

Low temperature x-ray diffraction study of the phase transitions in $\text{Sr}_{1-x}\text{Ca}_x\text{TiO}_3$ ($x = 0.02, 0.04$): Evidence for ferrielectric ordering

Cite as: Appl. Phys. Lett. **95**, 232910 (2009); <https://doi.org/10.1063/1.3273863>

Submitted: 25 September 2009 . Accepted: 31 October 2009 . Published Online: 11 December 2009

Sanjay Kumar Mishra and Dhananjai Pandey



View Online



Export Citation

ARTICLES YOU MAY BE INTERESTED IN

[Powder neutron diffraction study of the antiferroelectric phase transition in \$\text{Sr}_{0.75}\text{Ca}_{0.25}\text{TiO}_3\$](#)

Journal of Applied Physics **91**, 4447 (2002); <https://doi.org/10.1063/1.1432475>

[BaTiO₃-based piezoelectrics: Fundamentals, current status, and perspectives](#)

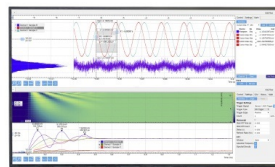
Applied Physics Reviews **4**, 041305 (2017); <https://doi.org/10.1063/1.4990046>

[Epitaxial growth of \$\text{SrCaTiO}_3\$ films on GaN by molecular beam epitaxy with a \$\text{TiO}_2\$ buffer layer](#)

Journal of Applied Physics **127**, 214104 (2020); <https://doi.org/10.1063/5.0007144>

Challenge us.

What are your needs for periodic signal detection?



Zurich Instruments

Low temperature x-ray diffraction study of the phase transitions in $\text{Sr}_{1-x}\text{Ca}_x\text{TiO}_3$ ($x=0.02, 0.04$): Evidence for ferroelectric ordering

Sanjay Kumar Mishra¹ and Dhananjai Pandey^{2,a)}

¹*Solid State Physics Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085 India*

²*School of Materials Science and Technology, Institute of Technology, Banaras Hindu University, Varanasi 221 005, India*

(Received 25 September 2009; accepted 31 October 2009; published online 11 December 2009)

X-ray diffraction studies on $\text{Sr}_{1-x}\text{Ca}_x\text{TiO}_3$ in the temperature range 12 to 300 K reveal cubic to tetragonal ($I4/mcm$) antiferrodistortive and tetragonal to orthorhombic ($Ic2m$) polar phase transitions at ~ 170 and 225, 32, 34 K, respectively, for $x=0.02$ and 0.04. It is shown that the polarization in the orthorhombic phase is along the $\langle 110 \rangle$ pseudocubic direction, in agreement with the experimentally reported easy polarization direction by Bednorz and Muller. However, in disagreement with them the moments are found to be ferroelectrically coupled in the neighboring (001) planes that is responsible for the anomalously low values of the spontaneous polarization in the polar phase. © 2009 American Institute of Physics. [doi:10.1063/1.3273863]

SrTiO_3 has been the paradigm of structural phase transition studies.¹ It is also one of the most common ingredients of BaTiO_3 -based ceramic capacitors.² The room temperature cubic perovskite structure of SrTiO_3 (space group $Pm\bar{3}m$) transforms to a tetragonal phase in the $I4/mcm$ space group below 105 K due to the freezing of one of the triply degenerate R_{25} modes in which the adjacent octahedra rotate about one of the cubic $\langle 100 \rangle$ directions in an anti-phase manner.³ Although the tetragonal phase is reported to be stable down to the lowest temperature,⁴ its dielectric constant gradually increases on cooling below room temperature and becomes nearly two orders of magnitude greater at ~ 4 K below which it levels off. While the increasing value of the dielectric constant at low temperatures is linked to a zone center soft mode,¹ its saturation below 4 K has been attributed to quantum fluctuations (i.e., zero point vibrations) of the lattice which stabilize the paraelectric state.⁵ Ca^{2+} substitution not only increases the antiferrodistortive phase transition temperature^{6,7} but also suppresses the quantum fluctuations, as revealed by the appearance of a peak in the temperature variation of the dielectric constant. It has been shown by Bednorz and Muller⁸ that above a critical Ca^{2+} concentration of $x_c=0.0018$, XY type “ferroelectricity” is stabilized in SrTiO_3 with sharp and diffuse ferroelectric transitions for $x_c \leq x \leq 0.016$ and $0.016 < x \leq 0.12$, respectively. Ranjan *et al.*⁹ and Mishra *et al.*⁹ have shown the presence of an antiferroelectric phase in $\text{Sr}_{1-x}\text{Ca}_x\text{TiO}_3$ (SCTx) for $0.12 < x \leq 0.40$. For Ca^{2+} concentrations $x_c < x < 0.12$, the dielectric constant of SCT in the ‘ferroelectric’ state decreases with increasing x but its value ($> 10^4$) remains an order of magnitude larger than that of the conventional ferroelectrics like BaTiO_3 (Ref. 8). On the otherhand, the measured saturation polarization values ($\sim 0.5 \mu\text{C}/\text{cm}^2$) are anomalously low^{10,11} in the “ferroelectric” phase as compared to that in BaTiO_3 , which is $\sim 25 \mu\text{C}/\text{cm}^2$. There is no satisfactory explanation for such a low value of saturation polarization ($\sim 0.5 \mu\text{C}/\text{cm}^2$) in a ‘ferroelectric’ phase with extremely

