence of novel features hitherto not reported. It is shown that the Pb_{0.70}Ca_{0.30}TiO₃ system undergoes an intermediate phase

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transition, viz., tetragonal→monoclinic, before attaining the paraelectric (cubic) phase. The phase transition from tetragonal to monoclinic phase is of “first order type” and occurs at ~4 GPa while the second “predominantly second order type” phase transition, from monoclinic to cubic phase, occurs around 15 GPa. Present investigation also presents the proof for occurrence of disorder in the paraelectric phase of $\text{Pb}_{0.70}\text{Ca}_{0.30}\text{TiO}_3$. Another novel feature of reappearance of ferroelectricity in the paraelectric phase above a critical pressure (~20 GPa) has also been observed in our studies. The reasons for reappearance of ferroelectricity are also discussed in this paper. These new results are also compared with those reported for the case of pure PbTiO_3 [Refs 33, 40].

2 Experimental

$\text{Pb}_{0.70}\text{Ca}_{0.30}\text{TiO}_3$ (henceforth abbreviated as PCT30) sample was prepared using the solid state thermo-chemical route using analytical grade PbCO_3 , CaCO_3 and TiO_2 powders as starting ingredients. Details of sample preparation have already been published elsewhere [18]. For collecting synchrotron X-ray diffraction and Raman data, the sintered PCT30 pellet was first crushed into fine powders and then annealed at 500°C for 10 h to remove the strains which may get introduced during crushing. Room temperature structural characterization was carried out using powder X-ray diffraction [18] and all the peaks could be indexed using a tetragonal structure (space group P4mm).

The angle dispersive powder synchrotron X-ray diffraction (ADXRD) measurements at high pressures were carried out at the ‘powder X-ray diffraction beam line (MCX beamline, 7.1)’ of ELETTRA Synchrotron source, employing X-rays of wavelength 0.6965 Å (calibrated with LaB_6). X-ray diffraction experiment as a function of pressure was carried out in the range of 0–35 GPa. Each diffraction pattern was collected in the 2θ range 4–42° with the step width 0.02151°. For collecting pressure dependent diffraction data, the powder was loaded in a diamond anvil cell (DAC) having a pair of diamond anvils with culet diameter of 400 µm. A pre-indented hardened stainless steel gasket with a central hole of diameter 150 µm and initial thickness of 60 µm was used. A mixture of methanol–ethanol (4:1) was used as pressure transmitting medium. The pressure was determined in situ by using Ag powder as pressure calibrant. Images of the powder diffraction rings were collected with a Mar345 image plate detector and read using a resolution of 100 µm×100 µm pixel size. Typically, 30 min of exposure time was employed for measurements at high pressures. The images were integrated over the rectangular

sector of the recorded powder rings using the FIT2D software [41]. The obtained powder patterns were further corrected for the absorption by the diamond anvils. The converted normal 2θ vs. intensity diffraction pattern was used for data analysis.

For high pressure Raman measurements, tiny disks of sample ~20 µm in diameter and ~10 µm in thicknesses were loaded into a diamond anvil cell (DAC). The cell was placed inside the tungsten gasket hole of diameter 100 µm, pre-indented to a thickness of 44 µm. Before loading the pressure transmitting medium, the high pressure cell was first dried at 120°C. The high pressure experiments below and above 8 GPa were carried out using the 4:1 ethanol-methanol mixture and Ar gas as pressure transmitting medium respectively. The pressure was determined using the Ruby fluorescence method by placing Ruby chips of approximate size 3–5 µm. Laser with the 457.9 nm line of a Spectra Physics 2025–05 argon ion laser was used for excitation. The laser light entered the diamond cell at an incident angle of 25° and was focused to a 15 µm spot on the sample. The laser power was kept to about 30 mW in order to avoid heating of the sample. The Raman spectrum was collected using an f/19 objective lens and focused into the monochromator through a pinhole to minimize the interference from the diamond fluorescence. The Raman spectra were analyzed using a SPEX 1402 double monochromator (1800 l/mm grating) with a liquid nitrogen cooled CCD detector (model LN/CCD—1100 PB), using a ST-130 CCD detector controller unit from Princeton Instruments. The spectral resolution was about 0.4 cm^{-1} and the spectra were sampled at 0.4 cm^{-1} in a range of 140–1,000 cm^{-1} .

3 Results and discussions

3.1 Structural studies

Figure 1 shows the evolution of three selective perovskite peaks namely, (100), (110) and (211). This figure clearly depicts the two pressures (viz., 8 GPa and 14 GPa) above which perceptible changes in the nature of diffraction peaks are observed. Above 6 GPa, the nature of peak splitting suddenly changes with the relative intensities of the set of peaks (100 and 001) becoming comparable to each other. Similar behaviour is observed for the (110 and 011) set of peaks. The representative set of (211; 112) and (101; 110) peaks also start to merge into each other with increasing pressure. The second perceptible change in the nature of diffraction pattern is observed above 14 GPa. Above this pressure we clearly observe singlet (100), (110) and (211) peaks. This is a clear signature of a structural transition to a paraelectric cubic phase above 14 GPa. The change in the

