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Titanium charge state drives antiferrodistortive phase transition in $\text{La}_x\text{Sr}_{1-x}\text{TiO}_3$

<https://doi.org/10.1515/zkri-2025-0047>

Received September 9, 2025; accepted January 15, 2026;

published online February 12, 2026

Abstract: The structure of $\text{La}_x\text{Sr}_{1-x}\text{TiO}_3$ single-phase perovskites ($0.10 \leq x \leq 0.30$) was studied using synchrotron X-ray Powder Diffraction for Rietveld and Pair Distribution Function analysis. Electron Spin Resonance and X-ray Raman Scattering Spectroscopy confirmed that Sr substitution by La is charge compensated via electron injection into the conduction band. High-resolution diffraction (110–490 K) revealed phase transitions to a tetragonal phase with antiferrodistortive tilting (a^0a^0c , in Glazer notation). Fitting the Ginzburg-Landau mean field equation indicated a transition regime between second-order and tricritical. The critical temperature (T_C) and tilt order parameter (Φ_0) increase with La content up to $x = 0.20$, then decrease at $x = 0.30$. This non-monotonic behavior reflects an emerging local symmetry lowering toward $Cmcm$, supported by increased octahedral tilting and Bond Valence Sum analysis. The enhanced tilting offsets compensate for reduced thermal contraction of Ti^{3+} -rich TiO_6 octahedra below T_C .

Keywords: lanthanum-doped strontium titanate; distortions in perovskites; synchrotron powder diffraction; pair distribution function; X-ray Raman scattering

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1 Introduction

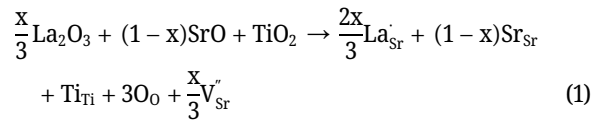
Perovskite materials based on strontium titanate (SrTiO_3 , hereafter referred to as STO) have garnered significant interest over the years due to their wide range of physical properties and applications in electronics,^{1–3} sensors,^{4,5} photo(electro)catalysts,^{6–8} and anodes for solid oxide fuel cells (SOFC).^{9,10} Among the modification methods employed to improve the properties of STO, lanthanum doping has attracted significant interest due to the improved electronic and catalytic properties compared to the undoped parent perovskite.^{11–14}

The phase transitions driven by composition and temperature hold invaluable insight into the relationship between physical properties and the underlying defective structures in solid solutions.^{14–17} The undoped SrTiO_3 undergoes an antiferrodistortive (AFD) cubic-to-tetragonal transition below 105 K, associated with the tilting of TiO_6 octahedra along the c -axis, described in the Glazer notation as a^0a^0c .^{18–20} However, even a modest substitution of strontium with smaller cations at the A-site has been reported to increase the transition temperature.^{18,21–23}

Although La-doped SrTiO_3 (SLTO) materials have been studied for several decades, gaps remain in the literature regarding the space groups involved in their phase transitions. Most studies found SLTO as $Pm\bar{3}m$ cubic at room temperature and above.^{16,24–27} Below room temperature, the tetragonal $I4/mcm$ and $P4/mmm$ groups, as well as the orthorhombic $Pbnm$, $Cmmm$, and $Ibmm$ space groups, have been proposed.^{17,27}

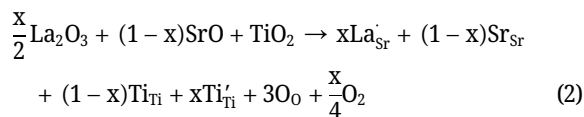
In the present work, we analysed samples of composition $\text{Sr}_{1-x}\text{La}_x\text{TiO}_3$ ($x = 0, 0.10, 0.15, 0.20, 0.30$) and $\text{Sr}_{0.7}\text{La}_{0.2}\text{TiO}_3$. The first series will be hereafter indicated as St (i.e. stoichiometric) as the site occupation factors of the A site sum to one per formula unit. The last sample will be referred to as CC (i.e. charge-compensated) because the formal charge at the A site sums up to 2. The study of the CC alongside the St samples seeks to compare how the distinct mechanisms of achieving charge neutrality impact the electronic and structural features of stoichiometric SLTO samples across the phase boundaries. SrTiO_3 , in principle, belongs to both the St and the CC series.

For any CC compositions, the mechanism of La doping can be described by following defect equation:



Thus, the higher positive charge of La³⁺ with respect to Sr²⁺ is compensated by negatively charged Sr vacancies, V_{Sr}^{••}. For both this equation and the following one, formal charges of vacancies have been assigned based on the Kroger-Vink notation.²⁸

For stoichiometric samples, multiple charge-compensation mechanisms have been proposed. Some researchers suggest that the formation of strontium vacancies is the main mechanism,^{29,30} in some cases resulting in the formation of ordered SrO layers between perovskite-type layers,³¹ and an overall stoichiometry Sr_{1-x}La_xTiO_{3+x/2} (or Sr_{1-3x/2}La_xTiO₃·x/2SrO). Other works propose that the additional positive charge introduced by substituting Sr²⁺ with La³⁺ is compensated by electrons added to the conduction band, leading to the partial reduction of Ti⁴⁺ to Ti³⁺,^{18,31,32} according to equation (2):



The discrepancies between the reported mechanisms might arise from the very high sensitivity of SLTO compositions towards processing variables such as temperature, oxygen partial pressure, and sintering time.³³

St samples have generally been reported to display higher electronic conductivities the higher the La³⁺ content, correlating with the greater number of electrons injected in the conduction band.^{32,34} These experimental findings have been corroborated by ab-initio calculations, which demonstrate that the density of states (DOS) of these materials can be accurately described by a rigid band model, where the Fermi level shifts towards the conduction band as the lanthanum content increases.^{35,36}

Here, we analysed the temperature and compositional dependence of single-phase SLTO powders by means of *in situ* high-resolution X-ray powder diffraction (HR-XRPD) over the 110 K–490 K range. Additionally, to investigate the presence of defects and possible local (< few nm) symmetry breaking, we used Pair Distribution Function (PDF) analysis allied to X-ray Raman Scattering spectroscopy and Electron Spin Resonance (ESR). Finally, we present Bond Valence Sum (BVS) calculations to reconcile the structural and electronic features of the compositions under study. We decided to limit our investigation to compositions with x ≤ 0.3 to study pure perovskite phases: Ruddlesden–Popper secondary phases such as SrLa₂Ti₂O₈, La₂Ti₂O₇, and La₄Ti₃O₁₂ have been reported for x ≥ 0.4.^{34,37}

2 Methods

2.1 Synthesis

SLTO powders were prepared by solid-state reaction of SrCO₃ (Sigma-Aldrich 99.9 %), La₂O₃ (Sigma-Aldrich 99.9 %) and TiO₂ (Sigma-Aldrich 99.8 %). Stoichiometric mixtures of reagents were uniaxially pressed into disks and fired in Pt crucibles for 4 h at T = 1400 K, 4 h at T = 1550 K, and finally twice 4 h at T = 1650 K in static air atmosphere with intermediate regrinding.

By this approach we synthesized the “stoichiometric” (St) series of formula Sr_{1-x}La_xTiO₃, with x = 0, 0.10, 0.15, 0.20, and 0.30, presenting a formally full occupation of the A-site by Sr²⁺ and La³⁺ ions. Additionally, we synthesized a “charge compensated” (CC) sample of formula Sr_{0.7}La_{0.2}TiO₃, where two La³⁺ ions were inserted in the structure every three Sr²⁺ sites, forming in this way 0.1 vacancies per formula unit. In Table 1, we report a summary of the studied samples. For the sake of brevity, samples will be referred to as SLTO_{x-y}, where x is the percentage of Sr and y the percentage of La on the perovskite A site.

2.2 Oxygen K-edge X-ray Raman scattering (XRS)

Spectra of the STO, SLTO₈₀₋₂₀ and SLTO₇₀₋₂₀ samples were collected using the large-solid-angle spectrometer for non-resonant inelastic X-ray scattering at beamline ID20 of the ESRF, Grenoble, France. X-rays from three consecutive U26 undulators were monochromatized first by a Si(111) high-heat-load double crystal monochromator and a subsequent Si(311) channel-cut post-monochromator. The monochromatic photons were then focused to a spot size of approximately 50 × 50 μm² at the sample position. The samples were pressed loosely into pellets using graphite as a binder. XRS spectra were collected by scanning the incident energy between 10.21 and 10.27 keV in steps of 0.2 eV. This

Table 1: List of samples and their labels.

Sample	Formula	A site vacancy per formula	Stoichiometry
SLTO ₇₀₋₂₀	Sr _{0.70} La _{0.20} TiO _{3+δ}	0.1	CC
SLTO ₇₀₋₃₀	Sr _{0.70} La _{0.30} TiO _{3+δ}	0	St
SLTO ₈₀₋₂₀	Sr _{0.80} La _{0.20} TiO _{3+δ}	0	St
SLTO ₈₅₋₁₅	Sr _{0.85} La _{0.15} TiO _{3+δ}	0	St
SLTO ₉₀₋₁₀	Sr _{0.90} La _{0.10} TiO _{3+δ}	0	St
STO	SrTiO ₃	0	St/CC

resulted in energy loss spectra with respect to the Si(660) analyzer reflection at approximately 9.7 keV. Intensities from different analyzer crystals positioned at small scattering angles were collected and averaged over resulting in an average momentum transfer of $3.2 \text{ \AA}^{-1}$. The overall energy resolution was 0.7 eV. Data acquisition took about 4 h per sample. Data merging and background subtraction was done as described in³⁸ using the XRStools software package. As the O–K edge was scanned several times during each measurement, during merging the individual scans were checked for consistency, summed and normalized to the area between 520 and 560 eV energy loss for the O K-edge.

2.3 Ab-initio calculations

FDMNES was used to carry out ab-initio calculations of the O K-edge XRS spectra. The calculations used a simplified structural model based on the tetragonal phase ($I4/mcm$) of SrTiO_3 and taking into account the nominal stoichiometries of each sample. The simulations were performed using multiple scattering theory within the muffin-tin (MT) approximation for the potential shape, following the Green's function approach. The calculations were non-relativistic and employed the Hedin–Lundqvist exchange potential, as implemented in the FDMNES code. The MT radii were adjusted to ensure good overlap between neighboring spherical potentials. To simulate experimental conditions, the calculated spectra were convoluted with an arctangent function to account for the core-hole lifetime and photoelectron damping, followed by a Gaussian convolution representing the experimental energy resolution. The resulting spectra were then scaled to match the integrated intensity of the experimental data.

2.4 Electron spin resonance

ESR spectra were collected at a Bruker ELEXSYS spectrometer equipped with an ER4102ST standard rectangular cavity at X band (9.4 GHz) frequency between 150 and 290 K on all the La-doped St. samples. Spectra were also collected on the CC sample at 150 K and RT and on the STO sample at 77 K. The derivative dP/dH^{-1} of power P absorbed was recorded as a function of the static magnetic field H .

