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Resolving the controversies about the ‘nearly cubic’ and other phases of $\text{Sr}_{1-x}\text{Ca}_x\text{TiO}_3$ ($0 \leq x \leq 1$): I. Room temperature structures

Sanjay Kumar Mishra¹, Rajeev Ranjan¹, Dhananjai Pandey¹ and H T Stokes²

¹ School of Materials Science and Technology, Institute of Technology, Banaras Hindu University, Varanasi-221005, India

² Department of Physics and Astronomy, Brigham Young University, Provo, UT 84602, USA

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Abstract

Results of a powder x-ray diffraction study are presented to show that the so-called ‘nearly cubic’ phase region of $\text{Sr}_{1-x}\text{Ca}_x\text{TiO}_3$, in fact, corresponds to two different types of crystal structures. The ‘nearly cubic’ phase occurring in the composition range $0.35 < x < 0.41$ is antiferroelectric in nature and its most plausible space group is $Pbcm$, while the crystal structure of the ‘nearly cubic’ phase for $0.41 \leq x < 0.70$ belongs to the space group $Pbnm$. This space group persists up to $x = 1.0$, even though the ‘nearly cubic’-like features disappear for $x \geq 0.70$. There are two other phase boundaries which occur around $0.05 < x < 0.06$ and $0.35 < x < 0.36$ and correspond to the change of structures with space groups $Pm3m$ to $Ibmm$ and $Ibmm$ to $Pbcm$, respectively.

1. Introduction

The mixed system $\text{Sr}_{1-x}\text{Ca}_x\text{TiO}_3$ has attracted considerable attention over the years [1–20]. While the end members, SrTiO_3 and CaTiO_3 , are well known quantum paraelectrics [21, 22], the mixed compositions are reported to exhibit quantum ferroelectric, relaxor ferroelectric and antiferroelectric transitions [14, 19, 8–10]. Both the end members and the mixed compositions also exhibit several antiferrodistortive structural phase transitions, which are linked with the phonon instabilities at the R ($q = \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$) and M ($q = \frac{1}{2}, \frac{1}{2}, 0$) points of the cubic Brillouin zone. The antiferrodistortive phase transitions induced by R and M point instabilities involve tilting of the oxygen octahedra in anti-phase and in-phase manners, respectively [23, 24]. Thus, SrTiO_3 , which has a cubic perovskite structure at room temperature, undergoes an anti-phase tilt transition to a tetragonal structure (space group $I4/mcm$, tilt system $a^0a^0c^-$ in the notation of Glazer [23, 24]) below 105 K [25, 26]. This structure seems to remain stable down to the

lowest temperature [27]. The other end member, CaTiO_3 , has orthorhombic structure (space group $Pbnm$, tilt system $a^-a^-c^+$) at room temperature and transforms to a tetragonal structure (space group $I4/mcm$, tilt system $a^0a^0c^-$) somewhere between 1373 and 1423 K and finally to the cubic perovskite structure above 1523 K [28]. Kennedy *et al* [29] have speculated about the existence of yet another intermediate phase with $Cmcm$ space group (tilt system $a^0b^+c^-$) in between the orthorhombic ($a^-a^-c^+$) and the tetragonal ($a^0a^0c^-$) phases. Vogt and Schmahl [30], on the other hand, suggest a direct transition from the orthorhombic to cubic phase without any intermediate phase.

The mixed $\text{Sr}_{1-x}\text{Ca}_x\text{TiO}_3$ (SCT $_x$) system shows complete solid solubility in the entire composition range ($0.00 \leq x \leq 1.00$). Several controversies with regard to the evolution of the structure of various crystalline phases of $\text{Sr}_{1-x}\text{Ca}_x\text{TiO}_3$ as a function of composition and temperature abound in the literature. Granicher and Jakits [1] reported the existence of cubic, tetragonal, 'nearly cubic', rhombohedral and orthorhombic phases at room temperature with increasing x . McQuarrie [2] reported occurrence of only cubic, tetragonal and orthorhombic phases. Ball *et al* [4] have proposed three phase boundaries corresponding to the crossover from the cubic (space group $Pm3m$) to tetragonal (space group $I4/mcm$, tilt system $a^0a^0c^-$) phase, the tetragonal $I4/mcm$ to an orthorhombic (space group $Bmmb$, tilt system $a^0b^+c^-$) phase and the orthorhombic $Bmmb$ phase to another orthorhombic phase (space group $Pbnm$, tilt system $a^-a^-c^+$) at $x > 0.05, 0.35$ and 0.60 , respectively. The $Bmmb$ space group (or $Cmcm$ in the standard setting) for the composition range $0.35 \leq x \leq 0.60$ corresponds to the 'nearly cubic' phase earlier reported by Granicher and Jakits [1]. Ranjan *et al* [7], on the other hand, proposed that the structure of SCT for $x = 0.50$, which falls within the 'nearly cubic' phase composition range, belongs to the orthorhombic $Pbnm$ space group. Yamanaka *et al* [15] have also proposed the orthorhombic $Pbnm$ space group for $x \geq 0.40$. The suggestions of Ball *et al* [4] and Ranjan *et al* [6] about the $Cmcm$ and the $Pbnm$ space groups for the 'nearly cubic' phase of SCT are based on Rietveld analysis of powder x-ray diffraction and neutron diffraction data, respectively. However, it is now known that it is not possible to distinguish between these two space groups using Rietveld analysis of powder diffraction data since both the models give identical goodness of fit [11]. Conventional and convergent beam electron diffraction studies have, however, unambiguously confirmed the correctness of the space group $Pbnm$ proposed earlier by Ranjan *et al* [6] and ruled out the $Cmcm$ space group [11, 17] for $x = 0.50$. Recently, Ranjan *et al* [9, 10] and Mishra *et al* [16] have also reported a 'nearly cubic'-like structure at low temperatures for $x = 0.30$ and 0.25 , and have attributed this structure to an antiferroelectric phase. This antiferroelectric phase gives rise to a new set of superlattice reflections not accountable in terms of the simple in-phase or anti-phase tilting of the oxygen octahedra. The space group of this 'nearly cubic'-like antiferroelectric phase has been shown to be $Pbcm$ [10], although the possibility of a still lower symmetry cannot be ruled out. It is thus evident that both the $Pbnm$ space group for $x = 0.50$ at room temperature, and the $Pbcm$ space group for $x = 0.25$ and 0.30 at low temperatures, can give rise to 'nearly cubic'-like features in powder diffraction patterns. The room temperature structure of the SCT compositions exhibiting 'nearly cubic'-like powder diffraction patterns can therefore correspond to either the $Pbnm$ or the $Pbcm$ space group.