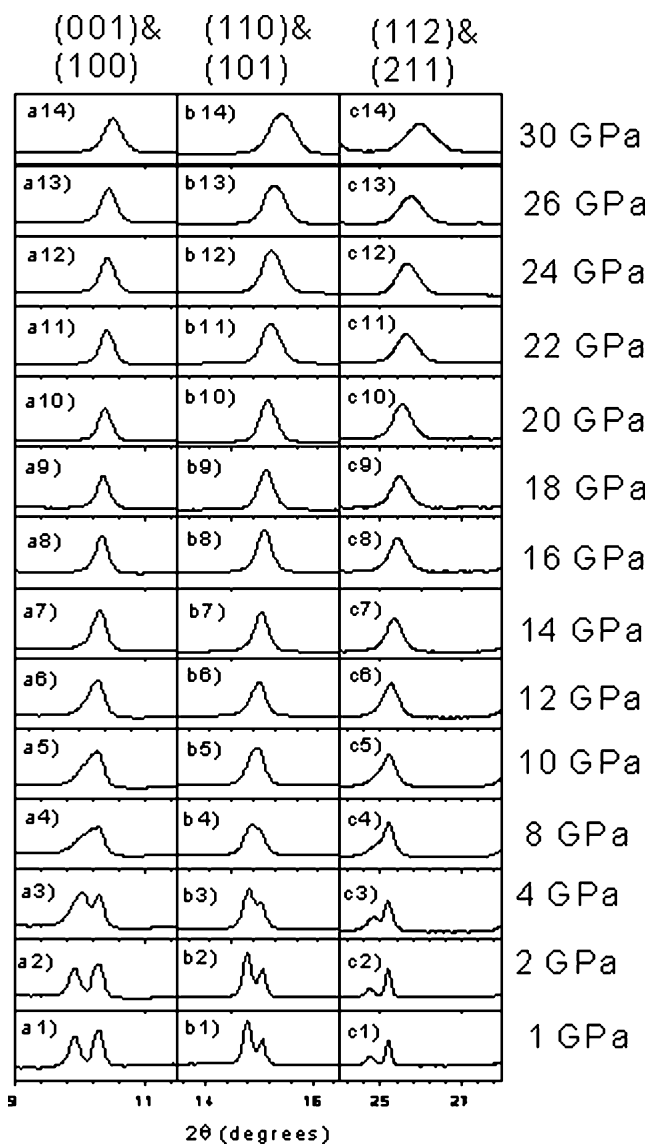


Fig. 1 Evolution of representative (100; 001), (110; 101) and (211; 112) diffraction peaks as a function of pressure in $\text{Pb}_{0.70}\text{Ca}_{0.30}\text{TiO}_3$

nature of diffraction peaks around 6 GPa suggests towards the modification of the parent tetragonal phase. As no new peak(s) is observed above 6 GPa, it is very difficult to conclusively claim about the new structural phase into which the system may be transforming. Before proceeding, it should be noted that in Fig. 1, the background of the diffraction peaks has not been removed differently. As the main purpose of this figure is to show the pressure dependent evolution of individual peaks, the y-axis of the peaks have been zoomed vertically to different extent. The peaks therefore look of comparable intensity. The actual peak intensity variation is shown in Fig. 2. Further, with increasing pressure in the paraelectric phase, the diffraction peaks show increased broadening. This indicates the presence of an essential order–disorder characteristic at

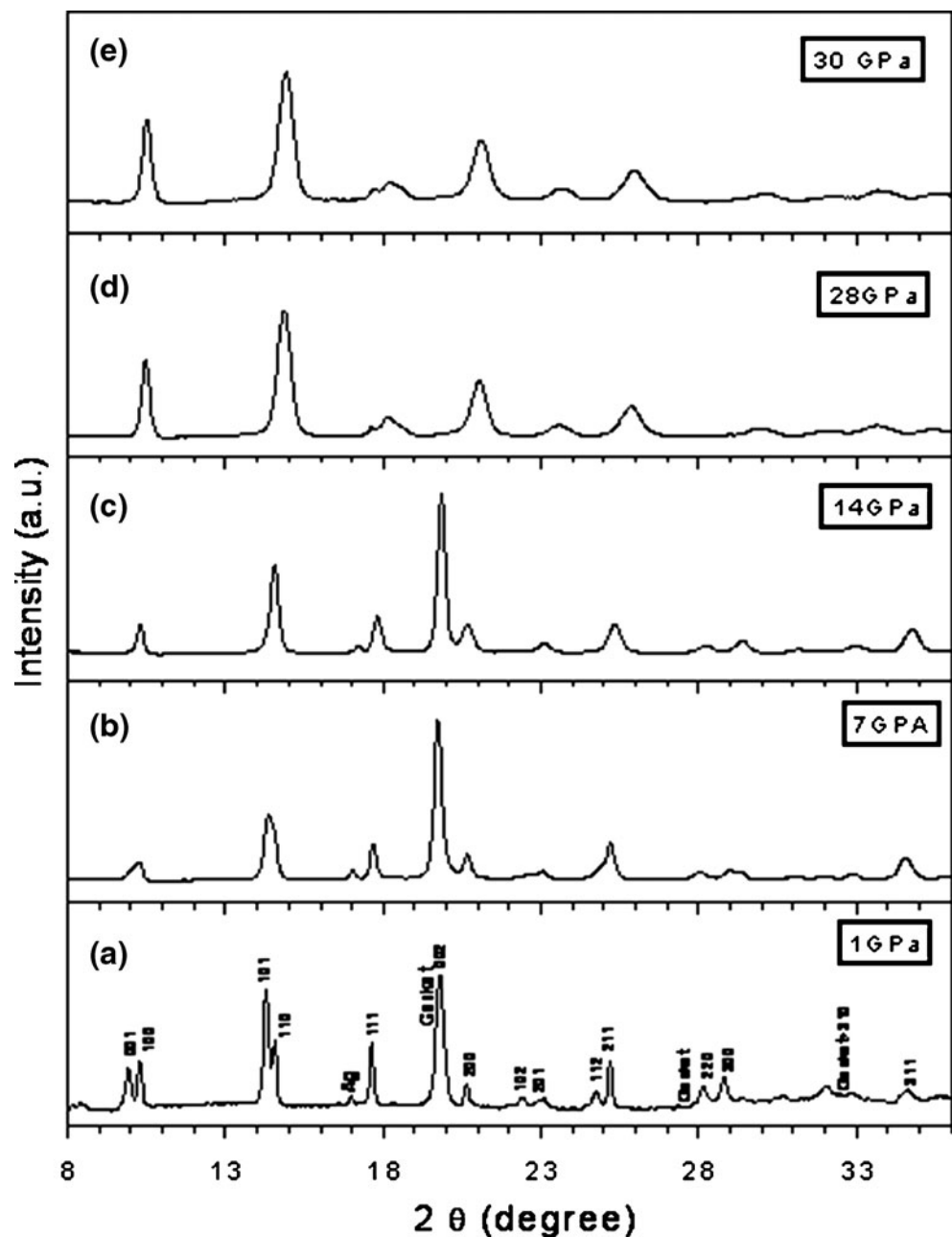
high pressures. This is contrary to the result which reported absence of order–disorder characteristic in pure PbTiO_3 above 12 GPa [27] but supports the results recently suggested by Jaouen et. al. [31] using Ti K edge XANES data. For the sake of completeness, Fig. 2 gives the complete diffraction spectra of PCT30 at 5 representative pressures. From this figure, the occurrence of increased broadening in all the diffraction peaks up to the highest achievable pressures becomes evident.

