Raman Response of Quantum Critical Ferroelectric Pb-Doped SrTiO$_3$

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Abstract: A quantum paraelectric SrTiO$_3$ is a material situated in close proximity to a quantum critical point (QCP) of ferroelectric transition in which the critical temperature to the ferroelectric state is suppressed down to 0 K. However, the understanding of the behavior of the phase transition in the vicinity of this point remains challenging. Using the concentration $x$ of Pb in solid solution Sr$_{1-x}$Pb$_x$TiO$_3$ (PST$_x$) as a tuning parameter and applying the combination of Raman and dielectric spectroscopy methods, we approach the QCP in PST$_x$ and study the interplay of classical and quantum phenomena in the region of criticality. We obtain the critical temperature of PST$_x$ and the evolution of the temperature-dependent dynamical properties of the system as a function of $x$ to reveal the mechanism of the transition. We show that the ferroelectric transition occurs gradually through the emergence of the polar nanoregions inside the non-polar tetragonal phase with their further expansion on cooling. We also study the ferroelastic cubic-to-tetragonal structural transition, occurring at higher temperatures, and show that its properties are almost concentration-independent and not affected by the quantum criticality.

Keywords: quantum paraelectrics; strontium titanate; solid solutions; lattice dynamics; dielectric response

1. Introduction

There has been significant interest in quantum phenomena in strontium titanate oxide, SrTiO$_3$, over the past decades. It has been observed that, upon cooling up to 30 K, the dielectric permittivity of this material follows the Curie–Weiss law with the characteristic Curie–Weiss temperature of ~37 K but then deviates from this behavior, saturating to a giant value of more than 20 000 at ~3 K [1]. Critical lattice dynamics reveals similar behavior. It has been observed that, unlike in conventional ferroelectrics, the frequency of the soft mode does not become unstable but also saturates at low temperatures [2,3]. It is widely accepted [1,4,5] that ferroelectric ordering in SrTiO$_3$ at low temperatures is suppressed by the quantum fluctuations of the polar Ti ions, preventing their stabilization in the off-center potential energy minima positions, hence the formation of the ferroelectric state. In other words, SrTiO$_3$ belongs to the noble systems in which the behavior is defined by quantum properties, widely known as quantum materials [6]. It is believed that the regime of proximity to the quantum critical point (QCP) [7] is realized in SrTiO$_3$, which makes this material not only a natural laboratory to study the fundamental properties of quantum criticality but also a suitable system for application in the emerging non-von Neumann quantum and neuromorphic computing circuits.
The pristine SrTiO$_3$ is located slightly outside the QCP. To achieve the genuine quantum ferroelectric transition at $T = 0$ and to study the crossover from quantum to classical criticality, one should apply the continuous driving force that suppresses the quantum fluctuation, restoring the ferroelectric order. Various means of stabilizing ferroelectricity in SrTiO$_3$, including substrate-induced [8] and pressure-induced [9] strains, substitution of $^{18}$O isotope [4], and defect generation [10] were suggested. However, the most commonly used way is chemical doping with the substitution of Sr by cation A (A = Ca, Ba, Pb, etc.) with the formation of Sr$_{1-x}$A$_x$TiO$_3$ solid solution [11–13]. The advantage of this method is the well-targeted attainability of the QCP and the ferroelectric phase at a certain $x$, although the question of whether the polar state at a small $x$ arises because of the polar ion displacement or because of the freezing of impurity-induced dipoles has been debated for many decades [14–16]. It is believed, however, that in Sr-based compounds, the quantum effects are strongly developed and prevent the frozen-glass behavior [12] that we also assume in our article.

In the present study, we explore the Sr$_{1-x}$Pb$_x$TiO$_3$ (PST$_x$) solid solutions with $x = 0.005$, 0.02, 0.04 by means of Raman and dielectric spectroscopies to investigate the effect of quantum fluctuations and the interaction of vibrational modes on the phase states in the vicinity of the QCP. We established that ferroelectric transition already takes place for the lowest Pb concentration $x = 0.005$ at the critical temperature of ~16 K. We demonstrate that this solid solution is very close to the QCP where the thermal and quantum fluctuations compete. Solid solutions with $x = 0.02$ and 0.04 possess higher critical temperatures, 56 K and 72 K, respectively, and are characterized by the more classical ferroelectric behavior. For all three Pb concentrations, we show that the ferroelectric transition occurs gradually through the emergence of the polar nanoregions inside the non-polar paraelectric phase. We give a detailed analysis of the temperature-dependent Raman spectra for these compounds in the temperature interval of 12–300 K and demonstrate that they also reveal a structural transition from the cubic $Pm\bar{3}m$ to the non-polar tetragonal $I4/mcm$ phase at a temperature of ~90 K.