high dielectric constant. The present work seeks to provide a structural basis for this low value of spontaneous polarization. We have investigated the phase transitions in SCT for $x=0.02$ and 0.04 (SCT02 and SCT04) in the temperature range 12 to 300 K by Le-Bail and Rietveld techniques of x-ray powder diffraction using the FULLPROF¹² package. Our results suggest that the anomalously low spontaneous polarization value of SCT is linked with the ‘ferroelectric’ nature of the hitherto regarded “XY type-ferroelectric” phase of SCT. The calculated spontaneous polarization values, obtained using the Rietveld refined atomic positions and Born-effective charges, as given in Ref. 13, are found to be in excellent agreement with the values reported by Bianchi *et al.*¹⁰ and Mitsui and Westphal.¹¹

SCT02 and SCT04 powders were prepared by solid-state thermochemical reaction at 1423 K for 6 h and then sintered at 1573 K for another 6 h. Crushed and annealed powders from sintered pellets were used for diffraction studies. Temperature dependent powder x-ray diffraction data for the 2θ range 20° to 110° at various temperatures from 12 to 300 K were collected on a 18 kW Rigaku (RINT 2000/PC series) rotating anode based high resolution x-ray powder diffractometer operating in the Bragg-Brentano focusing geometry fitted with a low temperature attachment and also a curved crystal monochromator in the diffraction beam.

The cubic to tetragonal antiferrodistortive phase transition in SrTiO_3 occurring at ~ 105 K is accompanied with the doubling of the elementary perovskite cell leading to characteristic splitting of main perovskite peaks along with the appearance of superlattice reflections.⁴ This transition occurs in SCT02 and SCT04 also but with higher transition temperatures. The tetragonal cell parameters (a_t , b_t , and c_t) of the low temperature phase are related to the elementary perovskite cell parameters (a_p , b_p , and c_p) as: $a_t=b_t \approx \sqrt{2} a_p$, $c_t \approx 2c_p$. The Miller indices of the main perovskite and superlattice reflections of the tetragonal phase with a $a^0a^0c^-$ tilt system are represented by all even (eee) and all odd (ooo) integers, respectively, when indexed with respect to a doubled pseudocubic ($2a_p \times 2b_p \times 2c_p$) unit cell (see Glazer¹⁴ for details). Figures 1(a) and 1(b) depict the evolution of the 311 superlattice and 800 perovskite reflections as a function of

^{a)}Author to whom correspondence should be addressed. Electronic mail: dpandey_bhu@yahoo.co.in.

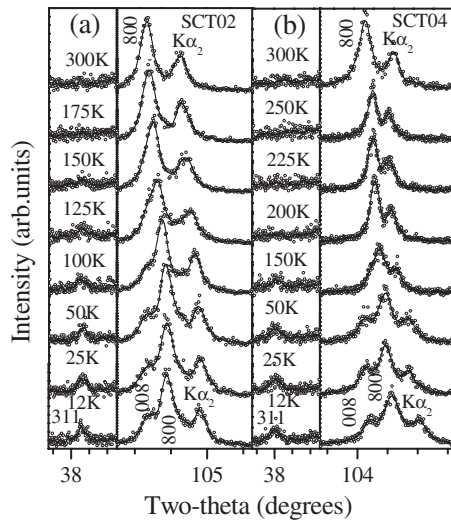


FIG. 1. Evolution of the XRD profile of the 311 superlattice and 800 perovskite reflections of (a) SCT02 and (b) SCT04. The indices are with respect to a doubled pseudocubic perovskite cell.