Absence of any new diffraction peaks above 4 GPa suggests that the new intermediate phase will have unit cell dimensions very close to that of the parent tetragonal phase and therefore determination of unit cell parameters using the tetragonal unit cell is quite justified. Variation of unit cell parameters as a function of pressure was determined using the procedure of LeBail fitting by considering the tetragonal ($P4mm$) unit cell for the ferroelectric phase (below 14 GPa) and cubic ($Pm3m$) unit cell for the paraelectric phase (above 14 GPa). Figure 3 depicts the variation of unit cell volume and unit cell a- and c-parameters as a function of pressure. The unit cell c-parameter shows a larger variation in comparison to the unit cell a-parameter. But the variation of both a- and c-parameters shows two distinct changes in slope. The first discontinuity is observed around 4 GPa while the second is observed around 15 GPa. Similar feature is observed in the variation of unit cell volume. This figure clearly suggests the occurrence of two phase transitions at around 4 GPa and 15 GPa, respectively.

But, as reported above, the evolution of diffraction pattern show no new peak(s) above 4 GPa (the pressure at which discontinuity is observed in the pressure–volume curve). As pseudo-symmetry is a well known problem in perovskites, it is difficult to confidently claim about the occurrence of phase transition around 4 GPa. Further, it has been reported [18, 21, 33] and also experienced by us that it is extremely difficult to carry out Rietveld refinement in $\text{Pb}_{1-x}\text{Ca}_x\text{TiO}_3$ compositions with $x < 0.40$. Samples in this range show enhanced peak broadening due to the intrinsic lattice strain in the predominantly tetragonal phase of PCT system. This makes it difficult to get good quality unique Rietveld fits without invoking many other parameters such as anisotropic thermal parameters, strain broadening parameters, occupancy, etc. The broadening can also be a consequence of mixed structural-phase region setting in. But this is difficult to claim with the available high pressure synchrotron data. Also, because of the order–disorder characteristics observed in PbTiO_3 based systems, the local symmetry can be different from that of the bulk symmetry which cannot be deciphered by techniques such as X-ray diffraction.

Further, the non-appearance of any new peak above 4 GPa even when the unit cell variation predicts the

Fig. 2 X-ray diffraction spectra as a function of pressure in $\text{Pb}_{0.70}\text{Ca}_{0.30}\text{TiO}_3$ at five representative pressures. 2 pressure values are above and 2 pressure values are below the transition pressure of ~ 15 GPa



occurrence of phase transition can be a direct consequence of the small domain size of the new crystal lattice as compared to the coherence length of the XRD technique. Further, if these domains are randomly distributed within the lattice, direct detection is sometimes difficult as has been observed in few other disordered systems [42]. Since, Raman spectroscopy technique is very sensitive towards small changes in atomic positions or formation of microdomains within the sample, occurrence of phase transition is expected to clearly manifest itself by modifying the Raman spectra of the sample. Therefore, it becomes interesting to investigate the evolution of phonon modes which may be linked with the lattice instability. The results

of pressure dependent Raman measurements carried out in PCT30 system in the range 0–40 GPa are discussed in the next section.

3.2 High pressure Raman spectroscopic studies

At room temperature, PCT30 has a tetragonal structure with C_{4v}^1 space group symmetry. The phonon mode assignment for the tetragonal phase of the PCT30 system can be done following the widely accepted mode assignment given by Foster et al. [43, 44] for pure PbTiO_3 as depicted in Fig. 4. The different mode frequencies were determined by fitting 9 Lorentzians in the frequency range 150 to 850 cm^{-1} . Figure 5