In this paper, we show that the correct space groups for the 'nearly cubic' phase of SCT in the composition ranges $0.35 < x \leq 0.40$ and $0.40 < x < 0.70$ are $Pbcm$ and $Pbnm$, respectively. In addition, we also present results for the composition ranges $0 \leq x < 0.36$ and $0.70 \leq x \leq 1$ to give a complete and up-to-date picture of the various phase boundaries as a function of composition (x) in the mixed SCT system. A brief group theoretical discussion of the nature of these phase boundaries is also presented.

2. Experimental details

Specimens of SCT were prepared by the solid state reaction method using powders of SrCO_3 , CaCO_3 and TiO_2 each of minimum 99.5% purity. These powders were thoroughly mixed in stoichiometric amounts in a ball mill containing a zirconia jar and balls using acetone as the mixing medium. Calcination of the mixed powder was carried out at 1150°C for 6 h. The calcined powder was pressed into circular pellets of 13 mm diameter and ~ 1.25 mm thickness using a uniaxial hydraulic press at an optimized load of 65 kN. Sintering of the green pellets was carried out at 1300°C for 6 h in air. For powder x-ray diffraction experiments, the sintered pellets were crushed to fine powder and subsequently annealed at 800°C to remove strains introduced, if any, during crushing. X-ray diffraction was carried out using an 18 kW Rigaku rotating anode based powder diffractometer having a Cu target and fitted with a graphite monochromator.

3. Principle of data analysis

As discussed by Glazer [23, 24], most of the non-cubic perovskite structures can be described in terms of small distortions of the cubic perovskite structure. These distortions may be brought about by tilts of the octahedra and displacements of the cations/anions. The octahedral tilt leads to the splitting of the cubic x-ray powder diffraction lines and also to the appearance of superlattice reflections. The Miller indices of the superlattice reflections based on a doubled pseudo-cubic cell carry information about the nature of the octahedral tilts in the structure. All-odd (o) integered (‘ooo’ type indices) superlattice reflections correspond to the anti-phase (–) tilt of the adjacent octahedra whereas the superlattice reflections with two odd and one even integer indices (i.e. ‘ooe’ type) to the in-phase (+) tilt of the adjacent octahedra [23, 24]. From a knowledge of the Miller indices of the superlattice reflections and nature of the distortion of the cubic lattice, as revealed by the splitting of the cubic powder diffraction peaks, one can drastically restrict the number of plausible space groups [23, 24] to be considered in the Rietveld refinement. In the present work, Rietveld refinement was carried out with the Fullprof programme³ using x-ray powder diffraction data in the two-theta range 20° – 120° . A pseudo-Voigt function was used to model the peak profiles. The background was fitted using a sixth order polynomial. Except for the occupancy parameters of the atoms, which were fixed corresponding to the nominal composition, all other parameters, i.e., scale factor, zero displacement, isotropic profile parameters, lattice parameters, isotropic thermal parameters and positional coordinates, were refined.

4. Results

4.1. Definition of the ‘nearly cubic’ and outside the ‘nearly cubic’ regions

Figure 1 depicts the x-ray diffraction profiles of 444 and 800 Bragg reflections (the indices are with respect to a doubled pseudocubic cell) for SCT compositions with $x = 0.00, 0.06, 0.12, 0.35, 0.40, 0.50, 0.60, 0.70, 0.80$, and 1.00 . For $x = 0.00$, the 444 and 800 peaks are singlets characteristic of a cubic structure. For $0.06 \leq x \leq 0.35$, the 444 peak is a singlet while 800 is split into two peaks. This has been interpreted in terms of a pseudo-tetragonal distortion of the elementary cubic perovskite cell [4]. For $0.35 < x < 0.70$, the 444 peak is still a singlet whereas the splitting of the 800 peak is not discernible; instead, a broad hump is

³ Rodriguez J-Carvajal. FULLPROF. A Rietveld Refinement and Pattern Matching Analysis Program. Laboratoire Leon Brillouin (CEA-CNRS), France.