temperature for SCT02 and SCT04, respectively. It is evident from these figures that the 800 profile is a doublet at low temperatures, as expected for the low temperature tetragonal phase. It is also evident from this figure that the intensity of the superlattice reflection resulting from cell doubling, as also the splitting of the 008 peak, disappears at high temperatures, as expected for the high temperature cubic phase. The variations of the equivalent elementary perovskite cell parameters, as obtained by Le Bail refinement, with temperature depicted in Fig. 2(a) reveals the cubic to tetragonal antiferrodistortive phase transition temperature $T_c=170$ and 225 K for $x=0.02$ and 0.04, respectively. Ca^{2+} substitution thus increases the T_c in agreement with an earlier report.⁷ Although the XRD profiles shown in Fig. 1 do not depict any qualitative change in the low temperature ‘ferroelectric phase’, the refined tetragonal cell parameters do show anomalies around 30 K [see Fig. 2(a)], which is close to the transition temperatures reported in the literature using dielectric measurements.⁸

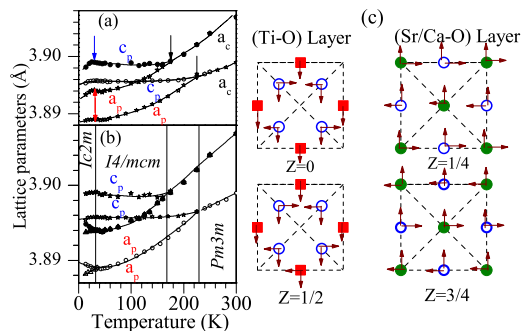


FIG. 2. (Color online) Evolution of the equivalent elementary perovskite cell parameters of the tetragonal phase of SCT02 and SCT04 as a function of temperature showing (a) the phase transition to the cubic phase around 170 and 225 K, marked with arrows, and (b) orthorhombic splitting of the “ a_p ” parameter of the tetragonal phase below ~ 32 K. The anomaly at ~ 32 K is linked with the transition to the polar phase, and is marked with arrow in Figs. 2(a) and 2(b). (c) A schematic representation of the direction of the ionic displacements in the individual layers of the orthorhombic ferroelectric phase with respect to their ideal positions in the cubic phase. $\text{Sr}^{2+}/\text{Ca}^{2+}$, Ti^{4+} , and O^{2-} ions are represented by filled circles (green), filled squares (red), and open circles (blue), respectively.

The centrosymmetric $I4/mcm$ space group of the paraelectric tetragonal phase cannot represent the structure of the ferroelectric phase of SCT02 and 04. The onset of ferroelectric polarization transforms under $Pm\bar{3}m$ as the components of the Γ_4^- irreducible representation (IR). Antiphase tilting of oxygen octahedra transforms under $Pm\bar{3}m$ as the components of the R_4^+ IR.¹⁵ Using the software package “ISOTROPY 2000”¹⁵ to couple Γ_4^- and R_4^+ IRs, we obtained many space groups. Since the paraelectric phase of SCT is tetragonal ($I4/mcm$), we impose the constraint that the ‘ferroelectric space’ group should be a subgroup of $I4/mcm$ for a second order phase transition. This constraint reduced the number of possible space groups for the ferroelectric phase to two, namely: $I4cm$ and $Ic2m$ (bca setting of $Ima2$). Previous Raman scattering studies on SCT with $x=0.007$ (Ref. 6) have shown that the E_g mode is split into two lines in the “ferroelectric phase,” whereas it is a singlet in the tetragonal phase. Hence the tetragonal $I4cm$ space group, for which E_g mode has to be a singlet, cannot represent the ferroelectric phase. Thus, the orthorhombic space group $Ic2m$ is the only space group likely to represent the ferroelectric (polar) phase of SCT. For this space group, the E_g mode will indeed be a doublet. The equivalent elementary perovskite cell parameters obtained at various temperatures by Le–Bail analysis of the full diffraction profiles in the 2θ range 20 to 110 degrees using the $Ic2m$ space group are depicted in Fig. 2(b) for SCT02 and SCT04, respectively. The cell parameters (A_0 , B_0 , and C_0) of the orthorhombic $Ic2m$ phase are related to the elementary perovskite cell parameters (a_p , b_p , c_p) as: $A_0 \approx \sqrt{2}a_p$, $B_0 \approx \sqrt{2}b_p$, and $C_0 \approx 2c_p$. It is evident from this figure that the a_p lattice parameter of the tetragonal paraelectric phase splits below ~ 32 K into a_p and b_p of the orthorhombic phase, in good agreement with the transition temperature ($T_c \sim 32$ K) at which the dielectric peak is observed.⁸ However, the orthorhombic distortion of the lattice is very small and can easily be mistaken for a tetragonal symmetry. The absence of any discontinuous change in the cell parameters at the transition temperature (~ 32 K) supports second order character of the transition.