2.5 X-ray experiments and data analysis

High-Resolution X-ray Powder Diffraction (HR-XRPD) patterns were collected in transmission geometry at the ID22

beamline at ESRF.³⁹ The powder samples were loaded into 0.7 mm diameter Kapton[®] capillaries and mounted parallel to the diffractometer axis. Two experimental setups were employed to acquire data optimized for either Rietveld refinement or Pair Distribution Function (PDF) analysis, respectively. In the former case we used an X-ray wavelength $\lambda = 0.399970(2) \text{ \AA}$ and a 9-element detector array.⁴⁰ Samples were first measured at fixed temperature (110 K) averaging two scans in the $0^\circ \leq 2\theta \leq 48^\circ$ range ($Q_{\text{max}} = 12.8 \text{ \AA}^{-1}$). St samples were also measured while ramping from 90 K to 470 K at a heating rate of 1 K min^{-1} , in the $0^\circ \leq 2\theta \leq 44^\circ$ range, so that one pattern was collected every 10 K. Rietveld refinements were done using GSAS.^{41,42} Refinement variables were scale factor, cell parameters, isotropic atomic mean square displacement parameters, as well as background (Chebyshev polynomial), and peak profile (Pseudo-Voigt) parameters. Data for PDF analysis were collected at 110 K on all the St samples (SLTO₉₀₋₁₀, SLTO₈₅₋₁₅, SLTO₈₀₋₂₀, and SLTO₇₀₋₃₀) using a wavelength $\lambda = 0.176927(1) \text{ \AA}$ and a 2D CCD detector (Perkin Elmer XRD 1611CP3) with $100 \times 100 \mu\text{m}^2$ pixel size. An empty capillary was measured in the same setup for background subtraction during PDF calculations. Each measurement collected 200 10-second frames. Wavelength, sample-detector distance, and azimuthal integration parameters were calibrated using a LaB_6 reference. The detector mask was created with the program FIT2D,⁴³ while calibration and azimuthal integration were done in pyFAI.⁴⁴

For real space analysis we used the reduced PDF, $G(r)$, obtained from the sine Fourier transform of the experimental total scattering function, $S(Q)$, defined as:⁴⁵

$$G(r) = 4\pi r [\rho(r) - \rho_0] = \frac{2}{\pi} \int_{Q_{\min}}^{Q_{\max}} Q[S(Q) - 1] \sin(Qr) dQ$$

where $\rho(r)$ is atomic pair density function and indicates the probability of finding an atom at a distance r from another atom, while ρ_0 is the atom number density. $G(r)$ curves were computed using the PDFgetX3 program⁴⁶ using data up to $Q_{\text{max}} = 28.0 \text{ \AA}^{-1}$. Structural models were fit to the $G(r)$ curves using PDFgui.⁴⁷

2.6 Bond valence sum

Within this method, the formal oxidation state V_i of a ion i is the sum of the valences S_{ij} of bonds between it and its neighbours j according to the equation $V_i = \sum_j S_{ij} = \sum_j \exp\left(\frac{r_0 - r_{ij}}{B}\right)$, where r_0 and B are constant parameters depending on the couple of atoms involved in the bond and r_{ij} is the experimental interatomic distance between the two atoms. The Bond Valence

Sums (BVS) for La, Sr and Ti cation were calculated using EXPO2013.⁴⁸

3 Results and discussion

3.1 XRS

The normalized XRS spectra of STO, SLTO_{80-20} and SLTO_{70-20} collected at the O–K edge (at $Q = 3.6 \text{ \AA}^{-1}$) are reported in Figure 1A. The spectra of the two La doped samples are superimposed, while the STO spectrum is offset for sake of clarity.

The XRS spectrum of SrTiO_3 is very close to the one reported in Figure 40 by Frati et al.⁴⁹ Peaks in Figure 1A are labelled according to the hybridization of oxygen 2p states with cationic states. According to the literature,^{49,50} the peaks correspond to transitions toward final states derived from O 2p states hybridized with: a) Ti 3d states (in the 530–534 eV range), b) Sr 4d states (between 535 and 538 eV), and c) Ti s and p states (at 542–546 eV). The spectrum of pure LaTiO_3 ⁵⁰ shows a first peak (related to Ti 3d states) at the same position as in SrTiO_3 , and a broad second peak attributed to hybridization of O p with La 5d states (see pink segments in Figure 1A). Since Ti is formally present as $3d^1$ in LaTiO_3 and $3d^0$ in SrTiO_3 , the ratio of the Ti 3d and La 5d peak intensities in LaTiO_3 is smaller than the ratio of the Ti 3d and Sr 4d peak intensities in SrTiO_3 .⁴⁹

The main differences between the spectra of SLTO_{80-20} and SLTO_{70-20} (Figure 1A) are the higher intensities of the La 5d peak below 535 eV and of the Ti 3d peak in the CC sample. The former can be explained by the larger La/Sr ratio in SLTO_{70-20} (0.286 vs 0.25). The latter is the result of the defect

equations (1) and (2). Unlike the CC specimen, in St compositions La doping injects electrons in the conduction band, partially filling the Ti 3d states. To support this interpretation, we carried out ab-initio calculations of the O K-edge absorption spectra (Figure 1B). In the FDMNES software, two semi-empirical parameters, *screening* and *dilatorb*, can be adjusted to fine-tune the simulated electronic structure. The *dilatorb* parameter modifies the spatial extent of the valence orbitals, thereby altering the degree of covalency. A higher *dilatorb* value enhances orbital overlap between the absorber and neighboring atoms, leading to greater covalency and influencing the effective oxygen charge at the O K-edge. The *screening* parameter, on the other hand, adjusts the electronic population in partially occupied valence orbitals of the absorber by adding an electron to the first unoccupied state. This compensates for charge transfer due to hybridization with neighboring ions.^{51–53} Hence, this parameter, applied to the absorber atom, helps to simulate the interaction of the absorber and its neighbors by artificially adding the extra screening charges coming from the neighbors. More specifically, in this work, screening helps to tune the interaction of oxygen and the transition metal (TM). Accordingly, two different screening values (0.7 and 0.9) were used for calculations. The lower the screening value the larger the time spent by the Ti–O bonding electrons on the Ti ion and, in other words, the smaller the positive charge ion Ti. As reported in Figure 1B, the peak intensity ratio around $\approx 531 \text{ eV}$ and $\approx 535 \text{ eV}$ is lower in the blue curve, which corresponds to a lower screening value, compared to the red curve with higher screening. This trend indicates that a lower Ti oxidation state (i.e., a higher Ti 3d occupancy) reduces the relative intensity of the $\approx 531 \text{ eV}$ peak. This is consistent with the experimental observation that the

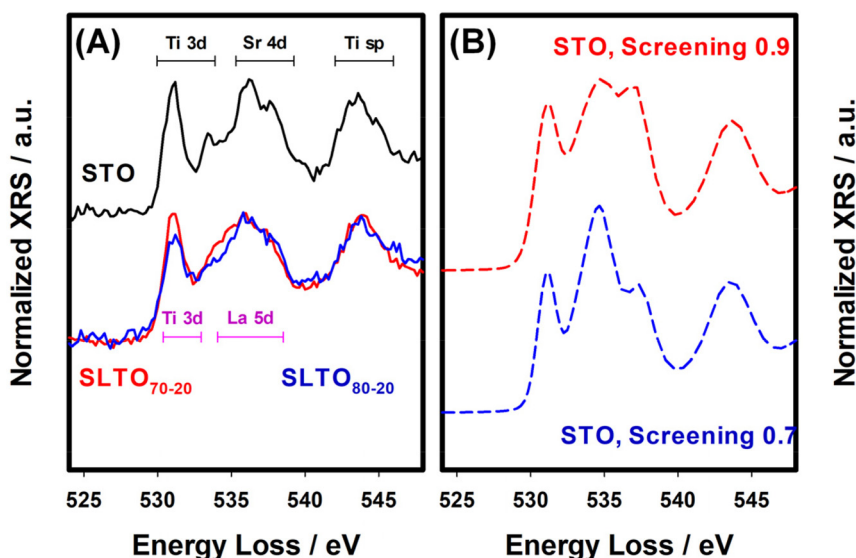


Figure 1: Obtained XRS results: In (A) normalized XRS spectra at the O–K edge of STO (black curve), SLTO_{70-20} (red curve) and SLTO_{80-20} (blue curve). The horizontal segments identify the energy ranges of final states with O 2p and cation characters as specified in the labels for STO (black segments and symbols) and LaTiO_3 (pink segments and symbols). See text for details. (B) Calculated XRS spectra at the O–K edge of STO applying different screening parameters.

SLTO₈₀₋₂₀ sample exhibits lower screening (and thus higher Ti 3d occupancy) compared to the SLTO₇₀₋₂₀ sample.

3.2 ESR

The only ESR signal obtained with SrTiO_3 was a six-line multiplet (Figure S1), similar to signals previously attributed to $\text{Mn}^{2+}\text{-V}_\text{O}$ associations⁵⁴ and/or to other Mn^{2+} or Mn^{4+} -based paramagnetic species.^{55,56} Inductive Coupled Plasma-Mass Spectrometry (ICP-MS) analysis confirmed the presence of manganese as an impurity in this sample, with a concentration of 0.0015 Mn atoms per formula unit. For the SLTO₇₀₋₂₀, the ESR spectral intensity decreases markedly with decreasing temperature, while the spectral shape remains unchanged (see panel A of Figure 2). The spectrum is composed of the lines A1 ($g \approx 2.07$), A2 ($g \approx 2.05$), C ($g \approx 2.01$), and B ($g \approx 1.98$). An unresolved additional line, marked with an asterisk, appears at $g \approx 2.03\text{--}2.04$ between A2 and C. Furthermore, faint signals corresponding to the six-line multiplet remain visible at room temperature.

According to Oliva and coworkers, the A1, A2 and C lines may be attributed to unpaired electrons localized on oxygen

(O^-) ions with different environments.⁵⁴ Additionally, the B feature at $g = 1.98$ is assigned to Ti^{3+} species. In the CC sample, the extra-charges introduced by La^{3+} substitution are compensated by Sr vacancies; thus, Ti^{3+} species are expected to be absent unless charge transfer occurs from oxygen to titanium due to Ti-3d states lying below the Fermi level, as reported among others by Shanthi and Sarma.³⁶ Additionally, even though the defect equation (Eq. (1)) for CC samples does not imply the formation of Ti^{3+} , a small amount of paramagnetic species detectable by ESR, including Ti^{3+} and O^- , could be introduced during the synthesis by compositional fluctuations in the bulk or surface defects, as pointed out by Oliva.⁵⁴

The enhanced signal-to-noise ratio with increasing T suggests that the EPR-active species are produced via an activated process.