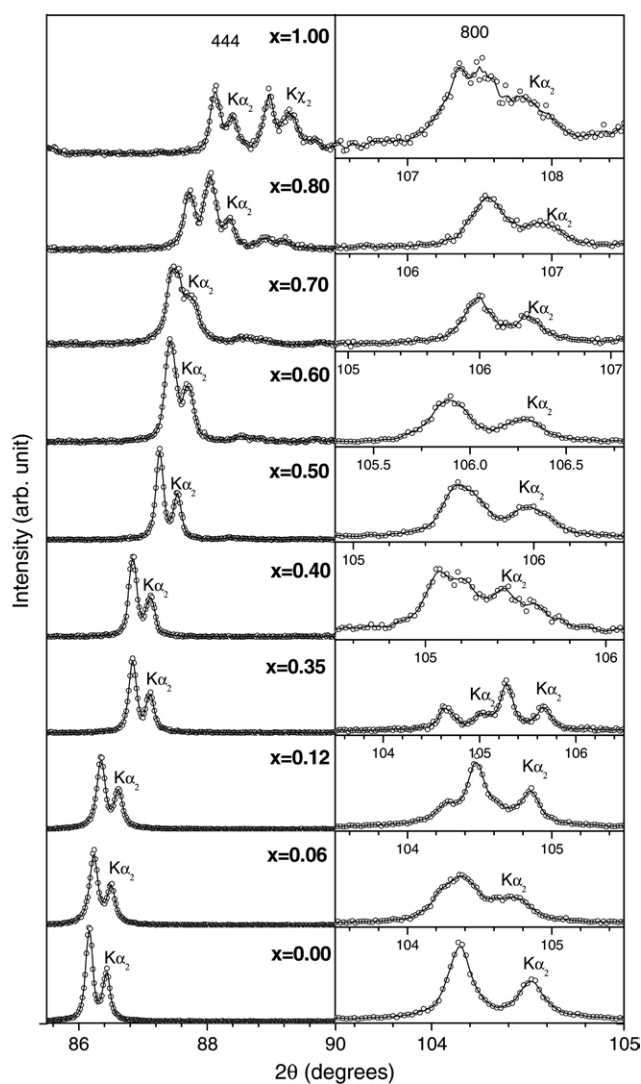


Figure 1. Evolution of the 444 and 800 elementary perovskite reflections as a function of composition (x) of $\text{Sr}_{1-x}\text{Ca}_x\text{TiO}_3$. The indices are with respect to a doubled pseudo-cubic unit cell.

observed. This composition range has been termed as ‘nearly cubic’ in the literature [1, 4]. For $x \geq 0.70$, the 444 peak appears as a doublet, which is less clear for $x = 0.70$ but has become quite evident for $x = 0.80$ and 1.00 in figure 1. The 800 peak for these two compositions is also a doublet. These features have been interpreted in terms of a pseudo-monoclinic distortion of the elementary cubic perovskite cell [4]. Thus the composition ranges $0.06 \leq x \leq 0.35$ and $0.70 \leq x \leq 1.00$ lie outside the ‘nearly cubic’ phase region of $0.35 < x < 0.70$.

4.2. Structures in the ‘nearly cubic’ region

Figure 2 shows a portion of the x-ray powder diffraction pattern of SCT in the two-theta range of 35° – 65° for various compositions in the range $0.35 \leq x \leq 0.43$. Except for $x = 0.35$,

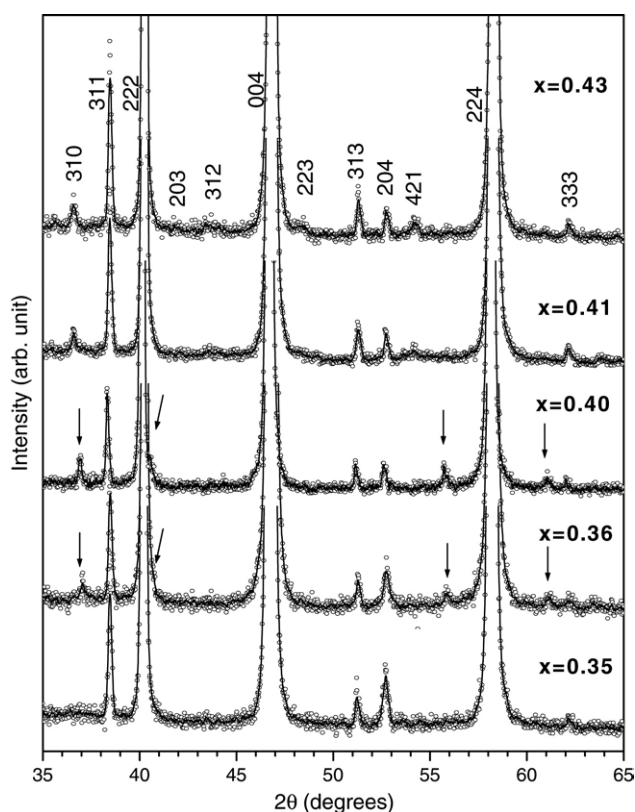


Figure 2. Powder x-ray diffraction patterns of $\text{Sr}_{1-x}\text{Ca}_x\text{TiO}_3$ with $x = 0.35, 0.36, 0.40, 0.41,$ and 0.43 in the two-theta range 35° – 65° . The arrows mark the additional superlattice peaks which are not related to simple octahedral tilts. The Miller indices are with respect to the doubled pseudocubic cell.

the rest of the compositions in this range belong to the ‘nearly cubic’ region. The profiles in figure 2 have been suitably zoomed to reveal the weak superlattice peaks. As a result of this zooming, some of the perovskite peaks (222, 004 and 224) appear truncated in this figure. The Miller indices of the superlattice reflections for $x = 0.41$ and 0.43 , indexed with respect to a doubled pseudocubic cell, are of all-odd (ooo), two-odd–one-even (ooe) and two-even–one-odd (oeo) types. Identical superlattice reflections are observed in the powder diffraction pattern for $x = 0.50$ [4, 6] for which the $Pbnm$ space group has been established unambiguously [11, 17]. In contrast, for $x \geq 0.41$, the Miller indices of the superlattice reflections for $x = 0.35$ (which is just outside the ‘nearly cubic’ composition range on the SrTiO_3 end) are of all-odd (ooo) type only. For the intermediate composition range $0.35 < x < 0.41$, one observes ooo type superlattice peaks along with four additional weak reflections around $2\theta = 37.1^\circ, 40.7^\circ, 56.2^\circ,$ and 61.2° , as can be seen from figure 2 for $x = 0.36$ and 0.40 . The presence of these four new weak reflections clearly indicates that the structure of SCT in the composition range $0.36 \leq x \leq 0.40$ is different from the structure for $0.41 \leq x < 0.70$ of the ‘nearly cubic’ phase region as well as for $0.06 \leq x \leq 0.35$, which is outside the ‘nearly cubic’ phase region.