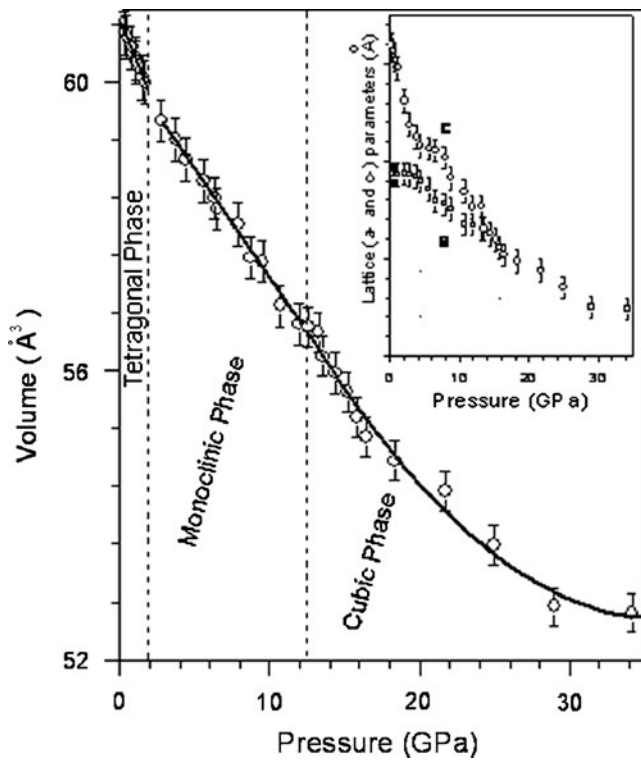


Fig. 3 Variation of unit cell volume as a function of pressure in $\text{Pb}_{0.70}\text{Ca}_{0.30}\text{TiO}_3$. The inset depicts the variation of unit cell a- and c-parameters in $\text{Pb}_{0.70}\text{Ca}_{0.30}\text{TiO}_3$

shows the evolution of Raman spectra of PCT30 in the pressure range 0–40 GPa. Clear signatures of changes in the Raman spectra starts to appear above 3.5 GPa. This strengthens the claim for the existence of a new phase transition in the PCT30 system suggested in the XRD studies discussed earlier. Above 3.5 GPa, it is not possible to index all the Raman modes using the expected number of phonon modes for a tetragonal (space group $P4mm$) phase as new Raman modes are observed around 160,230,380,576, and

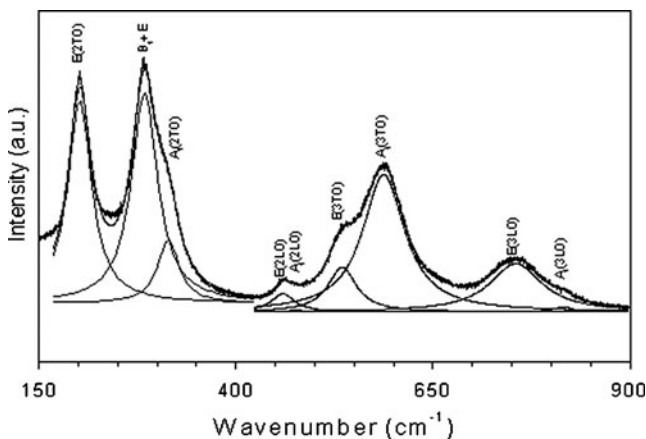


Fig. 4 Raman mode assignment in $\text{Pb}_{0.70}\text{Ca}_{0.30}\text{TiO}_3$ spectrum collected at ambient pressure

676 cm^{-1} (see Fig. 5(b)). This figure also clearly shows two pressures at which the nature of phonon modes change; one around 4 GPa and the second around 15 GPa. It is worthwhile to mention that the continuously rising background observed in Raman spectra shown in Fig. 5 is due to the inherent property of the sample at high pressures. The intense rising background at high pressures is due to the luminescence from the sample as well as diamonds in the anvil cell. As pressure increases, the Raman intensity goes down. Therefore the laser power and the accumulation time had to be suitably increased to get a proper intensity value. But, as the signal to noise ratio only depends on the instrument and it will not change with change in applied pressure, the observed Raman signal is that what is expected from the sample.

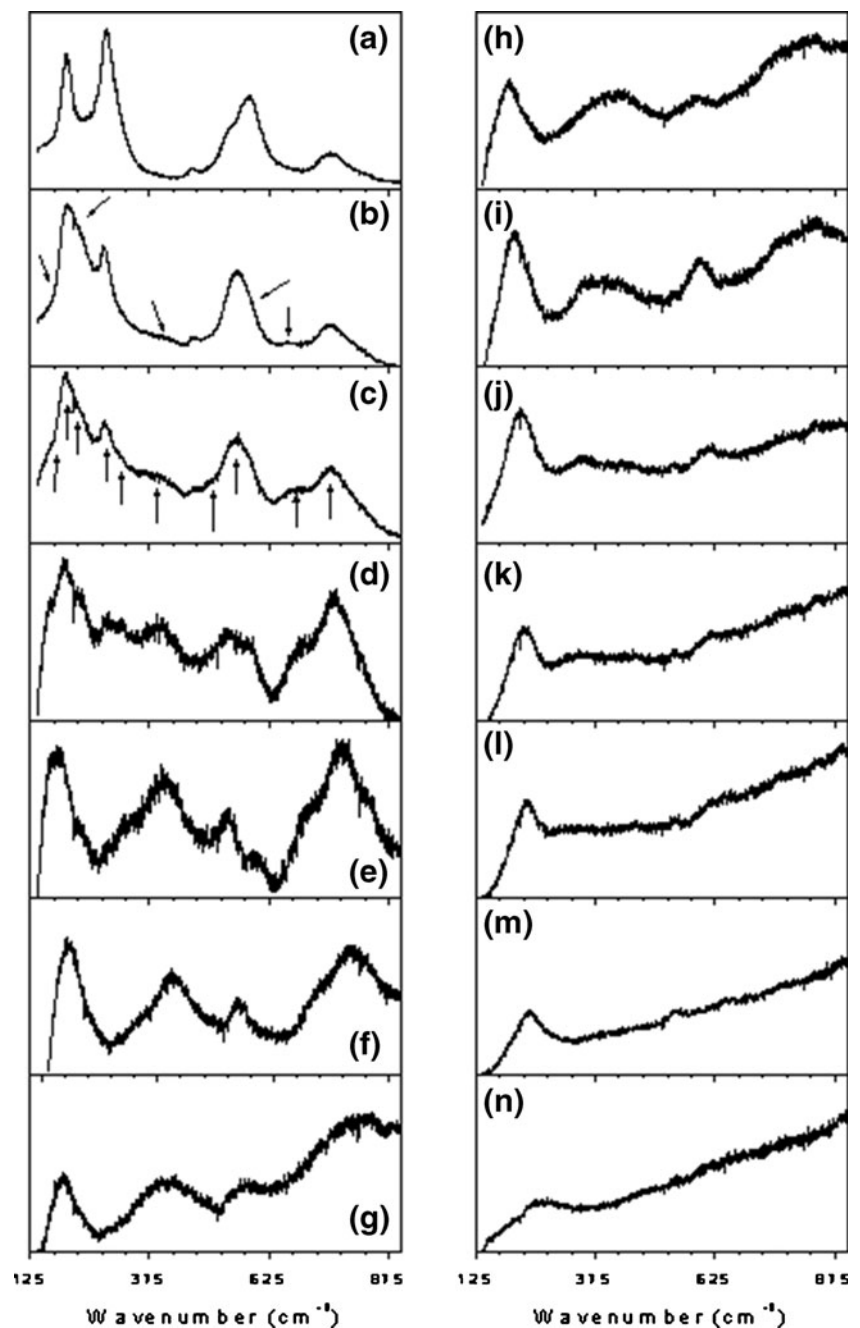
Further, it may be noted that uniform pressure from all sides on the sample could be attained in our Raman spectrometer sample holder/cell since the pressure transmitting media was hydrostatic and the sample size ‘very small’. This ensured uniformly spread changes in the sample. Consequently, it does not affect the Raman characteristics even if the spectrum is obtained from a slightly different sample area. Raman results given in Fig. 5 are discussed below. The first Raman peak appears to get broadened around 4 GPa.