2. Materials and Methods

The ceramic Sr$_{1-x}$Pb$_x$TiO$_3$ solid solutions with $x = 0.005$, 0.02, 0.04 were prepared from stoichiometric mixtures of SrCo$_3$, TiO$_2$, and PbO oxides according to the standard technique of solid-phase synthesis. The samples were calcined in the platinum crucible in the lead oxide ambient at $T = 1400$ K for 3 h and sintered at $T = 1650$ K for 1 h. Samples were pressed at 50 MPa in the form of 2 mm thick pellets with a diameter of 10 mm.

Synchrotron powder diffraction data were collected at the P24(EH2) PETRA III beam-line, DESY (Hamburg, Germany), using a 2D marCCD 165 detector at temperature of 250 K. The monochromatic beam at wavelength $\lambda = 0.5607$ Å was slitted down to $300 \times 300$ µm$^2$. The 200 µm diameter glass capillaries were used for mounting the finely ground powder samples. The sample-to-detector distance ($D \approx 75$ mm) and the detector parameters were calibrated using a LaB6 NIST reference powder sample; calibration and subsequent integration were conducted using the Dioptas software [17]. The Rietveld refinement of the collected data was conducted using the FullProf software [18]. The pseudo-Voigt profile was used to model the Bragg reflection profile. At 250 K, the cubic unit cell parameters of the PST$_x$ samples with $x = 0.005$, 0.02, 0.04 were $0.3910$ nm, $0.3908$ nm, and $0.3903$, respectively. No parasitic phases were detected (see Supplementary materials).

The Raman spectra were excited in the range of 12–800 cm$^{-1}$ using argon laser radiation with wavelength $\lambda = 514.5$ nm. They were recorded in a backscattering geometry using a Jobin Yvon T64000 spectrometer equipped with CCD and photon counting detector in the temperature range 15–150 K. An optical microscope with a 50× objective was used to focus the incident light as a 2 µm diameter spot on the sample. Low-temperature dependencies of the Raman spectra were received using a closed-cycle helium cryostat with temperature stability of ± 0.1 K. The measured Raman spectra were corrected for the Bose–Einstein temperature factor $(\frac{\hbar\omega}{kT} - 1)^{-1}$. 


Dielectric measurements at different temperatures were performed with an Agilent E4980 LCR-meter hooked to a Quantum Design Physical Properties Measurement System. Both sides of the pellets were covered with silver paste to create a capacitor-like structure. Capacitance C was measured at 10 kHz by assuming an equivalent parallel RC circuit, as is the standard for low leakage samples, and the corresponding relative permittivity $\varepsilon_r$ was calculated by means of the equation $\varepsilon_r = (C x d)/(\varepsilon_0 x A_r)$, where $d$ and $A_r$ are the dielectric thickness and the capacitor area, respectively. The measured temperature range was between 2 K and 290 K.

3. Results

At room temperature, the SrTiO$_3$ crystallizes in a cubic O$_h^1$ symmetry with the Pm$\overline{3}$m space group. The optical representation of the O$_h$ cubic phase includes three triply degenerated ferroelectric polar F$_{1u}$ modes and one triply degenerated “silent” F$_{2u}$-symmetry mode: $\Gamma_{\text{cub}} = 3F_{1u} + F_{2u}$. According to the symmetry selection rules, neither of them are Raman active. The ferroelectric F$_{1u}$ modes are conventionally called a Slater mode [19], an Axe mode [20], and a Last mode [21]. Moreover, each F$_{1u}$ mode splits into transverse (TO) and longitudinal (LO) components due to the long-range dipole–dipole interaction. Although they are not Raman active, they can be observed by various techniques, such as Hyper-Raman and neutron scattering, and IR spectroscopy [22,23]. A Slater mode describes mutually opposite vibrational displacements of the Ti and O ions along the z-axis. According to infrared, hyper-Raman, and neutron data, the TO$_3$ and LO$_3$ components of the Slater mode are observed at the frequencies of ~88 cm$^{-1}$ and ~175 cm$^{-1}$, respectively [24].