We carried out Rietveld refinement for $x = 0.40$ first using the $Pbnm$ and $Cmcm$ space groups proposed by earlier workers for the ‘nearly cubic’ phase of SCT. The orthorhombic lattice parameters (A_o, B_o and C_o) for the $Pbnm$ space group are related to the corresponding

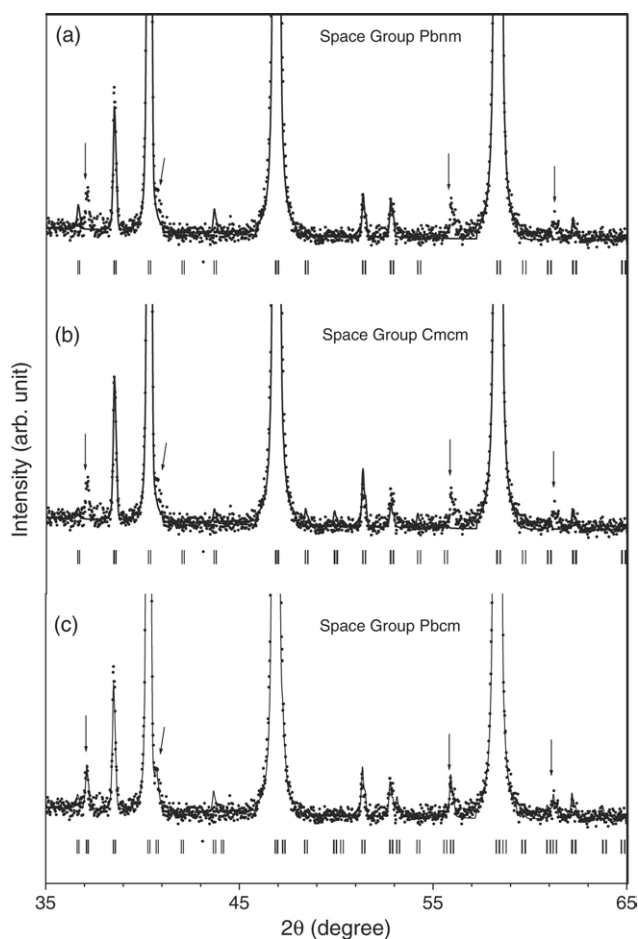


Figure 3. Observed (dots) and calculated (continuous line) profiles in the 2θ range 35° – 65° , obtained after the Rietveld refinement of $\text{Sr}_{1-x}\text{Ca}_x\text{TiO}_3$ with $x = 0.40$ using orthorhombic space groups (a) *Pbnm*, (b) *Cmcm* and (c) *Pbcm*.

elementary pseudocubic perovskite cell parameters (a_p , b_p and c_p) through the relations $A_o \approx \sqrt{2}a_p$, $B_o \approx \sqrt{2}b_p$ and $C_o \approx 2c_p$. In the *Pbnm* space group, Sr/Ca occupies the 4c Wyckoff site at $(0 \pm u, \frac{1}{2} \pm v, \frac{1}{4})$ and Ti occupies the 4a Wyckoff site at $(0, 0, 0)$. There are two types of oxygen atoms: O(1) at the 4c Wyckoff site at $(0 \pm u, 0 \pm v, \frac{1}{4})$ and O(2) at the 8d Wyckoff site at $(\frac{1}{4} \pm u, \frac{1}{4} \pm v, 0 \pm w)$. The orthorhombic lattice parameters (A_o , B_o and C_o) for the *Cmcm* space group are related to the corresponding elementary pseudocubic perovskite cell parameters (a_p , b_p and c_p) through the relations $A_o \approx 2a_p$, $B_o \approx 2b_p$ and $C_o \approx 2c_p$. In the *Cmcm* space group, two types of Sr/Ca atoms occupy the 4c Wyckoff sites at $(0, 0 \pm v, \frac{1}{4})$ and $(0, \frac{1}{2} \pm v, \frac{1}{4})$, and Ti occupies the 8d Wyckoff site at $(\frac{1}{4}, \frac{1}{4}, 0)$. There are three types of oxygen atoms: O(1) at the 8e Wyckoff site at $(\frac{1}{4} \pm u, 0, 0)$, O(2) at the 8f Wyckoff site at $(0, \frac{1}{4} \pm v, 0 \pm w)$ and O(3) at the 8g Wyckoff site at $(\frac{1}{4} \pm u, \frac{1}{4} \pm v, \frac{1}{4})$. Figures 3(a) and (b) depict the observed and calculated profiles of SCT with $x = 0.40$ for the *Pbnm* and *Cmcm* space groups obtained by Rietveld refinement. A clear mismatch between the observed and the fitted data is observed in this figure for the four new reflections marked with arrows. However, the

Table 1. Refined structural parameters of Sr_{1-x}Ca_xTiO₃ with x = 0.43 at 300 K using orthorhombic space group *Pbnm*.

Atoms	Positional coordinate			Thermal parameter
	X	Y	Z	
Sr/Ca	-0.001(1)	0.5067(2)	0.2500	0.55(2)
Ti	0.0000	0.0000	0.0000	0.43(2)
O(1)	-0.055(3)	-0.001(1)	0.25	-0.04(25)
O(2)	0.232(4)	0.266(4)	0.022(2)	1.5736
$A_o = 5.479\,93(34)\text{ \AA}$, $B_o = 5.480\,23(35)\text{ \AA}$, $C_o = 7.742\,32(11)\text{ \AA}$, volume = $232.51(2)\text{ \AA}^3$				
$R_p = 9.33$, $R_{wp} = 12.5$, $R_{exp} = 6.36$, $\chi^2 = 3.86$, $R_B = 5.87$				

fits for other superlattice reflections and the main perovskite reflections are quite satisfactory. This analysis undoubtedly proves the incorrectness of the *Pbnm* or the *Cmcm* space groups for the composition range $0.35 < x < 0.41$. In fact, irrespective of the space group proposed, it is not possible to index the new weak reflections on the basis of a doubled pseudocubic cell ($2a_p \times 2b_p \times 2c_p$). It is thus imperative to consider a larger supercell to account for the four new reflections.