For the St samples (see panel B of Figure 2), A1, A2 and C disappear, unlike the unresolved feature marked by an asterisk. The B signal dominates the ESR pattern only for samples with the lowest La concentration, as highlighted by the inset. Additionally, a broad signal D emerges with a maximum at ≈ 2930 G. Furthermore, the following monotonic trends are recognizable by increasing La^{3+} concentration:

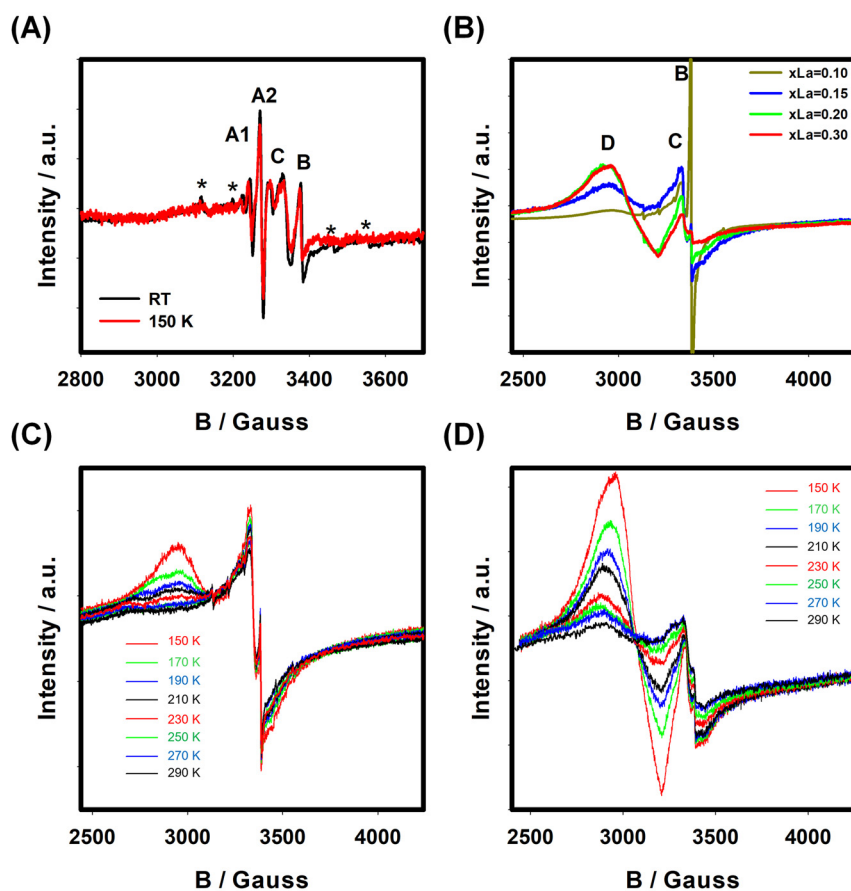


Figure 2: Details of the ESR spectra of: (A) SLTO₇₀₋₂₀ sample at 150 K (red curve) and RT (black curve); (B) SLTO₉₀₋₁₀ (grey curve), SLTO₈₅₋₁₅ (blue curve), SLTO₈₀₋₂₀ (green curve), SLTO₇₀₋₃₀ (red curve) at 130 K; (C) SLTO₈₅₋₁₅ at different T values, and (D) SLTO₇₀₋₃₀ at different T values. Labels are described in the text.

i) the six-line multiplet progressively disappears; ii) both the unresolved feature and the B signal decrease in intensity; iii) the broad D signal intensifies and becomes increasingly asymmetric. These trends suggest a reduction in the concentration of isolated Ti^{3+} ions in respect to the active species involved in the D band.

The spectra of St samples exhibit intriguing trends as a function of temperature, as shown in panels C and D of Figure 2 for SLTO_{85-15} and SLTO_{70-30} . The spectra of SLTO_{90-10} and SLTO_{80-20} samples are reported in Figure S2 of the Supporting Information. With increasing temperature, the D feature decreases in intensity relative to the B line, without any shift in its position across the entire temperature range. At 290 K, the D band is undetectable in the SLTO_{90-10} and SLTO_{85-15} samples but persists at higher La^{3+} concentrations. Additionally, the signal-to-noise ratio of the spectra deteriorates as the temperature increases. The near temperature-independence of the B feature's intensity suggests that it originates from isolated Ti^{3+} ions pinned at structural defects.

The increased intensity of the D feature with La doping suggests its connection to mobile electrons. This interpretation aligns with Equation (2) and with Hall effect measurements,⁵⁷ which reveals that the concentration of electrons in the conduction band corresponds to the La concentration. Accordingly, the D feature exhibit typical Dyson-like asymmetric shape of conductive materials.^{58–60} An extensive description of the phenomenon has been reported by Savchenko and co-workers.⁶⁰ However, determining the precise origin of this feature lies beyond the scope of this paper due to the complexity of spin-spin interactions among Ti^{3+} ions in octahedral coordination as described, for example, in titanium phosphates,⁶¹ and Magnéli phases.⁶²

3.3 XRPD data in the reciprocal space

3.3.1 Data collected at 110 K

The diffraction pattern of the STO sample collected at 110 K is fitted by the cubic model of undistorted perovskites (space group $Pm\bar{3}m$, n . 221). The patterns of all La-doped samples exhibit peak splitting and superlattice Bragg reflections consistent with the tetragonal phase (space group $I4/mcm$, n . 140) of strontium titanate below 105 K.^{63–65} We exclude other space groups, such as $Ibmm$, which was proposed for the SLTO_{70-30} sample,¹⁷ because we did not observe additional superstructure peaks like the (101) reflection. This reflection is systematically extinct for $I4/mcm$ due to the selection rule ($h0l$): $h, l = 2n$.⁶⁶

The atomic positions are for the $I4/mcm$ group are reported in Table 2. This structural model is characterized by an antiferrodistorsive (AFD) tilting of the TiO_6 along the c -axis, described in the Glazer tilt system as a^0a^0c .^{19,67} Along the c -axis, octahedra alternate between clockwise and anti-clockwise rotations of the same magnitude, characterized by the angle ϕ , directly related to the $x_{\text{O}2}$ coordinate: $\phi = \tan^{-1}(1-4x_{\text{O}2})$.

Figure 3A shows the 2θ range containing a superlattice reflection, the $(211)_T$ reflection, for all compositions at RT. Hereafter, the subscripts “T” and “C” refer to the tetragonal and to the cubic perovskite phases, respectively. Superlattice peaks as well as every $(hkl)_T$ reflection with $l = 2n+1$ arise solely from the scattering of oxygen ions at the O2 site, and their intensity increases when $x_{\text{O}2}$ deviates from 0.25 (and $y_{\text{O}2}$ from 0.75). Consequently, the magnitude of this reflection serves as a direct indication of the octahedral-tilting distortion.

The relationships between the translation vectors of the cubic ($\mathbf{a}_C$, $\mathbf{b}_C$ and $\mathbf{c}_C$) and of the tetragonal ($\mathbf{a}_T$, $\mathbf{b}_T$ and $\mathbf{c}_T$) axes are: $\mathbf{a}_T = \mathbf{a}_C + \mathbf{b}_C$, $\mathbf{b}_T = \mathbf{a}_C - \mathbf{b}_C$ and $\mathbf{c}_T = 2\mathbf{c}_C$; as to the cell metrics, $\mathbf{a}_T = \mathbf{a}_C \sqrt{2}$, $\mathbf{b}_T = \mathbf{b}_C \sqrt{2}$, and $\mathbf{c}_T = 2\mathbf{c}_C$. Figure 3B shows the $(004)_T$ and $(220)_T$ reflections arising from the split of the $(200)_C$ and related to the tetragonal strain η , according to:

$$\eta = \frac{2(c_C - a_C)}{(c_C + a_C)} = \frac{2(c_T - \sqrt{2}a_T)}{(c_T + \sqrt{2}a_T)} \quad (3)$$

Figure 3C shows the $(004)_T/(220)_T$ doublet in the SLTO_{80-20} sample at RT, together with the best fit using the tetragonal model. These peaks are asymmetric, with broad tails in the center of the doublet. This feature has been reported in the literature as indicative of microstrain gradients developing between different domains, for two ferroelectric perovskites: BaTiO_3 ⁶⁸ and PZN-PT ($\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3$ –8% PbTiO_3).⁶⁹ As observed for SrTiO_3 below its ferroelastic phase transition,⁶³ the microstrain should be attributed to domain walls (DW) regions separating couples of twin tetragonal domains below T_C within the same crystallites. The peaks are more accurately described when the Rietveld refinement includes an additional cubic $Pm\bar{3}m$ phase (Figure 3D), compared to only using the tetragonal model (Figure 3C). This approach maps the contribution to the scattering of DW, exploiting a distribution of cell parameters. On the other hand, above phase transition, the system can be accurately described by employing a single cubic phase, as shown in Figure S3 for the $(200)_C$ peak of sample SLTO_{80-20} .

The single-phase and the two-phase models return different cell parameters for the tetragonal phase; for example, for the SLTO_{80-20} sample, $\phi = 4.01$ (5°) and $\eta = 0.00227(1)$ for a single tetragonal phase and $\phi = 4.66^\circ$ and $\eta = 0.00251$ in the latter case.

Table 2: Results of Rietveld refinements on data collected at 110 K. Space group $Pm\bar{3}m$ Sr,L a 1a ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$); Ti 1b (0, 0, 0), O 3c (0, $\frac{1}{2}$, 0); space group $I4/mcm$. Atomic positions: Sr,L a 4b (0, $\frac{1}{2}$, $\frac{1}{4}$); Ti 4c (0, 0, 0); O1 4a (0, 0, $\frac{1}{4}$), O2 8h (x_{O_2} , $\frac{1}{2} + x_{\text{O}_2}$, 0).

Sample Space group	STO $Pm\bar{3}m$	SLTO ₉₀₋₁₀ $I4/mcm$	SLTO ₈₅₋₁₅ $I4/mcm$	SLTO ₈₀₋₂₀ $I4/mcm$	SLTO ₇₀₋₃₀ $I4/mcm$	SLTO ₇₀₋₂₀ $I4/mcm$
$a/\text{\AA}$	3.90068(2)	5.51608(5)	5.51658(4)	5.51788(4)	5.52269(1)	5.5012(1)
$c/\text{\AA}$	$\equiv a$	7.81272(1)	7.82062(1)	7.82123(1)	7.81760(3)	7.7944(2)
$V/\text{\AA}^3$	59.35(1)	237.72(1)	238.00(1)	238.13(1)	238.44(1)	235.88(1)
x_{O_2}	–	0.2366(2)	0.2327(1)	0.2324(3)	0.2348(3)	0.234(3)
$U(\text{Sr,L a})/\text{\AA}^2$	0.0374(3)	0.00426(3)	0.00485(3)	0.0052(2)	0.0054(3)	0.002(1)
$U(\text{Ti})/\text{\AA}^2$	0.0260(6)	0.00242(4)	0.0026(5)	0.0026(4)	0.0020(5)	0.004(2)
$U(\text{O})/\text{\AA}^2$	0.0074(3)	0.005(1)	0.005(1)	0.006(1)	0.0064(2)	0.006(5)
Φ	–	3.06(1)	3.94(2)	4.01(5)	3.47(2)	3.52(1)
η	–	0.00151(1)	0.002432(1)	0.00227(1)	0.00093(3)	0.00186(2)
Rp	0.0723	0.0610	0.0639	0.0576	0.064	0.0910
R(F ²)	0.0348	0.0323	0.0325	0.0327	0.05	0.0780
χ^2	12.22	16.55	9.278	10.55	16.7	8.465

Since adding a cubic phase to account for the DW introduced strong correlations among refined parameters, especially in the case of small tetragonal strain, we ultimately chose to report the refined values for the single tetragonal model (Table 2), noting that this may introduce a systematic bias on the refined parameters. The results obtained using the biphasic model are reported in the Supporting Information (Table S1). The Rietveld refinements of selected samples are shown in the Supporting Information (Figure S4).