An Axe mode corresponds to the oxygen vibrations leading to the bending of the oxygen frame. The TO$_2$ and LO$_2$ components of the Axe mode are found at the frequencies of ~175 and ~266 cm$^{-1}$, respectively. A Last mode represents the mutual vibrations of the TiO$_6$ octahedral framework and the Sr ions along the z-axis. Its TO$_4$ and LO$_4$ components can be detected at frequencies of ~545 and ~795 cm$^{-1}$, respectively [24]. The so-called “silent” F$_{2u}$ mode is a structural mode describing oxygen vibrations in the xy-plane. This mode does not exhibit a dipole moment or the polarizability change of the molecule [25].

Upon cooling down to 105 K, the SrTiO$_3$ undergoes the non-polar structural phase transition from the cubic O$_h^1$ to the tetragonal D$_{4h}^1$ phase with the I4/mcm space group caused by the antiphase rotations of the oxygen octahedra with multiple increases in the unit cell [26,27]. Such a tetragonal distortion leads to the splitting of the Slater, Axe, and Last modes with F$_{1u}$-symmetry into the A$_{2u}$ and E$_u$ components. A “silent” F$_{2u}$ mode transforms to the B$_{2u}$ and E$_u$ doublets. Since oxygen rotation does not lead to the ferroactive ion displacement, the A$_{2u}$ and E$_u$ modes are not Raman active. Note that the hydrostatic and chemical pressure or the epitaxial strains may induce the ferroelectric phase transition in the SrTiO$_3$ with symmetry lowering to the orthorhombic C$_{2v}$ phase with the mm2 point group [28]. In this ferroelectric phase, each of the A$_{2u}$ and B$_{2u}$ modes transforms into the modes with B$_2$ symmetry, and the E$_u$ modes split into the A$_1$ and B$_1$ modes. All of these modes are Raman active.

Moreover, at the structural phase transition to the tetragonal phase, we observe additional lines in the Raman spectra at 100 K. Their appearance is explained by the multiplication of the SrTiO$_3$ unit cell leading to the folding of the Brillouin zone; therefore, the modes from the R-point reflect the zone center. These modes can be interpreted as the A$_{2g}$, [A$_{2g}$ + B$_{1g}$], A$_{1g}$, and E$_g$, [A$_{1u}$ + E$_u$] which are observed at frequencies of ~795, 229, 52, 40, and 436, respectively, and the two groups of [B$_{1g}$ + E$_g$] modes are observed at the two frequencies of ~144 and 440 cm$^{-1}$ [29].

Figure 1 shows the temperature dependences of the Raman spectra of the PSTx solid solutions in a frequency range of 15–800 cm$^{-1}$. At 100 K, the Raman spectra contain a set of peaks corresponding to the two-phonon scattering lines observed in pure SrTiO$_3$ with the cubic phase Pm$\overline{3}$m [30]. The lowest frequency line at ~75 cm$^{-1}$ corresponds to the difference combination band that is caused by the phonon’s creation and annihilation processes [30]. Aside from a different combination band, the frequency region of 250–400 cm$^{-1}$ consists of
the lines corresponding to the creation of phonons from the different bands (the so-called additional combination band) and to the creation of the phonons from the same phonon branch (the so-called overtones). The frequency range of 600–800 cm$^{-1}$ also contains additional combination bands and overtones [30]. Since at 100 K the first-order Raman lines are not observed, we conclude that the PST$_x$ has a cubic structure in which a non-polar $Pm3m$ phase has no vibrations related to the molecule polarizability changes.

![Figure 1](image_url). Temperature-dependent Raman spectra of the Sr$_{1-x}$Pb$_x$TiO$_3$ solid solutions at concentrations $x = 0.005, 0.02, 0.04$ in the temperature range $12$–$100$ K.

Upon cooling, the Raman spectra of the PST$_x$ reveal the wing of the low-frequency line centered at the frequency below $15$ cm$^{-1}$ in the temperature range of $90$–$12$ K (see Figure 1). This line can be attributed to the $E_g$ mode, which indicates a structural phase transition at $90$ K. The same mode was observed by Taniguchi et al. [31] in the oxygen-isotope-exchanged SrTiO$_3$ at a temperature of $\sim 100$ K at the frequency of $\sim 8$ cm$^{-1}$. Note that the frequency and intensity of the $E_g$ mode increased upon cooling.

Moreover, at $\sim 90$ K, we observed the weak peak of $A_{1g}$ mode at frequency $\sim 25$ cm$^{-1}$ that increases with the temperature decreasing (as shown in Figure 2). The emergence of this peak evidences the structural transition to the non-polar tetragonal $I4/mcm$ phase. Thus, the temperature of the structural transition is coherent with the $T$-$x$ phase diagram for PST$_x$ solid solutions [32], where the transition temperature in the PST$_x$ with $x = 0.005, 0.02, 0.04$ is observed at $\sim 90$ K.