It has been shown by Ranjan *et al* [8–10] and Mishra *et al* [16] that $x = 0.30$ and 0.25 compositions undergo a paraelectric to antiferroelectric phase transition at 230 and 185 K, respectively. This transition is characterized by (i) an anomaly in the temperature dependence of the dielectric constant, with a negative Curie–Weiss temperature, and (ii) the appearance of new superlattice reflections in the x-ray and neutron powder diffraction patterns. The superlattice reflections observed by us in figure 2 at $2\theta = 37.1, 40.7, 56.2,$ and 61.2 for $x = 0.36$ and 0.40 are similar to the antiferroelectric superlattice reflections reported by Ranjan *et al* [10] for $x = 0.30$ below 230 K. PbZrO₃ and NaNbO₃ are typical examples of perovskite materials exhibiting antiferroelectric phase transition. Ranjan *et al* [10] have shown using Rietveld analysis that the new weak reflections characteristic of the antiferroelectric phase in SCT cannot be accounted for using a PbZrO₃ type structural model with *Pbam* space group. An excellent fit was, on the other hand, obtained with a NaNbO₃ type structural model (*Pbcm* space group), for which the orthorhombic *c*-lattice parameter is four times the elementary perovskite *c*-lattice parameter. Cochran and Zia [31] have suggested that this antiferroelectric structure is due to freezing of a Δ ($q = 0, 0, 1/4$) point phonon. We, therefore refined the structure of SCT with $x = 0.40$ using the *Pbcm* space group. For the *Pbcm* space group, the asymmetric unit of the structure consists of two Sr/Ca (Sr/Ca(1) and Sr/Ca(2)), one Ti and four O atoms (O(1), O(2), O(3), and O(4)). Sr/Ca(1) occupies the 4c Wyckoff site at $(\frac{1}{4} \pm u, \frac{3}{4}, 0)$ and Sr/Ca(2) the 4d Wyckoff site at $(\frac{1}{4} \pm u, \frac{3}{4} \pm v, \frac{1}{4})$, respectively. Ti occupies the 8e Wyckoff site at $(\frac{1}{4} \pm u, \frac{1}{4} \pm v, \frac{1}{8} \pm w)$. The oxygen atom O(1) occupies the 4c Wyckoff site at $(\frac{1}{4} \pm u, \frac{1}{4}, 0)$, O(2) the 4d Wyckoff site at $(\frac{1}{4} \pm u, \frac{1}{4} \pm v, \frac{1}{4})$, O(3) the 8e Wyckoff site at $(\frac{1}{2} \pm u, 0 \pm v, \frac{1}{8} \pm w)$ and O(4) the 8e Wyckoff site at $(0 \pm u, \frac{1}{2} \pm v, \frac{1}{8} \pm w)$. Figure 3(c) depicts the observed and calculated profiles for $x = 0.40$ after the final refinement using the *Pbcm* space group. It is evident that the four new weak reflections at $2\theta = 37.1, 40.7, 56.2$ and 61.2 are nicely accounted for using this space group. The agreement factors obtained at the end of the refinement are quite satisfactory. The overall fit and the difference profile is shown in figure 4 for the 2θ range 20° – 110° . The refined structural parameters for $x = 0.40$ are given in table 1. The nearly equal values of the elementary pseudocubic perovskite cell parameters $a_p = 3.8774\text{ \AA}$, $b_p = 3.8775\text{ \AA}$ and $c_p = 3.8744\text{ \AA}$, derived from A_o , B_o and C_o values given in table 1 using

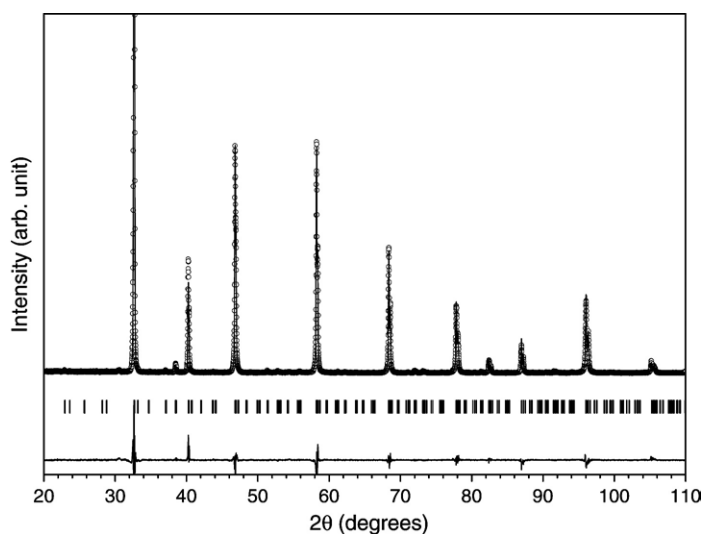


Figure 4. Observed (open circle), calculated (continuous line) and difference (bottom line) profiles in the 2θ range 20° – 110° , obtained after the Rietveld refinement of $\text{Sr}_{1-x}\text{Ca}_x\text{TiO}_3$ with $x = 0.40$ using orthorhombic space group $Pbcm$.

the relationships $A_o \approx \sqrt{2}a_p$, $B_o \approx \sqrt{2}b_p$ and $C_o \approx 4c_p$, clearly show that the structure of SCT for $x = 0.40$ belongs to the ‘nearly cubic’ type (i.e. $a_p \approx b_p \approx c_p$) but its space group is $Pbcm$ and not $Pbnm$ or $Cmcm$ as believed earlier.

For the sake of completeness, Rietveld refinement was also carried out for other structure in the ‘nearly cubic’ phase region taking $x = 0.43$ as a representative composition. The powder diffraction pattern for this composition is similar to that of $x = 0.50$ for which the $Pbnm$ space group has already been confirmed by electron diffraction studies [11, 17]. Figure 5 depicts the observed, calculated and difference profiles, obtained after the final cycle of refinement for $x = 0.43$ using this space group. The fit is quite good. Table 2 lists the various refined structural parameters along with the agreement (R) factors. The near equality of the elementary perovskite cell parameters, $a_p = 3.8748(9)$ Å, $b_p = 3.8751(1)$ Å and $c_p = 3.8711(6)$ Å, derived from the refined cell parameters given in table 2 using the relationships $A_o \approx \sqrt{2}a_p$, $B_o \approx \sqrt{2}b_p$ and $C_o \approx 2c_p$, clearly confirms the ‘nearly cubic’-like feature for $x = 0.43$ also.