Figure 4 reports selected refined parameters as a function of the La content. Panel A displays the cell volume of STO and the volume of the equivalent cubic cell for the tetragonal samples (i.e. $\frac{1}{4}$ of the tetragonal cell volume). In the St samples, the cell volume increases with La concentration, in accord with previous investigations,^{37,67} but in contrast with the trend reported by Eror and Balachandran.⁷⁰ Lattice expansion can be primarily attributed to the change in the average ionic radius introduced by La doping. According to Eq. (2), this introduces two competing effects: i) $\text{La}^{3+}/\text{La}^{2+}$ substitution, where La^{3+} has a smaller ionic radius than Sr^{2+} ($\text{La}_{\text{XII}}^{3+} = 1.36 \text{ \AA}$ and $\text{Sr}_{\text{XII}}^{2+} = 1.44 \text{ \AA}$ respectively)⁷¹ and ii) $\text{Ti}^{3+}/\text{Ti}^{4+}$ substitution, where Ti^{3+} has a larger radius (0.67 $\text{\AA}$) than Ti^{4+} 0.605 $\text{\AA}$ in octahedral coordination.^{26,71} Our XRS and EPR results confirm that charge compensation is achieved by the formation of Ti^{3+} from Ti^{4+} .^{26,31,71} Although the difference in ionic radii between La^{3+} and Sr^{2+} (0.08 $\text{\AA}$) is larger than the difference between Ti^{4+} and Ti^{3+} (0.065 $\text{\AA}$), the Ti–O distances are along the cubic axes and therefore contribute more to the lattice expansion than the Sr/La–O distances, which are parallel to the face diagonal of the cubic cell. This behavior is analogous to that of the $\text{Sr}_{1-x}\text{La}_x\text{FeO}_3$ perovskite, in which La doping induces $\text{Fe}^{4+} \rightarrow \text{Fe}^{3+}$ charge compensation. There, the

ionic radii of Fe^{4+} and Fe^{3+} (high spin⁷²) are 0.585 $\text{\AA}$ and 0.645 $\text{\AA}$, respectively, and the cell volume increases with La concentration, despite the smaller average ionic radius at the A site.⁷³ In absence of charge compensation at the B-site, as in the SLTO₇₀₋₂₀ CC sample, the cell volume decreases (Figure 4A).

Panels B and C of Figure 4 display the ϕ and η parameters, respectively. Both quantities increase with La doping, reaching a maximum for $x = 0.15$ – 0.20 , and diminishing for $x = 0.30$. The SLTO₇₀₋₂₀ sample displays similar ϕ but larger η than SLTO₇₀₋₃₀.

Finally, panel D of Figure 4 shows the refined atomic mean square displacement parameters (U_{iso}) of the St samples as a function of La concentration. The $U(\text{Ti})$ values remain almost unaffected by La doping, while the positive slopes of $U(\text{Sr,L a})$ and $U(\text{O})$ show that in the investigated solid solutions the disorder affects the A site more than the B site.

Having characterized the low-temperature structures, now we turn to their temperature evolution heating the St samples up to 490 K. Figure 5 reports as an example two portions of the XRPD patterns collected on the SLTO₈₀₋₂₀ sample. The main changes observed raising T are the progressive: i) intensity decrease and disappearing of the (211)_T reflection (panel A) and ii) merging of the (004)_T and (220)_T peaks into a single one, which are fingerprints of the antiferrodistortive (AFD) tetragonal-to-cubic phase transition.

This phase transition has been investigated extensively in SrTiO_3 by different authors^{64,65,74–77} as well as on other several perovskite compounds^{78,79} and solid solutions.^{74,80}

The calculated phonon spectrum of cubic strontium titanate presents two negative frequency modes at the R ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$) and the Γ (0, 0, 0) points;²⁰ one (irrep R_4^+) is associated to the

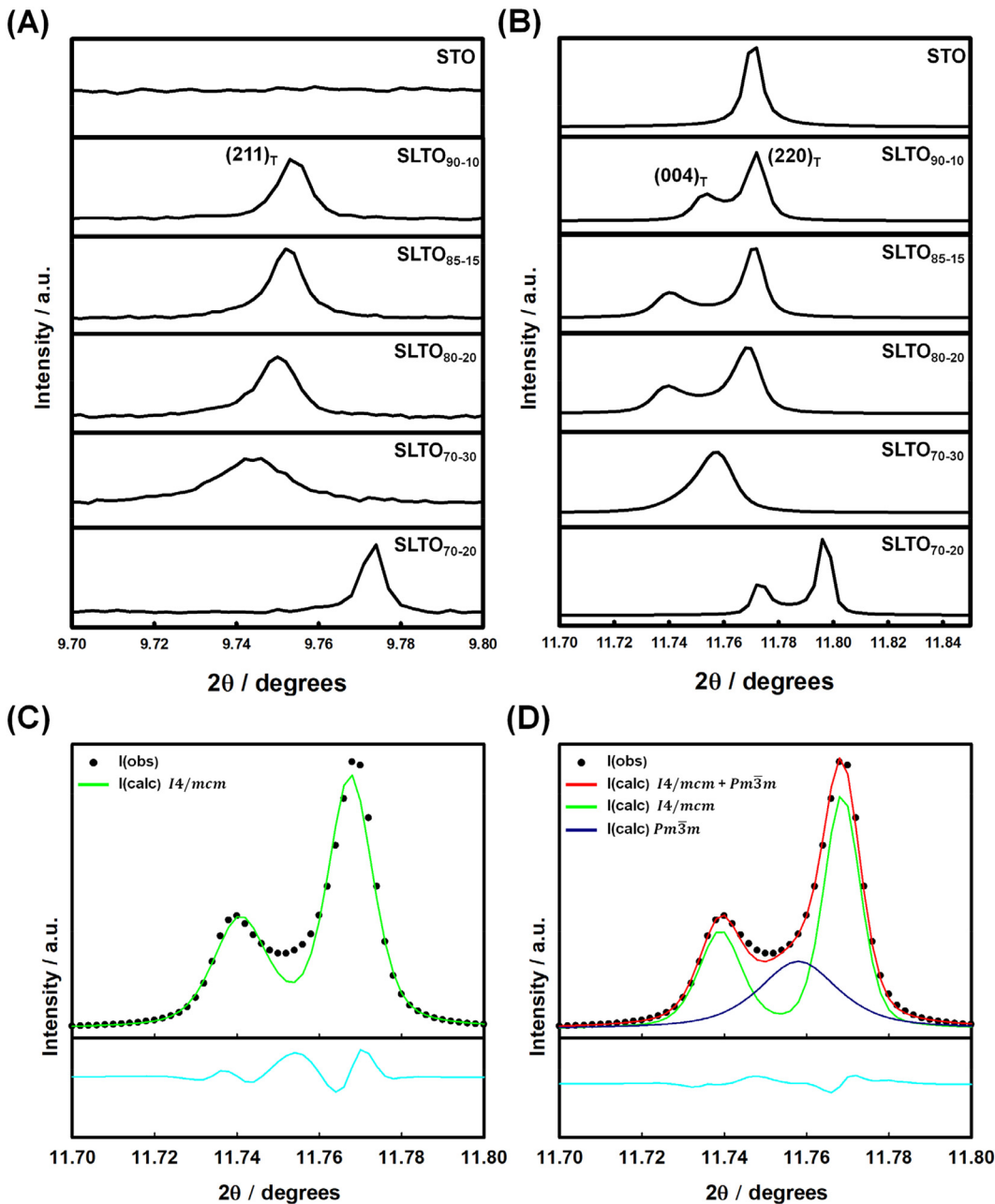


Figure 3: Portions of the experimental patterns obtained at 110 K (black lines) corresponding to (A) the (211)_T and (B) the (004)_T and (220)_T peaks. Portion of the experimental and of the calculated (full lines) patterns of SLT 80-20 sample employing (C) a single tetragonal $I4/mcm$ model and (D) a biphasic ($I4/mcm + Pm\bar{3}m$).

AFD instability²⁰ and is responsible of the observed phase transition from $Pm\bar{3}m$ to $I4/mcm$ that take place at 105 K. The second, at the zone-center Γ_4^- point, leads to a ferroelectric (FE) transition,⁸¹ which never condenses in the long-range structure of SrTiO_3 . Emerging ferroelectric features have been evidenced at ≈ 45 K in walls between antiphase ferroelastic domains,⁸² while bulk FE has been induced by uniaxial stress⁸³ or isotope doping.^{84,85} In the absence of stresses and

isotopic enrichment, an anomalous increase in the dielectric constant is observed at low temperatures, which is quantum-mechanically stabilized below 4 K in the paraelectric phase.⁸¹ According to the work of Vanderbilt⁸⁶ and Sai⁸⁷ the two instabilities tend to cancel each other out. Aschauer and Spaldin described a more complex scenario where competition/cooperation of the two instabilities can be finely tuned through the tilting angle and the tetragonal strain. Based on