The crystal structure of the low temperature phase in the $Ic2m$ space group consists of the stacking of TiO, Sr/CaO, TiO, and Sr/CaO layers at $z=0, \frac{1}{4}, \frac{1}{2},$ and $\frac{3}{4}$ of the unit cell, as shown in Fig. 2(c). In the layers at $z=\frac{1}{4}$ and $\frac{3}{4}$, the $\text{Sr}^{2+}/\text{Ca}^{2+}$ and O^{2-} ions have component displacements both along $+/-[100]$ and $+/-[010]$ directions of the orthorhombic cell. However, the component displacements along $+/-[100]$ in the $z=1/4$ and $z=3/4$ planes cancel out leaving net effective displacement only along the $[010]$ direction of the orthorhombic phase. Similarly, for the layers at $z=0$ and $\frac{1}{2}$, the net displacements of Ti^{4+} and O^{2-} ions are along the $[0\bar{1}0]$ direction of orthorhombic ferroelectric phase. Thus the direction of polarization in the TiO as well as Sr/CaO layers is along $+/-[010]$ direction of the orthorhombic phase. This is in agreement with the observation of Bednorz and Muller⁸ that the $\langle 110 \rangle$ pseudo-cubic direction, which becomes $\langle 010 \rangle$ direction in the orthorhombic cell, is the easy direction of polarization in the low temperature polar phase.

Having identified the most plausible space group for the low temperature polar phase, we carried out Rietveld analysis of the 12 K XRD data in the 2θ range 20° – 110° for SCT02 and SCT04 using the $Ic2m$ space group. Although the

TABLE I. Refined structural parameters of the ferroelectric phase of SCT02 and SCT04 at 12 K using orthorhombic structure (space group $Ic2m$).

Atoms	$\text{Sr}_{0.98}\text{Ca}_{0.02}\text{TO}_3$ (SCT02)				$\text{Sr}_{0.96}\text{Ca}_{0.04}\text{TO}_3$ (SCT04)			
	x	y	z	$B(\text{\AA})^2$	x	y	z	$B(\text{\AA})^2$
Sr/Ca	0.0018(9)	0.0091(7)	0.25	0.67(7)	0.0028(2)	0.0083(5)	0.25	0.89(5)
Ti	0.00000	0.4894(7)	0.50	0.008(5)	0.00000	0.4904(9)	0.50	0.011(7)
O ₁	-0.023(3)	0.552(7)	0.25	0.052(1)	-0.021(6)	0.5298(2)	0.25	0.24(7)
O ₂	0.267(3)	0.7148(7)	0.001(2)	0.67(7)	0.2412(2)	0.7938(7)	0.003(4)	0.70(7)
$A_0=5.5073(3)$ \AA; $B_0=5.5066(2)$ \AA; $C_0=7.7977(1)$ \AA				$A_0=5.4979(3)$ \AA; $B_0=5.4997(2)$ \AA; $C_0=7.7908(1)$ \AA				
$R_p=11.90$; $R_{wp}=18.73$; $R_e=12.97$; $\chi^2=2.08$				$R_p=8.87$; $R_{wp}=13.0$; $R_e=9.36$; $\chi^2=1.94$				