We thus conclude that the space groups for the ‘nearly cubic’ phase regions $0.35 < x < 0.41$ and $0.41 \leq x < 0.70$ are $Pbcm$ and $Pbnm$, respectively.

4.3. Structures outside the ‘nearly cubic’ region

Of the two composition ranges outside the ‘nearly cubic’ phase region mentioned in section 4.1, the x-ray powder diffraction patterns for $0.06 \leq x \leq 0.35$ contain superlattice reflections with all-odd type Miller indices only (see the pattern for $x = 0.35$ in figure 2). This suggests that the structure has only ‘–’ or anti-phase octahedral tilts [23, 24]. Similar superlattice reflections are observed in the tetragonal phase of SrTiO_3 stable below 105 K and for which the space group $I4/mcm$ with the $a^0a^0c^-$ tilt system has been confirmed [23–26]. In analogy with SrTiO_3 , most of the workers [4, 5, 15, 20] have proposed the $I4/mcm$ space group for SCT for the composition range $0.06 \leq x \leq 0.35$. Ranjan *et al* [10] have, however, assigned the orthorhombic space group $Ibmm$ with the $a^-a^-c^0$ tilt system for this composition range. Rietveld analysis of the powder diffraction data is not of any help in making a choice between

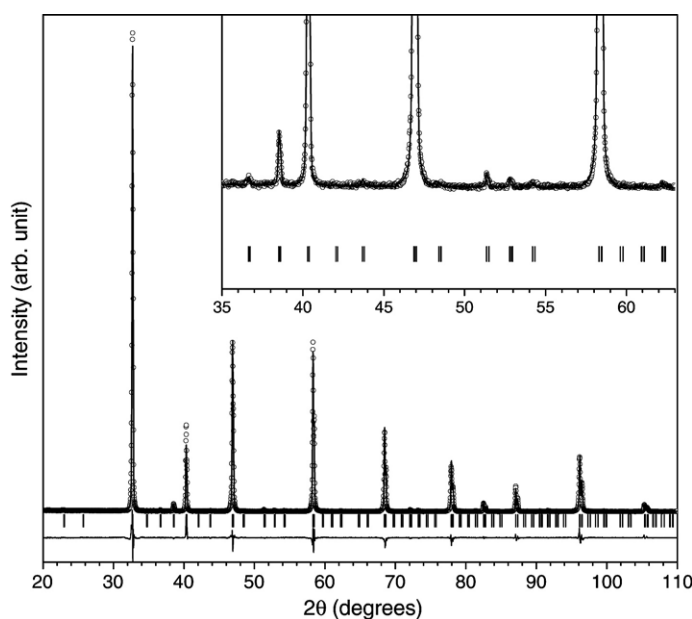


Figure 5. Observed (open circle), calculated (continuous line) and difference (bottom line) profiles in the 2θ range 20° – 120° , obtained after the Rietveld refinement of $\text{Sr}_{1-x}\text{Ca}_x\text{TiO}_3$ with $x = 0.43$ using orthorhombic space group $Pbnm$. The inset shows the zoomed pattern for the 2θ range 35° – 65° to highlight the fits for the weak superlattice peaks due to octahedral tilts.

Table 2. Refined structural parameters of $\text{Sr}_{1-x}\text{Ca}_x\text{TiO}_3$ with $x = 0.40$ at 300 K using orthorhombic space group $Pbcm$.

Atoms	Positional coordinate			Thermal parameter
	X	Y	Z	
Sr/Ca(1)	0.255 93(7)	0.7500	0.000	1.33(1)
Sr/Ca(2)	0.245 15(6)	0.757 36(9)	0.2500	0.557(2)
Ti	0.251 1(1)	0.260 32(8)	0.1237(7)	0.703(4)
O(1)	0.268 1(4)	0.2500	0.000	3.171(2)
O(2)	0.208 64(3)	0.247 3(3)	0.2500	0.891(1)
O(3)	0.515 4(1)	0.028 0(7)	0.1376(8)	1.117(5)
O(4)	−0.012 4(1)	0.487 0(6)	0.1120(6)	2.756(3)

$A_0 = 5.483\,50(9)\text{ \AA}$, $B_0 = 5.485\,95(9)\text{ \AA}$, $C_0 = 15.497\,52(17)\text{ \AA}$, volume = $466.2(1)\text{ \AA}^3$
 $R_p = 9.78$, $R_{wp} = 13.1$, $R_{exp} = 8.20$, $\chi^2 = 2.55$, $R_B = 5.34$

the $I4/mcm$ and the $Ibmm$ space groups as both give comparable agreement factors. Evidence in support of the orthorhombic symmetry of these compositions comes from Raman scattering studies [18]. The $I4/mcm$ space group predicts seven first order lines in the Raman spectra that are indeed observed in the tetragonal phase of SrTiO_3 and SCT with $x = 0.007$ below their respective antiferrodistortive phase transition temperatures [32, 19]. For $x = 0.06$ and 0.12 , however, one observes four more Raman lines than those expected on the basis of the $I4/mcm$ space group [18]. The disorder modes in the cubic phase of SCT for $x < 0.06$ and $0.06 \leq x \leq 0.35$ are also quite different indicating the difference in the local structures which are characteristic of the structure of the lower temperature non-cubic phase [18]. This rules out