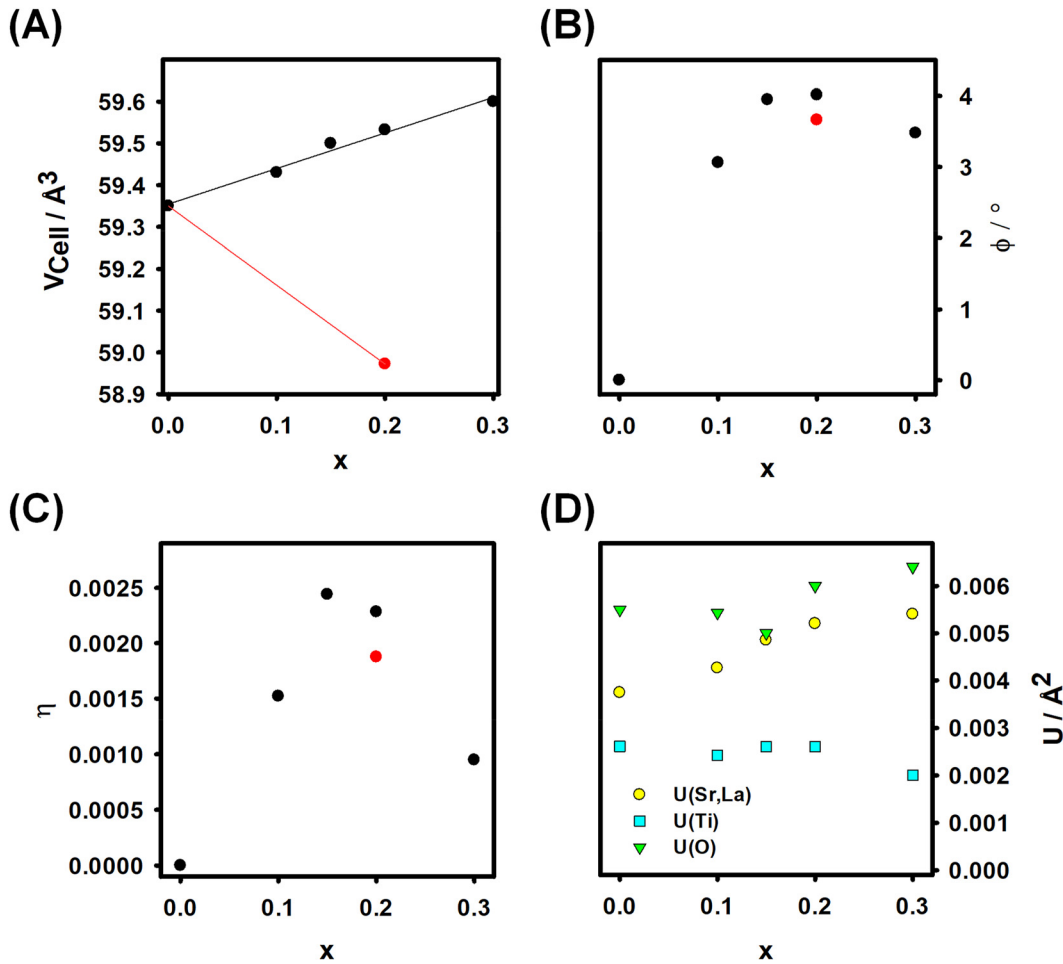


Figure 4: Parameters calculated for (black) stoichiometric ($\text{Sr}_{1-x}\text{La}_x\text{TiO}_3$), and (red) charge-compensated ($\text{Sr}_{1-3x/2}\text{La}_x\text{TiO}_3$) samples at 110 K; (A) cell volume of the parent cubic cell, i.e. the refined cell volume for STO and $\frac{1}{4}$ of the cell volume for the tetragonal phases; (B) octahedral tilt angle ϕ , (C) tetragonal strain η ; (D) atomic mean square displacement parameters U for St samples; La,Sr (yellow circles), Ti (cyan squares) and O (green triangles). Error bars are reported but are smaller than symbols.

their computational work, tilting angles (ϕ) larger than 6° energetic factors stabilize a FE state driven by cation off-centering along [001], provided that the cell is allowed to relax in order to develop tetragonal strain and cause the expansion of the Ti–O bond along the c -axis.

Within the second-order Jahn-Teller (JT) model, the Ti displacement along the $[101]_c$ direction recovers some π -bonding along the c -axis. In other words, for larger tilting angles, the elongation of the axial Ti–O bond plays a central role in lowering the energy of the FE distortion. Accordingly, Pr doped SrTiO_3 solid solutions, which exhibit tilting angles as large as 8° at the local scale, demonstrate high-temperature electrostriction usually associated with a relaxor FE behavior.⁸⁰ Although high dielectric constants have been measured at 25°C for slightly La-doped SrTiO_3 samples ($x < 0.02$), with a decrease observed for higher La concentrations,³¹ spectroscopic ellipsometry measurements revealed

that La doping progressively suppresses the FE instability in stoichiometric samples.⁸⁸

Focusing on the $Pm\bar{3}m$ to $I4/mcm$ AFD phase transition, the group-subgroup relationship⁸⁹ allows for a continuous transition. The thermodynamic of these transitions have been extensively investigated within the framework of the Ginzburg-Landau Theory.^{65,75} Here, the tilting angle is considered the order parameter of the transition, and the temperature dependence of ϕ below the phase transition is described using the mean field equation (Equation (4)):

$$\phi = \phi_0 \left(1 - \frac{T}{T_C} \right)^\beta \quad (4)$$

where T_C is the transition temperature, ϕ_0 is the tilting angle at 0 K, and β is related to the order of the phase transition ($\beta = \frac{1}{2}$, $\beta = \frac{1}{4}$ for second-order and tricritical transitions,

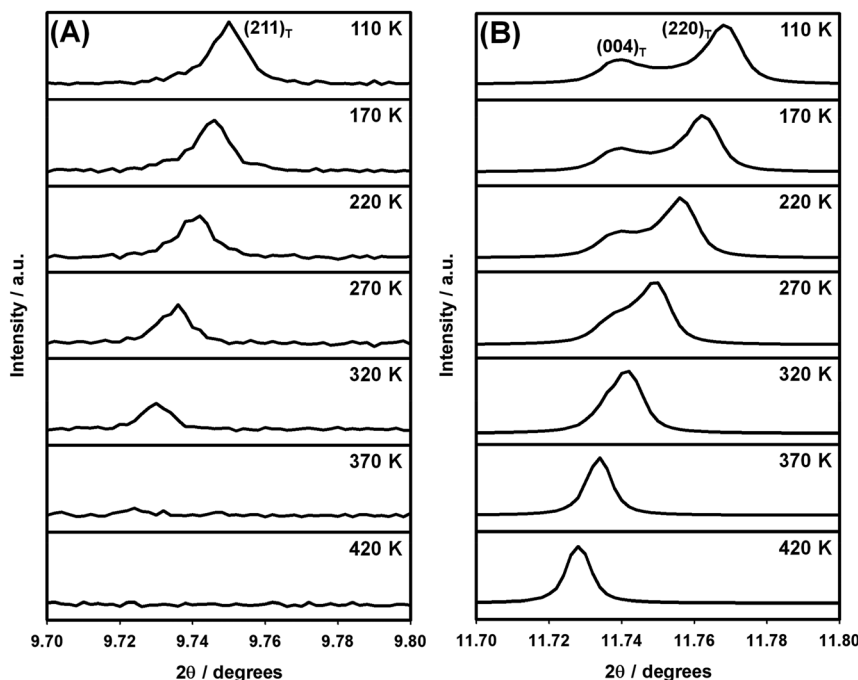


Figure 5: Temperature-dependent changes for the (A) $(211)_T$ and (B) the $(004)_T$ and $(220)_T$ peaks for SLTO_{80-20} sample.

respectively).⁶⁵ Although the phase transition in STO is continuous,⁷⁴ it has been suggested that it is close to a tricritical point,^{65,74,75,77} which causes the deviation of β from $1/2$. For detailed descriptions of this phase transition in SrTiO_3 within the framework of Landau theory, we refer to Hayward and Salje,⁶⁵ and Carpenter⁷⁵ and the references therein. A more accurate

Table 3 reports the β , ϕ_0 and T_C values calculated applying equation (4) to the experimental tilting angles versus T (Figure 6A). All β values lie in the 0.41–0.46 range, indicating an intermediate regime between second-order and tricritical transitions. As mentioned earlier, using a single tetragonal phase for refining the XRPD data could introduce small systematic errors in the parameters. Figure S6 of the SI reports the ϕ versus T curve for the SLTO_{80-20} sample obtained using a biphasic model in the Rietveld refinement. The calculated parameters of the mean field equation are $T_C = 391(1)$ K, $\phi_0 = 5.00(6)^\circ$ and $\beta = 0.40(1)$.

It is important to note that, except for the SLTO_{90-10} sample, which exhibits a calculated transition temperature around 270 K, all other samples undergo the tetragonal-to-cubic transition above RT, in the 350 K–390 K range (see Figure 6B). A more accurate determination of the process' thermodynamics could be obtained by calorimetric means but are out of the scope of the present manuscript. Given that pure SrTiO_3 undergoes this transition at 105 K,^{90,91} it can be generalized that the introduction of lanthanum in the A-site stabilizes the tetragonal symmetry at higher temperatures, as a result of the smaller ionic radius of La^{3+} compared to Sr^{2+}

Table 3: Fitted values of T_C , ϕ_0 and β for the different samples and Goldschmidt t value (t).

Sample	$\phi_0/^\circ$	T_C/K	β	t
SLTO_{90-10}	3.8(4)	270(0.7)	0.45(1)	0.9046
SLTO_{85-15}	4.5(3)	365(0.4)	0.41(1)	0.9020
SLTO_{80-20}	4.8(4)	391(1.1)	0.43(1)	0.8994
SLTO_{70-30}	4.0(2)	356(0.5)	0.46(1)	0.8942

and Ti^{4+} compared to Ti^{3+} , both of which progressively decrease the Goldschmidt tolerance factor t Ti^{3+} .⁹² The decrease in t also favors the tilting distortion (see Figure 6B).

We note that in solid solutions experiencing the same $Pm\bar{3}m \rightarrow I4/mcm$ transitions, but where no Ti^{3+} is formed, such as $\text{Sr}_{1-x}\text{Ca}_x\text{TiO}_3$, T_C monotonically raise on Ca doping from 105 K of SrTiO_3 to more than 1600 K of CaTiO_3 .⁷⁵ As shown in Figure 6B, increasing T_C and ϕ values are observed up to SLTO_{80-20} , while these trends are inverted in SLTO_{70-30} .

Regarding the tetragonal distortion, Figure 6C shows the refined reduced lattice parameters $a_c (=a_T/\sqrt{2})$ and $c_c = c_T/2$ as a function of T for the St samples, while Figure 6D reports the η values.

In the cubic phase, Sr/La lies in the center of a cuboctahedral oxygen cage with 12 identical (Sr/La)–O distances, while Ti is surrounded by an oxygen octahedron with 6 identical Ti–O distances. The tetragonal strain and the tilting distort both Ti and Sr/La coordination environments. The (Sr/La)–O bonds split into four short, four medium and four