The new Raman mode around 380 cm^{-1} which starts to appear around 4 GPa grows in intensity with increasing pressure. It is well known that the width (FWHM) parameter of a Raman mode is inversely proportional to the lifetime of the associated phonon. Therefore, the appearance followed by sharpening of the peak with increasing pressure clearly indicates two things viz., (a) establishment of a new phase and (b) establishment of the long range order with increasing pressure. Above 15 GPa, this peak once again changes its nature and starts to loose its intensity clearly showing the start of second phase transition. This is quite expected as the structure starts to attain an average paraelectric (cubic) phase above this pressure (as shown by XRD studies earlier).

The next striking feature is the appearance of the mode at 222 cm^{-1} (marked by arrow in Fig. 5). This mode is directly related with the displacement of Ti-cation and tilts of the BO_6 octahedra and has also been observed in a few other relaxor ferroelectrics such as PMN and NBT [25, 45]. This mode also appears around 3.5 GPa and starts to disappear above 15 GPa.

Another evidence for phase transition comes from the evolution of the phonon mode around 150 cm^{-1} . As has been reported earlier [45], this mode is directly related to the displacement of the Pb atom. This mode starts to appear around 4 GPa and shows softening with increasing pressure. This can only occur with increasing dominance of the new structure inside the crystal lattice. But this mode

Fig. 5 Evolution of Raman spectra in $\text{Pb}_{0.70}\text{Ca}_{0.30}\text{TiO}_3$ as a function of pressure at (a) 1.9 GPa, (b) 3.5 GPa, (c) 4.5 GPa, (d) 6.6 GPa, (e) 9.7 GPa, (f) 12.4 GPa, (g) 14.1 GPa, (h) 15.2 GPa, (i) 17.7 GPa, (j) 20.9 GPa, (k) 22.4 GPa, (l) 24.6 GPa, (m) 31.3 GPa and (n) 40 GPa



rapidly loses its intensity above 15 GPa. This further confirms that the system becomes predominantly cubic above 15 GPa.

The above results suggests that the new structure has its origin in the displacement of both Ti and Pb atoms. This indicates towards a monoclinic or a rhombohedral structure. But the rhombohedral structure similar to ones seen in other doped PbTiO_3 system can be ruled out as we did not observe any new superlattice peak above 4 GPa in the diffraction pattern discussed earlier. Further, by comparing the Raman spectra of monoclinic (Cm) phase observed in few other doped ferroelectric systems [25, 45–47], we can

suggest a probable establishment of an intermediate monoclinic phase in the PCT30 sample in the pressure range 4–15 GPa. This claim is suitably explained little later in the text.

Another important observation worth mentioning is the presence of large fluctuation in Raman spectra in the range 6.6–12.4 GPa. This can be a result of large stress felt by the lattice because of the competing structures namely (a) the new phase which is trying to establish itself globally within the lattice and (b) the starting parent tetragonal phase. This is a typical case of “nucleation” problem in the case of first order phase transition.

3.3 Deciphering the structure of the new phase

Most of the perovskite type ferroelectric materials based on BaTiO_3 and PbTiO_3 show a simple cubic structure at high temperatures and undergo a structural phase transitions to distorted structures upon cooling [48, 49]. Using the phenomenological sixth order Landau theory, Devonshire [50] was able to explain the observed phases and phase transition sequences. Very recently, Vanderbilt and Cohen, by extending the Landau theory up to the eighth order could also predict the existence of lower symmetric monoclinic phases in PbTiO_3 based ferroelectric materials [11, 29]. Following the experimental observations and theoretical calculations done on $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ showing the existence of a monoclinic phase between the tetragonal and cubic phase of the material, same strategy was applied to PCT system.