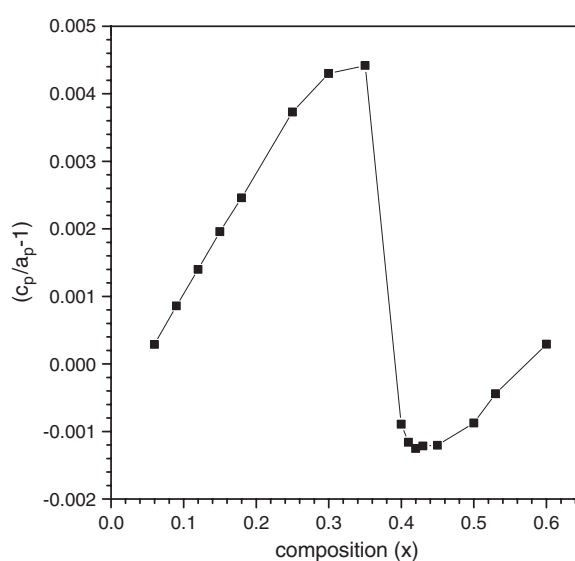


Figure 6. Variation of pseudo-tetragonal distortion ($c_p/a_p - 1$) with composition (x).

the $I4/mcm$ space group for the composition range $0.06 \leq x \leq 0.35$. As shown by Mishra *et al* [18], these additional Raman lines are consistent with the $Ibmm$ space group. It may be mentioned that although the lattice parameters obtained for the $Ibmm$ space group bear a pseudotetragonal relationship (i.e. $a_p \approx b_p$), they do not fit into Glazer's model [23, 24] of the $a^-a^-c^0$ tilt system for which $a_p \approx b_p > c_p$. In the SCT compositions $0.06 \leq x \leq 0.35$, $a_p \approx b_p < c_p$, which may be linked with non-rigid rotation of the octahedra and/or the coupling of the primary order parameter (i.e. the tilt angle) with the lattice strain. Rietveld analysis of both the powder x-ray and neutron diffraction data for $x = 0.12$ lead to Ti–O bond lengths of 1.951 and 1.950 Å for the $Ibmm$ space group. These bond lengths are comparable to the Ti–O bond length of 1.9525 Å in cubic SrTiO₃ ruling out any significant distortion of the Ti–O bonds being responsible for the $a_p \approx b_p < c_p$. The pseudo-tetragonal distortion ($c_p/a_p - 1$) is sufficiently large for $x = 0.35$, and decreases with decreasing x , becoming zero for $x = 0.055$ (figure 6). A concomitant decrease in the intensity of the 311 pseudocubic superlattice reflection is also observed with decreasing x , which vanishes just below $x = 0.06$ (figure 7). Since the intensity of the superlattice reflections is a measure of the tilt angle of the octahedra, the vanishing intensity implies disappearance of the octahedral tilt for $x < 0.06$. This confirms that the structure of SCT becomes simple cubic ($Pm3m$) at room temperature for $x < 0.06$. For $x > 0.35$, the pseudotetragonal distortion drops abruptly at the onset of the so-called 'nearly cubic' phase region.

For the composition range $0.70 \leq x \leq 1.00$, which is outside the 'nearly cubic' phase region on the CaTiO₃ rich end, it is unanimously agreed by all workers [3–6, 11, 15] that the structure belongs to the $Pbnm$ space group with $a^-a^-c^+$ tilt system.

5. Discussion

The results presented in the previous section indicate the change of space group from $Pm3m$ to $Ibmm$ at $0.05 < x < 0.06$, $Ibmm$ to $Pbcm$ at $0.35 < x < 0.36$ and $Pbcm$ to $Pbnm$ at $0.40 < x < 0.41$. These phase boundaries are shown in figure 8, which depicts the variation

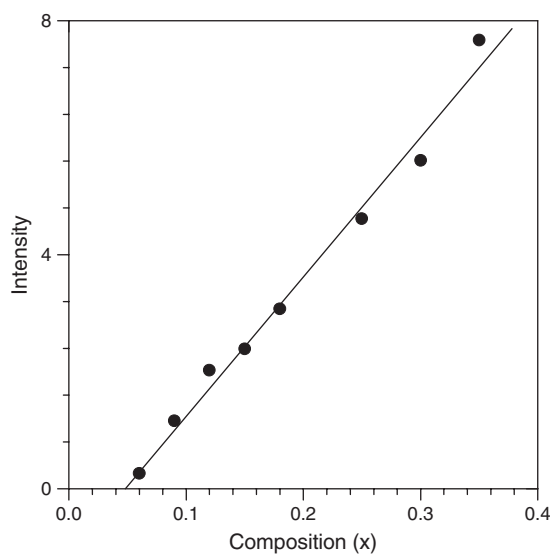


Figure 7. Variation of peak intensity of the 311 superlattice reflection, normalized with respect to the peak intensity of the neighbouring 220 reflection, with composition (x).

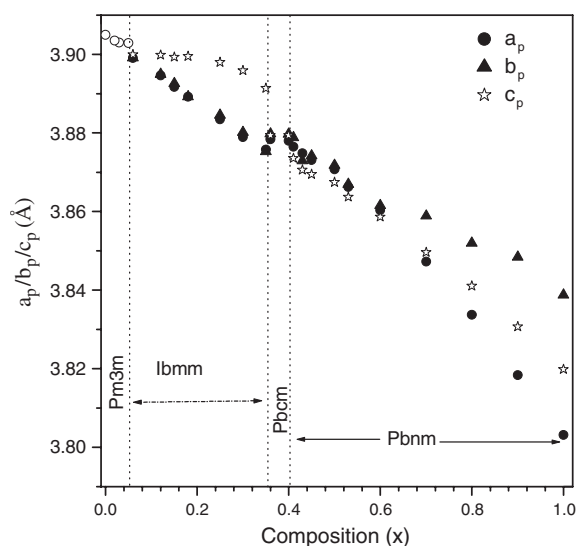


Figure 8. Variation of the elementary perovskite cell parameters (a_p , b_p and c_p) with composition (x) depicting the various phase boundaries at $x = 0.05 < x < 0.06$, $0.35 < x < 0.36$ and $0.40 < x < 0.41$.

of the elementary perovskite cell parameters (a_p , b_p and c_p) as a function of composition at room temperature. It is evident from this figure that these cell parameters are nearly equal in the composition range $0.35 < x < 0.70$.