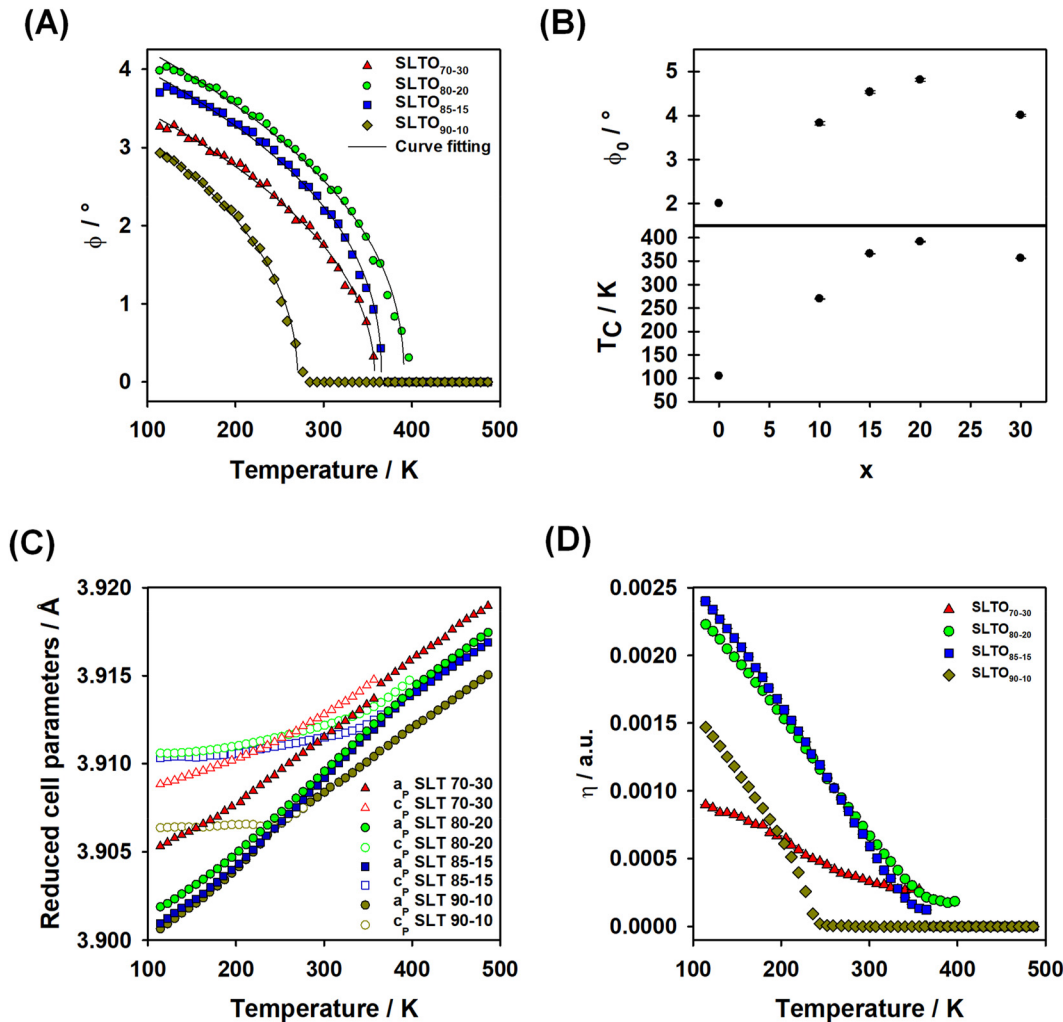


Figure 6: In (A) the tilting angle (ϕ) values are reported as a function of temperature SLT_{0.70-0.30} (red triangles), SLT_{0.80-0.20} (green circles), SLT_{0.85-0.15} (blue squares), and SLT_{0.90-0.10} (ochre diamonds) along with the fitted mean square equation curves are reported. In (B) we report the dependency of both critical temperature T_C and ϕ_0 from the lanthanum content. Data for STO are taken from Hui et al.⁶⁴ In (C) reduced lattice parameters a_p (full) and c_p (empty), while in (D) the tetragonal strain parameter η are plotted as a function of temperature. Error bars are reported in each panel but are smaller than symbols. Single curves for both panels A and D are reported in the SI (Figure S5).

long interatomic distances, whose values as displayed in Figure 7A as a function of $(T-T_C)$ for comparison. All curves show similar trends below the phase transitions. While the intermediate (Sr/La)–O1 distances follow the same trend as above T_C , the difference between the longest and shortest interatomic distances Δd , those involving the equatorial O2 oxygen ions, progressively increases due to the tilting distortion, reaching values as large as ≈ 0.18 Å at the lowest temperatures. Additionally, Δd increases with La doping up to $x = 0.20$, then decreases for $x = 0.30$.

The ratio between the Ti–O1 (axial, parallel to the c -axis) and Ti–O2 (equatorial, in the ab plane) bond lengths ($=d_{\text{Ti-O1}}/d_{\text{Ti-O2}}$), in the tetragonal phase depends on both T and composition, as shown in Figure 7B. Particularly, for STO⁶⁴

this ratio is larger than one in the whole T interval considered, as previously observed in STO,⁶⁵ in another quantum paraelectric material like EuTiO_3 ⁷⁸ and in the ferroelectric $P4mm$ phase of BaTiO_3 (≈ 1.011 at 300 K⁹³). It could be inferred that values of the Ti–O bond length ratio ≥ 1 characterize materials with a soft FE instability. Conversely, La-doping progressively leads to the compression of the TiO_6 octahedra, as noticeable by plotting the octahedron distortion parameter percentage (ODP%) defined as $\frac{2(d_{\text{Ti-O1}}-d_{\text{Ti-O2}})}{d_{\text{Ti-O1}}+d_{\text{Ti-O2}}}\times 100$ (Figure 7B).

A possible explanation could rely on the link between the Ti charge state and the nature of the FE distortion. As proposed by Aschauer and Spaldin²⁰, the Ti off-centering is related to its $3d^0$ electronic configuration (2nd order JT

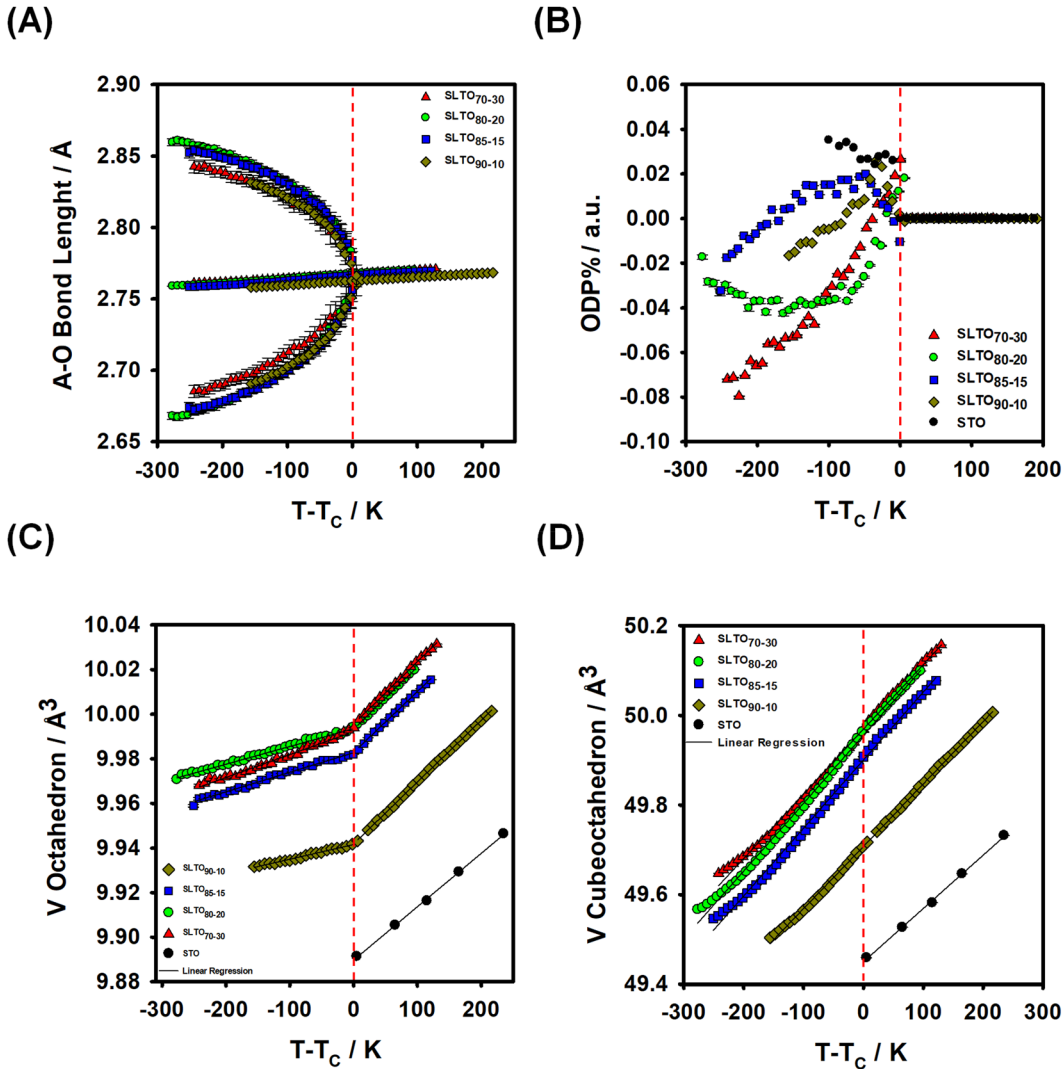


Figure 7: Temperature dependency of (A) A-O bond lengths, (B) Ti-O octahedron distortion parameter percentage, (C) TiO_6 octahedron volume, and (D) cubeoctahedron volume. All temperature values are relative to the critical temperature (T_c). In all plots red triangles refer to SLTO_{70-30} , green circles to SLTO_{80-20} , blue squares to SLTO_{85-15} , ochre diamonds to SLTO_{90-10} , and black circles to STO (STO data from Hui et al. ⁶⁴). In (C) and (D), the linear fits are reported as black lines. Error bars are reported in each panel but are smaller than symbols, aside from panel A. For visual clarity, in all panels the vertical red dashed lines represent $T - T_c = 0$.

effect) and is stabilized by the elongation of the axial $d(\text{Ti}-\text{O}1)$ distances. By this argument, increasing the Ti^{3+} ($3d^1$) concentration at the expense of Ti^{4+} ($3d^0$), should diminish the second order JT effect and, in turn, harden the FE instability.⁸⁸ On the other hand, this should also induce a (small) 1st order JT effect which, in turn, leads to compressive stress to the axial $\text{Ti}-\text{O}1$ bonds.⁹⁴

To compare this with the experimental data, the volumes of the TiO_6 octahedra V_{TiO_6} (that turns into a squared base bipyramid below T_c) and of the $(\text{Sr/La})\text{O}_{12}$ cuboctahedra ($V_{(\text{La,Sr})\text{O}_{12}}$) are shown in panels C and D of Figure 7, respectively.

$V_{(\text{La,Sr})\text{O}_{12}}$ values shrink with almost the same slope ($d(V_{(\text{La,Sr})\text{O}_{12}})/dT \approx 1.4 \times 10^{-3} \text{ Å}^3 \text{ K}^{-1}$) independently on sample composition in the whole investigated temperature ranges. Conversely, the temperature evolution of V_{TiO_6} is strongly affected by the phase transition. Above T_c $d(V_{\text{TiO}_6})/dT$ is $\approx 2.8 \times 10^{-4} \text{ Å}^3 \text{ K}^{-1}$ for all the samples, while below the phase transition it sharply decreases.

This effect must be related to the progressive tilting of the octahedra that enlarges the basis of the bipyramid. It follows that the phase transition should be related to the rigidity of the TiO_6 cage and tilting arises to contrast the thermal shrinking of the cell. Finally, we note that the slope

in SLTO_{70-30} is larger ($1.03 \times 10^{-4} \text{ \AA}^3 \text{ K}^{-1}$) than in all other samples with $0.10 \leq x \leq 0.20$ ($\approx 7.77 \times 10^{-5} \text{ \AA}^3 \text{ K}^{-1}$). Again, SLTO_{70-30} deviates from the trends observed in the less doped samples while displaying the same long-range tetragonal structure.

To shed light on the discrepancies between SLTO_{70-30} and the other solid solutions, we turn to PDF analysis carried out at the lowest investigated temperature (110 K).

3.4 PDF analysis

Figure 8 shows the low- r region of the $G(r)$ curves collected at 110 K for the St samples. The labels indicate the atomic pairs involved in each peak. a_c , $\sqrt{2}a_c$, $\sqrt{3}a_c$, $2a_c$ correspond to (the moduli of) the translation vectors along the cell axis, the face and cell diagonals and twice the cell axis of the cubic cell, respectively. La doping primarily affects the metal-oxygen distances: the Sr/La–O peaks centered at $\approx 2.7 \text{ \AA}$ and $\approx 4.8 \text{ \AA}$ progressively decrease in intensity and develop low- r shoulders. Meanwhile, the Ti–O peak at $\approx 4.4 \text{ \AA}$ exhibits significant broadening. Similar effects appear also at larger r distances. In contrast, the peaks involving only cation-cation distances are only slightly broadened and shifted toward larger r values.