quality of Rietveld fit obtained for $Ic2m$ was comparable to that for $I4/mcm$ space group, the $Ic2m$ space group was favored on the basis of the group theoretical analysis of the second order phase transition discussed above. Further, the observation of doublet character of the Eg band in Raman spectra out rightly rejects the centrosymmetric tetragonal space group $I4/mcm$. Table I depicts the refined structural parameters and agreement factors for the ferroelectric phase of SCT02 and SCT04, respectively, using the $Ic2m$ space group. The refined structural parameters for the $Ic2m$ space group reveal ferrielectric coupling of the dipole moments residing in the neighboring (001) layers of the orthorhombic phase, in contrast to the suggestions of Bednorz and Muller⁸ for ferroelectric order. The dipole moments are not only found to be antiparallel in the alternate (001) layers but also their magnitudes along the $[0\bar{1}0]$ and $[010]$ orthorhombic directions are not equal. Using the Born effective charges given in Ref. 13 for Sr/Ca ($q=2.56$ C), Ti ($q=7.26$ C), and O ($q=-3.27$ C) along with the refined positional coordinates given in Table I, we obtain a spontaneous polarization of 0.98 and 1.17 $\mu\text{C}/\text{cm}^2$ for $x=0.02$ and 0.04, respectively. These values are in good agreement with the values reported by Bianchi *et al.*¹⁰ and Mitsui and Westphal¹¹ on the basis of hysteresis loop measurements. Thus the extremely low value of spontaneous polarization, in spite of the very high dielectric constant of SCT02 and SCT04 is due to the partial cancellation of the dipole moments as a result of the ferrielectric coupling of the dipoles in the neighboring (001) planes of the orthorhombic phase.

To summarize, we have observed anomalies in the unit cell parameters at the antiferrodistortive and the polar phase

transition temperatures. Using symmetry arguments for second order phase transition and the known Raman scattering results, we have zeroed on the $Ic2m$ space group as the most plausible space group of the low temperature polar phase. This polar phase is not ferroelectric in nature, as hitherto believed, but is ferrielectric, as a result of which it shows very low polarization values.

¹M. E. Lines and A. M. Glass, *Principles and Applications of Ferroelectrics and Related Materials* (Clarendon, Oxford, 1977); A. D. Bruce and R. A. Cowley, *Adv. Phys.* **29**, 219 (1980).

²R. C. Buchman, *Ceramic Materials for Electronics: Processing Properties and Application* (Marcel Dekker, New York, 1991).

³G. Shirane and Y. Yamada, *Phys. Rev.* **177**, 858 (1969).

⁴J. M. Kiat and T. Roisnel, *J. Phys.: Condens. Matter* **8**, 3471 (1996).

⁵K. A. Muller and H. Burkard, *Phys. Rev. B* **19**, 3593 (1979).

⁶U. Bianchi, W. Kleeman, and J. G. Bednorz, *J. Phys.: Condens. Matter* **6**, 1229 (1994).

⁷S. K. Mishra, R. Ranjan, D. Pandey, R. Ouillon, J.-P. Pinan-Lucarre, P. Ranson, and P. Pruzan, *J. Solid State Chem.* **178**, 2846 (2005).

⁸J. G. Bednorz and K. A. Muller, *Phys. Rev. Lett.* **52**, 2289 (1984).

⁹R. Ranjan, D. Pandey, and N. P. Lalla, *Phys. Rev. Lett.* **84**, 3726 (2000); S. K. Mishra, R. Ranjan, D. Pandey, R. Ouillon, J.-P. Pinan-Lucarre, P. Ranson, and Ph. Pruzan, *Phys. Rev. B* **64**, 092302 (2001).

¹⁰U. Bianchi, J. Dec, W. Kleeman, and J. G. Bednorz, *Phys. Rev. B* **51**, 8737 (1995).

¹¹T. Mitsui and W. B. Westphal, *Phys. Rev.* **124**, 1354 (1961).

¹²J. Rodriguez-Carvajal, FULLPROF, Laboratory Leon Brillouin (CEA-CNRS) CEA/Saclay, 91191 Gif sur Yvette Cedex, France, 2006.

¹³Ph. Ghosez, J.-P. Michenaud, and X. Gonze, *Phys. Rev. B* **58**, 6224 (1998).

¹⁴A. M. Glazer *Acta Crystallogr.* **B28**, 3384 (1972); **A31**, 756 (1975).

¹⁵H. T. Stokes, D. M. Hatch, and B. J. Campbell, *ISOTROPY*, 2007 (<http://stokes.byu.edu/isotropy.html>).