The results obtained at low temperatures in [33] showed that the Raman spectra of the SrTiO$_3$ contain the $B_{1g}$ and $E_g$ modes at $\sim 144$ and $\sim 440$ cm$^{-1}$ corresponding to the Ti-O vibrations that are also responsible for the transition to the tetragonal $I4/mcm$ phase. However, in our experiment, these modes were not observed, presumably because of suppression of the Ti ions’ motions at a small amount of the Pb dopant.

The comparison of our Raman spectra of the PST$_x$ with the small $x$, the spectra of the pure SrTiO$_3$, and the spectra of the PST$_x$ with $x = 0.2$ is shown in Figure 3. We observed that even a small amount of the Pb dopant leads to drastic spectral changes in comparison with the pure SrTiO$_3$ ceramic. Note that the Raman spectrum of the PST$_x$ with $x = 0.2$ contains a clear dip at $\sim 67$ cm$^{-1}$ between two intensive peaks at $\sim 24$ cm$^{-1}$ and $\sim 86$ cm$^{-1}$. These peaks can be attributed to ferroelectric $TO_1$ modes of the $E$ and $A_1$ symmetry that correspond to the tetragonal $P4mm$ phase as shown in [34]. As can be seen
in Figure 3, Raman spectra of the PST\textsubscript{x} with \(x = 0.005, 0.02, 0.04\) also reveal two intensive peaks, centered at \(-22-29\) cm\(^{-1}\) and at \(-58-65\) cm\(^{-1}\) separated by the dip at \(-45\) cm\(^{-1}\). According to the phase \(T-x\) diagram [32], low-\(x\) PST\textsubscript{x} have the non-polar \(I4/mcm\) phase at low temperatures.

![Figure 2. The temperature evolution of the Raman spectra of the Sr\(_{1-x}\)Pb\(_x\)TiO\(_3\) solid solutions at concentrations \(x = 0.005, 0.02, 0.04\) in the temperature range 50–100 K. The experimental data are shown by the black circles. The red lines show the results of spectra deconvolution. The stars indicate the \(A_{1g}\) mode.](image)

According to the symmetry selection rules for the \(I4/mcm\) phase, these lines can be assigned to the TO\(_{1}\) mode, which splits into the two ferroelectric \(E_u\) and \(A_{2u}\) components. Note that, in pure oxygen-isotope-exchanged SrTiO\(_3\), the same modes appear at lower temperatures and frequencies, although these modes are forbidden in the Raman spectra of the paraelectric SrTiO\(_3\).

Analyzing the higher frequency region 150–800 cm\(^{-1}\) of the Raman spectra of the PST\textsubscript{x} at low temperatures, we observe the two narrow lines at \(-170\) and \(-540\) cm\(^{-1}\) appearing on the background of the two-phonon scattering. Their intensity rises strongly with the temperature decreasing. These lines refer to the transverse components of the Axe and Last modes, TO\(_2\) and TO\(_4\), respectively, which are prohibited by the symmetry selection rules in paraelectric SrTiO\(_3\). The appearance of these modes in the Raman spectra of paraelectric perovskite materials is usually attributed to the pre-transitional polarization fluctuations. For instance, in the Sr\(_{1-x}\)Ca\(_x\)TiO\(_3\) solid solutions [11] the appearance of these modes is associated with the ferroelectric phase transition [35]. Additionally, it was shown that, in the pure SrTiO\(_3\) ceramics or the BST\textsubscript{x} solid solutions, the TO\(_2\) and TO\(_4\) lines indicate the presence of the polar nanoregions originated from the microdeformations between the stochastically oriented microcrystallites, impurities, or oxygen vacancies [3].

Moreover, we observe the emergence of the sharp peak at \(-263\) cm\(^{-1}\) upon cooling. This line is attributed to the TO\(_3\) mode, originating from the \(F_{2u}\) “silent” structural mode. In the Raman spectra of the PST\textsubscript{x} with \(x = 0.005, 0.02,\) and \(0.04\), the “silent” mode appears at 60, 50, and 80 K, respectively. Since this mode is not related to the polarizability change, its emergence may be associated with the structural transformation into the orthorhombic phase. The longitudinal LO\(_3\) component of a “silent” mode is also observed in the Raman spectra at 474 cm\(^{-1}\), but it is too blurred for the correct estimation of its parameters.
Figure 3. The Raman spectra of the PST\(x\) solid solutions with small amount of Pb \((x = 0.005, 0.02, 0.04)\) and their comparison with the Raman spectra of the pure SrTiO\(_3\) and the PST\(x\) with \(x = 0.2\) at 50 K.