The $G(r)$ curves in the 2.3–10.0 $\text{\AA}$ interval were fitted using the $I4/mcm$ model, which adequately interpreted the high resolution XRPD data at the same temperature. In addition to the cell parameters and x_{O_2} , we refined four isotropic U parameters: $U(\text{Sr/La})$, $U(\text{Ti})$, $U(\text{O1})$ and $U(\text{O2})$. The calculated $G(r)$ curves for all ST samples are shown in Figure 8, panels B–E, alongside the experimental data and the residuals.

The $I4/mcm$ model adequately fits the experimental data for the samples with La concentration up to $x = 0.20$, while the same model proves inadequate in the case of SLTO_{70-30} .

Regarding the displacement parameters, $U(\text{Sr/La})$, $U(\text{Ti})$ and $U(\text{O1})$ (Figure 9, upper panel) all fall in the 0.002–0.010 $\text{\AA}^2$ range. Their values increase with higher La concentration, reflecting the static disorder introduced by doping. $U(\text{O2})$, being significantly larger than the other U parameters, indicates the disordering in the coordination octahedra and cuboctahedra but could also be influenced by the higher uncertainty in the oxygen-related parameters obtained from the X-ray PDF.

The refined tilting angles (Figure 9B) range from 7.4° to 8.5° , higher than the values obtained by Rietveld analysis ($3\text{--}4^\circ$, Figure 4). This discrepancy points to the coexistence of domains characterized by different order parameter orientations, as might be produced, for example, by the $R4+$ and $R3+$ irreducible representations of $I4/mcm$, both of which give rise

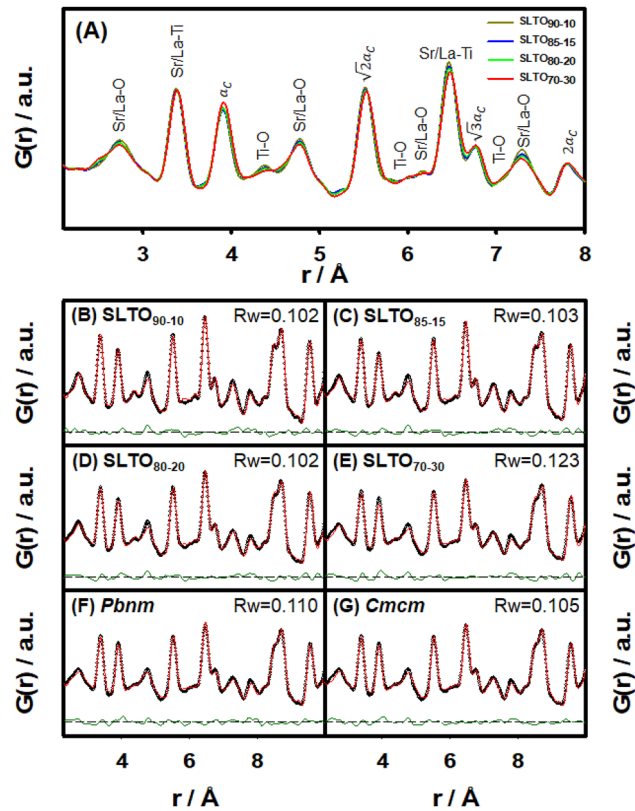


Figure 8: In (A) low- r fit range of the $G(r)$ collected at 110 K for SLTO_{90-10} (ochre), SLTO_{85-15} (blue), SLTO_{80-20} (green), and SLTO_{70-30} (red). Fits of using the $I4/mcm$ model for: (B) SLTO_{90-10} , (C) SLTO_{85-15} , (D) SLTO_{80-20} , and (E) SLTO_{70-30} . Additional fits are shown for SLTO_{70-30} using $Pbnm$ (F), and $Cmcm$ (G) models. In all panels symbols are the experimental data, the calculated curves are in red, while the green curve is the residuals.

to the same Bragg superlattice reflections. Another possibility might be the occurrence of another, distinct tilting mode, like $M2+$, limited to the local scale. Either way, the smaller Rietveld-refined ϕ values should represent the average value of the AFD tilting magnitude over domains characterized by different local distortions. Along with hkl -dependent Bragg peaks asymmetry shown in Figure 3, this suggests the presence of DW. It is generally accepted that, in perovskites with tolerance factors $t < 1$, the tilting of TiO_6 octahedra optimizes the bonding. Furthermore, the larger the ϕ angle, the larger the volume of TiO_6 , making tilting an effective mechanism to mitigate contraction upon cooling. Accordingly, the V_{TiO_6} values calculated by the PDF refinements are $\sim 1.5\%$ larger than those obtained by Rietveld refinements on data at the same temperature (see Figure 9, panel C).

The Bond Valence Model proposed by I.D. Brown and D. Aldermatt allow us to quantify these effects.^{95,96} In Figure 10 we report the results of Bond Valence Sum (BVS) calculations for titanium. For STO we used only the $Pm\bar{3}m$ model calculated by the Rietveld analysis at 110 K; for St samples, we first

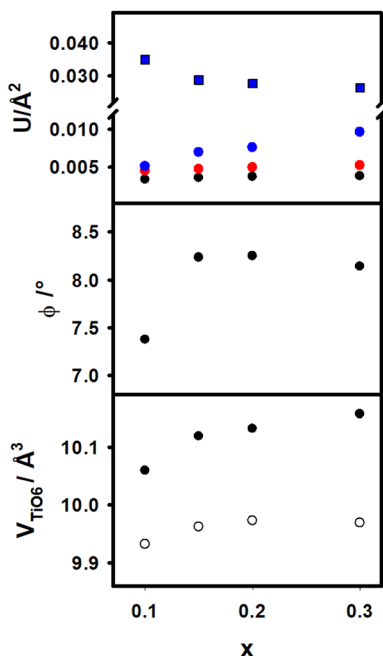


Figure 9: In (A) U values for Ti (black circles), La/Sr (red circles), O1 (blue circles) and O2 (blue squares); (B) ϕ and (C) volume of the TiO_6 octahedron refined applying the $I4/mcm$ model on PDF data collected at 110 K (full circles). The empty circles in panel C are the V_{TiO_6} values calculated from the rietveld refinements in the reciprocal space.

adopted an artificial “tilting-free” model starting from the Rietveld refined a and c parameters and constraining $x_{\text{O}_2} = 0.25$ and (black circles) to test the effect of the absence of tilting on the titanium BVS. Then we applied the $I4/mcm$ models derived from either the reciprocal space (red circles) or the real space (blue circles) Rietveld analysis. For SrTiO_3 the Ti and Sr BVS values were 4.16 and 2.13, respectively. Similar BVS are calculated starting from the data of Hui and coworkers: 4.18 and 2.14.⁶⁴ The mismatch between the calculated BVS and the expected formal charges of Ti (4.00) and Sr (2.00) could be due to the lower temperature of these measurements. For this reason, we normalized the BVS values to obtain BVS Ti = 4 for STO, as in the literature Ti(IV) has been reported as the predominating oxidation state in STO.^{97–99} It should be noted that this approach may introduce a systematic error, as small amounts of Ti(III) in STO cannot be fully excluded, potentially arising from surface defects. Since in St samples Sr and La share the same site, all the adopted models, supply average (Sr,La)–O distances only, hindering a meaningful analysis of La and Sr charge state. For this reason, only the BVS values of titanium are shown in Figure 10 and discussed in the following paragraphs.

The normalized BVS of the tilting free model are ≈ 4.0 for all the samples; increasing the tilting angle a systematic decrease of the BVS values is observed as well as a larger dependence on composition. Particularly, applying the

models refined against the PDF, the BVS results follow the linear trend $\text{BVS} = 4 - y$ (with y the Ti oxidation state according to Eq. (2)) up to $x = 0.20$, confirming the interplay between the titanium charge state and the tilting. Even in this case, SLTO_{70-30} deviates from the trends of the less doped samples.

As shown in Figure 8E, the $I4/mcm$ model fits the local structure SLTO_{70-30} sample worse than the other compositions. Since the tolerance factor in SLTO_{70-30} ($t = 0.984$) is comparable to that of perovskites showing $Pbnm$ ($Pnma$) symmetry above room temperature,⁷⁹ we explored the possibility of local symmetry breaks towards structures expected for $t < 1$, which could also act as precursors to phase transitions at temperatures lower than those investigated in this study.

Perovskite phases of symmetry $Pbnm$ (alternate setting of $Pnma$), characterized by the $a^+a^-c^+$ ($a^+b^-b^-$ for $Pnma$)¹⁰⁰ tilting pattern, have been identified e.g. in CaTiO_3 ,^{100–102} $\text{Sr}_{1-x}\text{Ca}_x\text{TiO}_3$ ($x > \approx 0.10$),⁷⁹ $\text{Eu}_{1-x}\text{Ca}_x\text{TiO}_3$ ($x > \approx 0.40$),¹⁰³ SrZrO_3 .¹⁰⁴ $Ibmm$ space group (alternate setting of $Imma$) has been proposed by Sunstrom and coworkers for $\text{Sr}_{1-x}\text{La}_x\text{TiO}_3$ at RT in the $0.2 \leq x \leq 0.7$ range.¹⁷ The tilting pattern is $a^+a^-c^0$ ($a^0b^-b^-$ for $Imma$ setting²⁷). Finally, the $Cmcm$ space group has been identified as an intermediate phase between $I4/mcm$ and $Pbnm$ in ZrTiO_3 ¹⁰⁴ and CaTiO_3 ¹⁰⁵ on lowering T and is characterized by the tilting pattern is $a^0b^+c^-$.

The $Ibmm$ space group, which has been proposed for the same $\text{Sr}_{0.7}\text{La}_{0.3}\text{TiO}_3$ composition, does not improve the $G(r)$ fit ($R_w = 0.121$), despite introducing an additional out-of-phase rotation of the octahedra. In contrast, adding an extra in-phase rotation ($M2^+$ ⁷⁵) perpendicular to the $R4^+$ of the main tetragonal phase, leading to $Pbnm$ or $Cmcm$, reduces the residuals to $R_w = 0.110$ and $R_w = 0.105$, respectively. The corresponding fits are shown in panels F and G of Figure 8. The additional in-phase tilting increases the volume of TiO_6 distorted octahedra, facilitating a reduction of its formal average oxidation state. Using the BVS method, the oxidation state of Ti was calculated to be $\text{Ti}^{+3.73}$, which is very close to $\text{Ti}^{+3.7}$, the expected value for stoichiometric samples according to Equation (2) (see green circles in Figure 10).

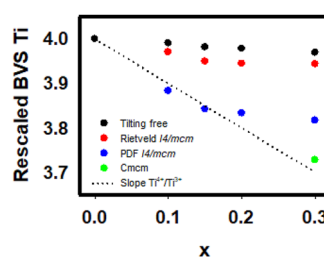


Figure 10: Rescaled bond valence sums for Ti. Black, red, blue and green circles report the calculated values applying “tilting free”, rietveld $I4/mcm$, PDF $I4/mcm$, and $Cmcm$ models. See text for details.