We now proceed to examine the nature of these phase boundaries using group theoretical considerations. In order to understand the nature of the various phase boundaries in SCT, we depict in figure 9 the variation of the c_p lattice parameter with composition on a magnified scale.

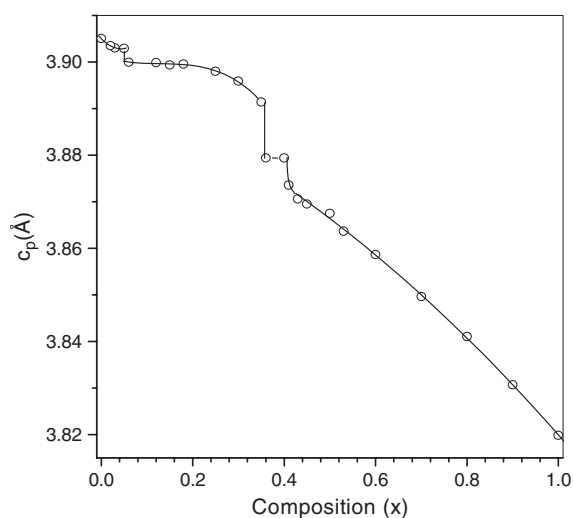


Figure 9. Variation of the elementary perovskite c -parameter (c_p) with composition (x).

It is evident from this figure that this cell parameter changes discontinuously at all the three phase boundaries. The discontinuous changes of c_p at $0.05 < x < 0.06$ and $0.40 < x < 0.41$ were missed by Ball *et al* since their data were collected at $\Delta x = 0.05$ intervals. The small discontinuity at $0.05 < x < 0.06$ is well outside the standard deviation whose value is smaller than the size of the circles in figure 9. Another feature missed by Ball *et al* in their study is the existence of the $Pbcm$ space group in the composition range $0.35 < x < 0.41$. The discontinuous change of the cell parameter in figure 9 implies the first order nature of the three boundaries. As discussed below, the first order nature of these boundaries is also consistent with Landau theory considerations.

For the phase boundary at $0.05 < x < 0.06$, we consider both $Pm3m-I4/mcm$ and $Pm3m-Ibmm$ possibilities. According to Howard and Stokes [33], both $I4/mcm$ and $Imma$ are subgroups of $Pm3m$ but Landau theory predicts that the $Pm3m-I4/mcm$ transition is continuous whereas the $Pm3m-Imma$ ($\equiv Ibmm$) transition is discontinuous (i.e. first order) in nature. The observed discontinuity in the c_p cell parameter is therefore consistent with the $Imma$ space group and not the $I4/mcm$ space group.

The next question that remains to be answered now is how the $Pbcm$ structure ($0.356 < x \leq 0.40$) is group-theoretically related to the $Imma$ and $Pnma$ ($\equiv Pbnm$) space groups for $x < 0.36$ and $x > 0.40$. Howard and Stokes [33] give the lattice vectors for both $Imma$ and $Pnma$ as $(0, 1, 1)$, $(2, 0, 0)$, $(0, 1, -1)$, in terms of the lattice vectors of $Pm3m$. Since in $Pbcm$ the lattice parameters are $A_o \approx B_o \approx \sqrt{2}a_p$ and $C_o \approx 4c_p$, we choose the lattice vectors of $Pbcm$ to be $(0, 1, -1)$, $(0, 1, 1)$, $(4, 0, 0)$, a set which is consistent with the choice for $Imma$ and $Pnma$ and also with the known lengths. We use these lattice vectors to transform the atomic positions in $Pbcm$ (table 1) into positions with respect to the $Pm3m$ lattice, and find that we can obtain the atomic positions in $Pm3m$ (with small distortions) if we put the origin of $Pbcm$ at $(1/2, 1/2, 0)$ with respect to the origin of $Pm3m$. Knowing the lattice vectors and origin of $Pbcm$, we use the ISOTROPY software [34] to decompose the $Pbcm$ distortions in terms of IRs of $Pm3m$. We find that the primary distortions belong to $R4+$ and Δ_5 . No $M3+$ distortions are present. Therefore, we conclude that the $Pbcm$ structure possesses $a^0b^-b^-$ tilt and an additional antiferroelectric distortion belonging to Δ_5 . $Pbcm$ is

a subgroup of *Imma* since the structure can change from *Imma* to *Pbcm* by an infinitesimal Δ_5 distortion. Using ISOTROPY, we determined that this distortion belongs to the Δ_4 IR of *Imma*. A phase transition from *Imma* to *Pbcm* would not be continuous, according to Landau theory [35], since the Lifshitz condition is not met for the IR Δ_4 . This prediction is consistent with the experimental observation which reveals a discontinuous change of c_p at the *Imma*–*Pbcm* phase boundary at $0.35 < x < 0.36$ (see figure 9). The discontinuous change in the c_p parameter at $0.40 < x < 0.41$, corresponding to the *Pbcm*–*Pnma* phase boundary, is also consistent with the group theoretical predictions according to which the *Pbcm*–*Pbnm* transition is of first order as *Pbcm* is not a subgroup of *Pnma* since both *Pnma* and *Pbcm* contain distortions not contained in the other. There is no infinitesimal distortion that can either bring *Pnma* into *Pbcm* or *Pbcm* into *Pnma*.

6. Conclusions

We have shown that in the 'nearly cubic' phase region of SCT with $0.35 < x < 0.70$ there are two different types of structures with space groups *Pbcm* and *Pbnm* stable for $0.35 < x < 0.41$ and $0.41 \leq x < 0.70$, respectively. The *Pbcm* space group is also found to exist for $x \geq 0.70$ outside the 'nearly cubic' phase region. The *Ibmm* space group seems to be more plausible than *I4/mcm* for the composition range $0.06 \leq x < 0.35$, which is also outside the 'nearly cubic' phase region. The three phase boundaries *Pm3m*–*Ibmm*, *Ibmm*–*Pbcm* and *Pbcm*–*Pbnm* are found to be of first order, consistent with group theoretical considerations.

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