When the structure transforms from tetragonal to monoclinic phase the degeneracy of the E phonon of the tetragonal phase is lost. This results in the splitting of the A modes. In the monoclinic (Cm) phase, $5A_1+5A_2$ numbers of modes are expected in the Raman spectra. 10 Raman modes can be clearly observed in the Raman spectra obtained above 4 GPa (marked by arrows in the spectra for 4.5 GPa). This clearly points towards the establishment of a new structure similar to the monoclinic phase with Cm space group in the present PCT30 system.

To conclusively show the stabilization of a monoclinic phase, it would be interesting to (a) used a different LASER as excitation to avoid (or reduce) luminescence and (b) carry out Polarized Raman investigations which, even in ceramics, can reveal different dependencies on approaching phase transitions.

3.4 Reappearance of ferroelectricity above 20 GPa

Recently, it has been reported that PbTiO_3 shows a non-monotonous behaviour with pressure and results in an increase of ferroelectricity in PbTiO_3 above 30 GPa pressure [24]. This phenomenon was theoretically explained by the calculations based on density functional theory and the pseudo-potential method. The ferroelectric state is enhanced above the critical pressure in order to reduce the overlap between the hybridization levels of Ti (d_{eg} level) and O ($2s$ level) atoms. These overlaps are bound to happen when the pressure increases and the atoms come closer to each other. In the present case, we observe that the PCT30 system also shows an anomalous behaviour similar to PbTiO_3 . But the striking difference is that this feature starts to appear above 20 GPa as compared to PbTiO_3 where this feature occurs >30 GPa. Raman modes (expected in the ferroelectric phase start to reappear in the spectrum). The lowering of the critical pressure can be understood as a direct consequence of the substitution of

Pb^{2+} by Ca^{2+} . Because of this substitution, the tetragonal distortion ($(c/a) - 1$) of the host PbTiO_3 matrix decreases from ~ 0.06 to ~ 0.03 at room temperature which means that the displacement of O^{2-} with respect to Ti^{4+} in PCT system is smaller than that observed in pure PbTiO_3 . Due to decreasing unit cell size with increasing pressure, the two atoms (O and Ti) start to come closer to each other. This logically means that the overlap between the hybridization levels of Ti and O atoms will start to occur at a much lower pressure as compared to that in PbTiO_3 (which has higher tetragonal distortion). This is what is observed in our present investigation.

This result shows that the prediction by Kornev et al. [24] regarding the possibility of enhancement in ferroelectricity with increasing pressures in most ferroelectric materials such as PbTiO_3 , BaTiO_3 , BaZrO_3 , $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$, etc. is correct. But our investigations have shown that the affect of substituents will also play a major role in deciding the critical pressure above which the ferroelectric phase will reappear. Therefore the value of critical pressure is not unique. We hope that this study will pave way for comprehensive and detailed investigations for critical pressures in various other doped ferroelectric materials based on PbTiO_3 and BaTiO_3 . Another recent result reported by Angel et al. [51] exhibit that all pressure media exhibit non-hydrostatic components at high pressures which can result in deviation from cubic symmetry. Also, shear forces and/or stress are other possible reasons for deviation from cubic symmetry and, thus, resulting in the reappearance of Raman modes in the high pressure phase.

4 Conclusions

Detailed X-ray diffraction and Raman spectroscopy studies have been carried out to establish the pressure dependent phase transitions in PCT30 system. Using Le Bail fitting of pressure dependent synchrotron X-ray data, it has been shown that PCT30 system undergoes two phase transitions. It is shown that the first discontinuous change in the unit cell parameters occurs around 4 GPa. The second phase transition, with no discontinuous change in the slope of variation in unit cell parameters, is observed around 15 GPa. The system changes to its paraelectric phase (cubic) above this pressure of ~ 15 GPa. Although clear signature of the new monoclinic phase is not observed in the XRD data, it is believed to be a direct consequence of the establishment of the small domain size (smaller than the coherence length of X-rays) in the new monoclinic phase. Clear signature for occurrence of phase transition around 4 GPa could be obtained using pressure dependent Raman measurements. Appearance of new phonon modes is shown. These phonon modes can be expected by consid-

ering the monoclinic (Cm) phase. Using the recent theoretical studies of Cohen et. al. [11, 29], it has been argued that the structure transforms to monoclinic (Cm) phase around 4 GPa. Presence of a critical pressure of ~20 GPa has been established for PCT30 system above which the ferroelectric phase starts to reappear. This critical pressure is much lower than the one predicted for pure PbTiO₃. Reasons for this lowering of critical pressure have been discussed in the paper.

Acknowledgement AC acknowledges the financial support from BRNS, BARC, Mumbai. GDM thankfully acknowledge financial support and access to ELETTRA under ELETTRA user's program sponsored by DST (India) and Italian foreign Ministry. GDM also wishes to thank Dr. Ludmila Chudinovskikh for her help and useful suggestions during Raman spectroscopy measurements.