The PDF analysis of SLTO_{70-30} sample was extended to larger r values. In the range $10 < r < 20 \text{ \AA}$, the $I4/mcm$ and $Cmcm$ models provided comparable results with R_w values of 0.067 and 0.064, respectively (see Figure S7 of the Supporting Information). Given that the $Cmcm$ model more degrees of freedom than $I4/mcm$, we conclude that the tetragonal symmetry describes effectively the structure beyond 1 nm. Finally, attempts to apply the $Pbnm$ and $Cmcm$ models to the $G(r)$ of SLTO_{80-20} sample brought to slightly worse residuals ($R_w = 0.108$ and 0.105 , respectively) than the tetragonal model.

According to our PDF analysis, the local structure of the SLTO_{70-30} sample is consistent with $Cmcm$ symmetry. The out-of-phase tilting along the c -axis displays long-range order, enabling Bragg peak splitting and the formation of superstructure peaks characteristic of the $I4/mcm$ space group. However, the local tilting angle along c is significantly larger than the average one (7° versus 4° , respectively), indicating the presence of domains with different tilting directions, separated by DW. This is supported by the hkl -dependent asymmetry observed in the Bragg peaks. An in-phase tilting perpendicular to the c -axis is also present, with a tilting amplitude of approximately 4° and a coherence length of about 1 nm. It is worth noting that there is a group-subgroup relationship between the $I4/mcm$ and $Cmcm$ space groups (which is absent between $I4/mcm$ and $Ibmm$ or $Pbnm$ ²⁷), allowing, in principle, continuous transformation from one phase to the other.

We propose that this feature also explains the limited coherence length of the in-phase tilting distortion: only a few octahedra are coherently tilted along the same a -axis before the tilting fades, generating DW. These DW, in turn, serve as sources of domain $Cmcm$ nanodomains, which enable the switching of the in-phase tilting axis. In the absence of a group-subgroup relationship, such a switching of the tilting axis would necessitate structural reconstruction at the DW.

As to less doped samples ($x \leq 0.20$), some disorder exists at low r , as testified by the large values of the $U(02)$ parameter, without bringing to a coherent symmetry decrease even at the local scale.

Thus, local deviations from an ordered tetragonal phase exists in all the investigated samples. However, only for $x > 0.20$ the instability at the M point (in phase tilting) produced coherently distorted $Cmcm$ nanodomains.

4 General discussion and conclusions

We have investigated the structural evolution of $\text{Sr}_{1-x}\text{La}_x\text{TiO}_3$ ($0.10 \leq x \leq 0.30$) perovskite samples (stoichiometric St

samples) in the $110 \text{ K} \leq T \leq 490 \text{ K}$ range, encompassing the antiferrodistortive $I4/mcm$ to $Pm\bar{3}m$ phase transition by means of the Rietveld analysis of high-resolution powder diffraction data. PDF measurements were also carried out at the lowest T (110 K). Additionally, EPR spectra were collected on the same samples plus SrTiO_3 and $\text{Sr}_{0.7}\text{La}_{0.2}\text{TiO}_3$ (charge compensated CC sample). Finally, XRS spectra at the O–K edge were collected at RT on selected samples (SrTiO_3 , $\text{Sr}_{0.7}\text{La}_{0.2}\text{TiO}_3$ (CC) and $\text{Sr}_{0.7}\text{La}_{0.3}\text{TiO}_3$ (St)).

In respect to the CC specimen, the XRS spectrum of the $\text{Sr}_{0.7}\text{La}_{0.3}\text{TiO}_3$ St sample displayed a decreased scattered intensity in the $\approx 530\text{--}532 \text{ eV}$ range, corresponding to O 2p/Ti 3d final states. This finding suggests that in St samples these states are partially populated, confirming that the excess positive charge of La dopant is reasonably compensated by electron injection in the conduction band. Accordingly, in the ESR spectra of the St samples features attributable to both isolated Ti^{3+} ions and itinerant electrons appear, with increasing population of the latter ones on La doping. Due to the limitations of the employed characterization and computational techniques, we cannot quantify the amount of the formed Ti^{3+} and thus we cannot fully exclude the formation of metal vacancies, as a secondary charge compensation mechanism.

According to high resolution XRPD measurements, at 110 K all the investigated La-doped samples are tetragonal, space group $I4/mcm$. The (hkl) dependence of the diffraction peaks asymmetry suggests that DW exist within each crystallite separating tetragonal regions with different tilting directions. The cell volume of St samples increases with La concentration, reasonably due to the substitution of Ti^{4+} with the larger Ti^{3+} prevailing over the contraction expected from the $\text{La}^{3+}/\text{Sr}^{2+}$ substitution. Accordingly, the CC sample, which has no Ti^{3+} , shows the lowest cell volume. La doping increases the tilting angle ϕ and the tetragonal strain η up to a peak at $x = 0.15\text{--}0.20$, while their values decrease for the $x = 0.30$ sample.

Temperature dependent XRPD data was used to study the structural phase transition to the cubic phase. The critical parameters β , ϕ_0 , and T_C were calculated applying the mean field equation (Eq. (4)) to the experimental ϕ values. All β values are in the 0.41–0.46 range, indicating an intermediate regime between second-order and tricritical transitions. ϕ_0 and T_C reveal a non-monotonic trend; both increase up to a maximum at $x = 0.20$, then start decreasing. The analysis of nearest neighbor interatomic distances reveals that below T_C the TiO_6 octahedron is slightly compressed, unlike in quantum paraelectric compounds like SrTiO_3 and EuTiO_3 and Ferroelectric BaTiO_3 , where it is elongated. As proposed by Aschauer and Spaldin²⁰, the Ti off centering is related to its 3d⁰

electronic configuration (2nd order JT effect) and is stabilized by the elongation of the axial d(Ti–O1) distances. Indeed, La doping both hardens the FE phonon, pushing the SLTO system away from the FE instability and transforming Ti^{4+} into Ti^{3+} at the expense of the concentration of $\text{Ti}^{4+}(3d^0)$ ions. While the 2nd order JT effect is decreased, Ti^{3+} ions could induce a (small) 1st order JT effect which, in turn, should imply compressive stress to the axial Ti–O1 bonds.⁹⁴

The PDF measurements shed light on the non-monotonic trends observed through XRPD. The local structure of St samples up to $x = 0.20$ is suitably fitted by the *I4/mcm* model, although the local octahedral tilt angle is enhanced ($\phi \approx 8^\circ$) with respect to the average structure ($\phi_0 \approx 4^\circ$). In $\text{Sr}_{0.7}\text{La}_{0.3}\text{TiO}_3$ an additional in-phase tilting mode along the *a*-axis is active at the local scale ($r < 1$ nm), which might represent the onset of another phase transition below the lowest temperature investigated here. On the other hand, the additional tilt mode is believed to coexist with the AFD octahedral tilting in distinct domains, resulting in the smaller ϕ and η values observed by Rietveld analysis and in the observation of peak broadening compatible with DW.

One last comment concerns the thermal contraction of the $(\text{Sr/La})\text{O}_{12}$ cuboctahedron and of the TiO_6 octahedron as the temperature decreases. As shown in Figure 7, $V_{(\text{La,Sr})\text{O}_{12}}$ shrinks at a nearly constant rate across the phase transition. Conversely, the thermal contraction rate (dV_{TiO_6}/dT) of the TiO_6 octahedron changes significantly, decreasing from $2.8 \times 10^{-4} \text{ \AA}^3 \text{ K}^{-1}$ above T_C to $7.77 \times 10^{-5} \text{ \AA}^3 \text{ K}^{-1}$ below T_C for samples with $x \leq 0.20$, with SLTO_{70-30} presenting a higher value below T_C ($1.03 \times 10^{-4} \text{ \AA}^3 \text{ K}^{-1}$). This suggests that the phase transition is related to the rigidity of the TiO_6 cage. This experimental finding was confirmed by Bond Valence Sum calculations, showing that tilting arises to contrast the thermal shrinking of V_{TiO_6} . Without tilting, the BVS values for La and Ti deviate significantly from their expected values based on the defect equation (eq. (2)) and both our findings and those reported in the literature. Increasing the out-of-phase tilting angle along *c*, i.e. applying the Rietveld ($\phi_0 \approx 4^\circ$) and the PDF ($\phi_0 \approx 8^\circ$) *I4/mcm* models, the BVS values for Ti decreases progressively reaching the expected values according to eq.(2) for the $x \leq 0.20$ samples. For the $x = 0.30$ sample the expected BVS value is obtained by applying the *Cmcm* model, which includes additional in-phase tilting along the *a*-axis. Thus, tilting seems to reduce the contraction upon cooling of the TiO_6 octahedra and is progressively enhanced by increasing the Ti^{3+} concentration.

Acknowledgments: We acknowledge the European Synchrotron Radiation Facility (ESRF) for provision of beamtime under proposal number HC-2324. The authors thank Dr.

Serena Cappelli for collecting the ESR data and Prof. Luigi Falciola for collecting ICP-MS data. M.P. and M.S. acknowledge funding by PRIN 2022 of Ministero dell'Università e della Ricerca (MUR); funded by the European Union (NextGenerationEU), project code 20224KN85Y, CUP G53D2300331006, project title “Fuel from CO₂: by co-electrolysis: advanced materials and devices For sustainable energy storage–FORCEFUL”. M.C. acknowledges the support from the Ministero dell'Università e della Ricerca (MUR) and the University of Pavia through the program “Dipartimenti di Eccellenza 2023–2027”.

Research ethics: Not applicable.

Informed consent: Not applicable.

Author contributions: M.P.: Investigation; Formal analysis; Visualization; Writing–Original Draft; Writing–Review & Editing; Funding acquisition. S.C.: Investigation; Writing – review and editing. M.C.: Investigation; Writing – review and editing. C.O.: Investigation; Formal analysis; Visualization; Writing–Original Draft; Writing–Review & Editing. A.L.: Investigation; Formal analysis; Visualization; Writing–Original Draft; Writing–Review & Editing. M.S.: Conceptualization; Investigation; Formal analysis; Visualization; Writing–Original Draft; Writing–Review & Editing; Funding acquisition.

Use of Large Language Models, AI and Machine Learning Tools: None declared.

Conflict of interest: The authors state no conflict of interest.

Research funding: M.P and M.S. acknowledge funding by PRIN 2022 of Ministero dell'Università e della Ricerca (MUR); funded by the European Union (NextGenerationEU), project code 20224KN85Y, CUP G53D2300331006, project title “Fuel from CO₂: by co-electrolysis: advanced materials and devices For sustainable energy storage–FORCEFUL”. M.C. acknowledges the support from the Ministero dell'Università e della Ricerca (MUR) and the University of Pavia through the program “Dipartimenti di Eccellenza 2023–2027”.

Data availability: Data is available upon request to the authors.

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Supplementary Material: This article contains supplementary material (<https://doi.org/10.1515/zkri-2025-0047>).