4. Discussion

For more detailed analysis of the Raman spectra, we deconvoluted them on the two-phonon and first-order Raman scattering using the damping oscillator functions (DHO model) and the Fano profile:

\[
I(\omega) = I_0 + \sum_j \frac{A_j \Gamma_0 \omega_{0j}^2 \omega^2}{(\omega_{0j}^2 - \omega^2)^2 + \Gamma_0^2 \omega^2} + A_j \left( q + E(\omega) \right)^2 \frac{1}{1 + E(\omega)^2},
\]

where \(I_0\) is the background intensity, \(\omega_{0j}\) is the frequency of the oscillator, \(\Gamma_0\) is the damping (half-width) of the oscillator, \(A_i\) and \(A_j\) are the strengths (intensity) of the oscillator and Fano profile, \(q\) is the asymmetry parameter of the Fano resonance, and \(E(\omega) = \frac{2(\omega - \omega_{0j})}{\Gamma_0}\).

Note that the TO\(_2\) polar phonon mode observed at ~170 cm\(^{-1}\) demonstrates an asymmetric profile of the Fano resonance with the parameter \(q > 0\). Such asymmetry was also previously observed in the SrTiO\(_3\)-based materials synthesized in various designs [35]. Usually, the Fano resonance with positive \(q\) is a feature of the interaction between a discrete phonon state and a continuous excitation background, such as multiphonon states [36].

According to the deconvolution of the Raman spectra, the temperature dependence of the frequency of the polar Slater modes with \(E_u\) and \(A_{2u}\) components, denoted as TO\(_1\), is shown in Figure 4. Note that the \(E_u\) component splits into \(A_1\) and \(B_1\) doublets in the orthorhombic phase as the temperature decreases. As a result, we observe three TO\(_1\) modes at low frequencies, demonstrating a soft mode behavior when the temperature changes. The temperature behavior of the TO\(_1\) mode frequency (about 70 cm\(^{-1}\)) reveals the minimum critical temperatures ~18 K and ~50 K for the \(x = 0.005\), ~50 K for the \(x = 0.02\), and ~70 K for the \(x = 0.04\). It is known that such soft mode behavior may indicate the macroscopic phase transition in the ferroelectrics [37,38]. Our results specify the symmetry of the low-\(T\) ferroelectric phase of PST\(x\) as an orthorhombic one that is in line with the symmetry of the ferroelectric phases in other near-quantum ferroelectrics [11,28,29,31] but is in contrast to [32] where this phase was suggested as tetragonal. Note, however, that the suggestion in [32] is based on the simple extrapolation of the tetragonal symmetry \(P4mm\)
of PbTiO$_3$ to PST$_x$ compounds. The TO$_2$ and TO$_4$ vibrations observed in the vicinity of 170 and 540 cm$^{-1}$ are hard modes that slightly depend on the temperature changes.

![Figure 4](image)

**Figure 4.** The temperature evolution of the TO$_1$ mode frequency of the Sr$_{1-x}$Pb$_x$TiO$_3$ solid solutions at selected concentrations $x = 0.005, 0.02, 0.04$. The dashed lines indicate the changes in slope for the temperature dependencies of the soft mode frequency.

The temperature changes for the intensity of the polar TO$_1$, TO$_2$, and the TO$_4$ modes of PST$_x$ with $x = 0.005, 0.02$, and $0.04$ are shown in Figure 5. It is worth noting that the three soft TO$_1$ modes reveal a strong interaction of phonons; therefore, we sum up the values of their intensities and present the total intensity of the collective TO$_1$ modes on the top row in Figure 5. Upon cooling, the intensities of all polar modes reveal a sharp increase, demonstrating a kink-like behavior. As can be seen in Figure 5, the bending points at the $x = 0.005, 0.02$, and $0.04$ are observed at temperatures of ~90 K, ~75 K, and ~100 K, respectively. As was shown for the Sr$_{1-x}$Ba$_x$TiO$_3$ solid solutions with small Ba content [3], the presence of prohibited lines in the paraelectric phase points out the existence of the polar nanoregions in the system. The abrupt growth in their intensity corresponds to the expansion of their dimensions. Note that studies of the SrTiO$_3$ by resonant piezoelectric spectroscopy [39] also revealed the polar resonances at temperatures below 80 K, which become stronger on further cooling. This was interpreted as the appearance of polarity in the ferroelastic domain walls. Such thermally induced effects are consistent with the temperatures of the emergence of the polar nanoregions in our Raman data. Thus, in the case of the PST$_x$, we can assume that the Pb-concentration increase also leads to the rise in critical temperature of the expansion of the polar nanoregions. For the concentrations $x = 0.02$ and $0.04$, we do observe such behavior. However, the temperature behavior for the sample with $x = 0.005$ is different, presumably due to the manifestation of the quantum effects.