References

1. S. Lee, Z.-K. Liu, M.H. Kim, C.A. Randall, Influence of nonstoichiometry on ferroelectric phase transition in BaTiO₃. *J. Appl. Phys.* **101**, 054119 (2007)
2. A.V. Belushkin, D.P. Kozlenko, N.O. Golosova, P. Zetterstrom, B. N. Savenko, A study of disorder effects at ferroelectric phase transition in BaTiO₃. *Phys. B: Condens. Matter* **385–386**, 85 (2006)
3. Y.L. Wang, A.K. Tagantsev, D. Damjanovic, N. Setter, V.K. Yarmarkin, A.I. Sokolov, Anharmonicity of BaTiO₃ single crystals. *Phys. Rev. B* **73**, 132103 (2006)
4. A. Kojima, H. Sasou, K. Tozaki, T. Okazaki, Y. Yoshimura, N. Tokunaga, H. Iwasaki, Simultaneous measurements of thermal, electrical, and acoustic properties of BaTiO₃—new feature of 403 K phase transition. *Int. J. Thermophys.* **26**, 1963 (2005)
5. R.E. Alonso, C.O. Rodriguez, G.A. Lopez, First-principles study of the electric field gradient at the cubic-tetragonal phase transition in barium titanate. *Phys. Rev. B* **69**, 212106 (2004)
6. H. Fu, R.E. Cohen, Polarization rotation mechanism for ultrahigh electromechanical response in single-crystal piezoelectrics. *Nature* **403**, 281 (2000)
7. E.K. Akdogan, A. Safari, Thermodynamic theory of intrinsic finite size effects in PbTiO₃ nanocrystals. II. Dielectric and piezoelectric properties. *J. Appl. Phys.* **101**, 064115 (2007)
8. E.S. El-Frikhe, A. Toumanari, D. Khatib, Theory of the cubic-tetragonal phase transition in PbTiO₃. *Phys. Stat. Sol. C: Curr. Top. Sol. St. Phys.* **3**, 3332 (2006)
9. R. Emre, H.C. Semelhack, R. Boettcher, R. Holger, J. Banys, A. Matthes, H.J. Glaesel, D. Hirsch, E. Hartmann, Study of the tetragonal-to-cubic phase transition in PbTiO₃ nanopowders. *J. Phys. C: Condens. Matter* **18**, 3861 (2006)
10. G.A. Rossetti Jr., N. Maffei, Specific heat study and Landau analysis of the phase transition in PbTiO₃ single crystals. *Phys. C: Condens. Matter* **17**, 3953 (2005)
11. D. Vanderbilt, M.H. Cohen, Monoclinic and triclinic phases in higher-order Devonshire theory. *Phys. Rev. B* **63**, 094108 (2001)
12. B. Noheda, D.E. Cox, G. Shirane, J.A. Gonzalo, L.E. Cross, S.E. Park, A monoclinic ferroelectric phase in the PZT solid solution. *Appl. Phys. Lett.* **74**, 2059 (1999)
13. R. Guo, L.E. Cross, S.E. Park, B. Noheda, D.E. Cox, G. Shirane, Origin of the high piezoelectric response in PbZr_{1-x}Ti_xO₃. *Phys. Rev. Lett.* **84**, 5423 (2000)
14. D.M. Hatch, H.T. Stokes, R. Ranjan, Ragini, S.K. Mishra, D. Pandey, B.J. Kennedy, Antiferrodistortive phase transition in Pb(Ti_{0.48}Zr_{0.52}O₃): Space group of the lowest temperature monoclinic phase. *Phys. Rev. B* **65**, 212101 (2002)
15. T.T.A. Faria, L.A. Bassora, D. Garcia, J.A. Eiras, Ultrasonic and dielectric investigation of the (Sr, Pb) TiO₃-SPT ferroelectric ceramics. *Ferroelectrics* **336**, 161 (2006)
16. N.V. Zaitseva, E.P. Smirnova, V.V. Lemanov, Symmetry and lattice parameters of SrTiO₃-PbTiO₃ solid solutions. *Phys. Solid State* **49**, 510 (2007)
17. S.P. de Lazaro, P.R. de Lucena, J.R. Sambrano, S.P. Paula, A. Baltran, J.A. Varela, E. Longo, Pb_{1-x}Ca_xTiO₃ solid solution (x=0.0, 0.25, 0.50, and 0.75): A theoretical and experimental approach. *Phys. Rev. B* **75**, 144111 (2007)
18. A. Chandra, D. Pandey, Evolution of crystallographic phases in the system (Pb_{1-x}Ca_x)TiO₃: A Rietveld study. *J. Mater. Res.* **18**, 407 (2003)
19. D. Damjanovic, T.G. Gururaja, L.E. Cross, Anisotropy in piezoelectric properties of modified lead titanate ceramics. *Am. Ceram. Soc. Bull.* **66**, 699 (1987)
20. Y. Ito, Temperature-compensated PbTiO₃ ceramics for surface acoustic wave applications. *Appl. Phys. Lett.* **35**, 595 (1979)
21. S.Y. Kuo, C.T. Li, W.F. Hsieh, Lattice dynamics of perovskite Pb_xCa_{1-x}TiO₃. *Phys. Rev. B* **69**, 184104 (2004)
22. K.M. Rittenmeyer, R.Y. Ting, Piezoelectric and dielectric properties of calcium and samarium modified lead titanate ceramics for hydroacoustic applications. *Ferroelectrics* **110**, 171 (1990)
23. V.I. Torgashev, Y.I. Yuzyuk, V.V. Lemanov, C.A. Kuntscher, Raman spectroscopic study of the concentration phase transition in Pb_{1-x}Ca_xTiO₃ solid solutions. *Phys. Solid State* **48**, 765 (2006)
24. I.A. Kornev, L. Bellaiche, P. Bouvier, P.-E. Janolin, B. Dkhil, J. Kreisel, Ferroelectricity of perovskites under pressure. *Phys. Rev. Lett.* **95**, 196804 (2005)
25. J. Kreisel, B. Dkhil, P. Bouvier, J.M. Kiat, Effect of high pressure on relaxor ferroelectrics. *Phys. Rev. B* **65**, 172101 (2002)
26. G.A. Samara, Pressure-induced crossover from long- to short-range order in compositionally disordered soft mode ferroelectrics. *Phys. Rev. Lett.* **77**, 314 (1996)
27. A. Sani, M. Hanfland, D. Levy, The equation of state of PbTiO₃ up to 37 GPa: a synchrotron x-ray powder diffraction study. *J. Solid State Chem.* **167**, 446 (2002)
28. J. Frantti, Y. Fujioka, R.M. Nieminen, Pressure-induced phase transition in PbTiO₃: A query for the polarization rotation theory. *J. Phys. Chem. B* **111**, 4287 (2007)
29. Z. Wu, R.E. Cohen, Pressure-induced anomalous phase transitions and colossal enhancement of piezoelectricity in PbTiO₃. *Phys. Rev. Lett.* **95**, 037601 (2005)
30. S. Tinte, K.M. Rabe, D. Vanderbilt, Anomalous enhancement of tetragonality in PbTiO₃ induced by negative pressure. *Phys. Rev. B* **68**, 144105 (2003)
31. N. Jaouen, A.C. Dhaussy, J.P. Itie, A. Rogalev, S. Marinel, Y. Joly, High-pressure dependent ferroelectric phase transition in lead titanate. *Phys. Rev. B* **75**, 224115 (2007)
32. A. Chandra, D. Pandey, M.D. Mathews, A.K. Tyagi, Large negative thermal expansion and phase transition in (Pb_{1-x}Ca_x)TiO₃ (0.30 ≤ x ≤ 0.45) ceramics. *J. Mater. Res.* **20**, 350 (2005)
33. A. Chandra, R. Ranjan, D.P. Singh, N. Khare, D. Pandey, The effect of Pb²⁺ substitution on the quantum paraelectric behaviour of CaTiO₃. *J. Phys. Condens. Matter* **18**, 2977 (2006)
34. A. Chandra, Comment on "Pb_{1-x}Ca_xTiO₃ solid solution (x=0.0, 0.25, 0.50, and 0.75): A theoretical and experimental approach". *Phys. Rev. B* **77**, 017101 (2008)
35. S. Singh, O.P. Thakur, P. Chandra, K.K. Raina, Improved piezoelectric properties via mechano-chemical activation in modified PCT ceramics. *Mater. Chem. Phys.* **94**, 7 (2005)
36. S. Allen, J.S.O. Evans, Negative thermal expansion and oxygen disorder in cubic ZrMo₂O₈. *Phys. Rev. B* **68**, 134101 (2003)

37. A.W. Sleight, Negative thermal expansion materials. *Curr. Opin. Solid. State. Mater. Sci.* **3**, 128 (1998)
38. O. Sigmund, S. Torquato, Composites with extremal thermal expansion coefficients. *Appl. Phys. Lett.* **69**, 3202 (1996)
39. J.S.O. Evans, Negative thermal expansion materials. *J. Chem. Soc. Dalton Trans.* **19**, 3317 (1999)
40. T.A. Mary, J.S.O. Evans, T. Vogt, A.W. Sleight, Negative thermal expansion from 0.3 to 1050 Kelvin in ZrW_2O_8 . *Science* **90**, 272 (1996)
41. A.P. Hammersley, S.O. Svensson, M. Hanfland, A.N. Fitch, D. Hausermann, Two dimensional detector software: From real detector to idealised image or two theta scan. *High Press. Res.* **14**, 235 (1996)
42. B.P. Mandal, V. Grover, M. Roy, A.K. Tyagi, X-ray diffraction and Raman spectroscopic investigation on the phase relations in Yb_2O_3 - and Tm_2O_3 -substituted CeO_2 . *J. Am. Ceram. Soc.* **90**, 2961 (2007)
43. C.M. Foster, M. Grimsditch, Z. Li, V.G. Karpov, Raman line shapes of an harmonic phonons. *Phys. Rev. Lett.* **71**, 1258 (1993)
44. C.M. Foster, Z. Li, M. Grimsditch, S.K. Chan, D.J. Lam, Anharmonicity of the lowest-frequency $A_1(TO)$ phonon in $PbTiO_3$. *Phys. Rev. B* **48**, 10160 (1993)
45. J. Kreisel, A.M. Glazer, P. Bouvier, G. Lucazeau, High-pressure Raman study of a relaxor ferroelectric: The $Na_{0.5}Bi_{0.5}TiO_3$ perovskite. *Phys. Rev. B* **63**, 174106 (2001)
46. J. Rouquette, J. Haines, V. Bornand, M. Pintard, P. Papet, C. Bousquest, L. Konczewicz, F.A. Gorelli, H. Sull, Pressure tuning of the morphotropic phase boundary in piezoelectric lead zirconate titanate. *Phys. Rev. B* **70**, 014108 (2004)
47. J. Rouquette, J. Haines, V. Bornand, M. Pintard, P. Papet, F.A. Gorelli, Pressure induced rotation of spontaneous polarization in monoclinic and triclinic PZT. *J. Eur. Ceram. Soc.* **25**, 2393 (2005)
48. A.L. Kholkin, I. Bdikin, Y.I. Yuzyuk, A. Almeida, M.R. Chaves, M.L. Calzada, J. Mendiola, Raman scattering in sol-gel derived $PbTiO_3$ films modified with Ca. *Mater. Chem. Phys.* **85**, 176 (2004)
49. J.F. Meng, R.S. Katiyar, G.T. Zou, Grain size effect on ferroelectric phase transition in PBT ceramics. *J. Phys. Chem. Solids* **59**, 1161 (1998)
50. A. Devonshire, Theory of barium titanate. *Philos. Mag.* **40**, 1040 (1949)
51. R.J. Angel, M. Bujak, J. Zhao, G.D. Gatta, S.D. Jacobsen, Effective hydrostatic limits of pressure media for high-pressure crystallographic studies. *J. Appl. Crystallogr.* **40**, 26 (2007)