Figure 6a shows how the low-temperature region of existence of the ferroelectric phase and the region of the emergence of the polar nanoregions (shaded area) evolve as a function of Pb concentration. The filled red and green circles present the characteristic temperatures obtained from Raman data, delimiting these regions. The filled blue circles present the independent measurements of the ferroelectric transition temperatures, obtained as maxima in the temperature dependencies of the dielectric constants (Figure 6b). For comparison, we also present the transition temperatures obtained in [32] from dielectric measurements (empty blue circles). All the data are in good agreement with each other; we found that
the ferroelectric transition occurs at temperatures of ~16 K, 56 K, and 72 K for the samples with \( x = 0.005, 0.02, \) and 0.04, respectively.

**Figure 5.** The temperature evolution of intensities of the TO\(_1\) modes (upper row) and of the TO\(_2\) and TO\(_4\) modes (bottom row) for the Sr\(_{1-x}\)Pb\(_x\)TiO\(_3\) solid solutions at \( x = 0.005, 0.02, 0.04 \). The dashed lines show the interpolation of the modes intensity.

**Figure 6.** (a) Characteristic temperatures of the emergence of the polar nanoregions (red circles) and critical temperatures of the ferroelectric transition (green and blue circles) for different Pb concentrations \( x \). The filled red and green circles correspond to the Raman measurements, and the filled blue circles to the dielectric measurements. The empty blue circles correspond to the dielectric data obtained in Ref. [32]. The high-temperature area of the plot corresponds to the paraelectric phase of PST\(_x\), the intermediate shaded area corresponds to the emergence of the polar nanoregions, and the low-temperature area corresponds to the ferroelectric phase. The dashed red line gives the fit of the results by theoretical formula, \( T_c = A(x - x_c)^2 \). (b) Temperature dependence of the dielectric permittivity for different Pb concentrations \( x \).

The dependence of the ferroelectric transition temperatures on concentration was fitted by the theoretical formula for the system with quantum criticality [40], \( T_c = A(x - x_c)^2 \), with \( A \approx 399 \) and \( x_c \approx 0.0025 \) (red dashed line in Figure 6a). The extrapolated critical concentration, \( x_c \approx 0.0025 \), corresponds to the quantum critical point in which a concentration-
driving quantum phase transition from the paraelectric to ferroelectric phase occurs at zero temperature as a function of increasing concentration [4,41,42].

For PSTx with \( x = 0.005 \), the ferroelectric transition occurs at a finite temperature, \( T_c = 16–18 \text{ K} \), that is, however, substantially reduced with respect to the temperature at which the polar nanoregions emerge (\( \sim 90 \text{ K} \)) and with respect of the temperature of the critical soft mode slope change (\( \sim 50 \text{ K} \)). We assume therefore that the quantum effects are also relevant at \( x = 0.005 \) and that the transition is conditioned by competing interaction between thermal and quantum fluctuations. With increasing \( x \), the ferroelectric transition temperature grows and the interval of pre-transitional polarization fluctuations shrinks. The system recovers classical thermal behavior.

5. Conclusions

Raman spectra of the PSTx solid solutions with \( x = 0.005, 0.02, \) and 0.04 were studied at \( T \sim 12–300 \text{ K} \) to obtain insight on the nature of the phase transitions emerging in this temperature interval. It was established that all samples undergo the structural transition from the cubic \( Pm\bar{3}m \) to the non-polar tetragonal \( I4/mcm \) phase at a temperature of \( \sim 90 \text{ K} \). Another transition corresponding to the transformation to the ferroelectric orthorhombic phase takes place at temperatures of \( \sim 16 \text{ K}, 56 \text{ K}, \) and \( 72 \text{ K} \) for \( x = 0.005, 0.02, \) and 0.04, respectively. This transition was shown to occur gradually through the emergence of the polar nanoregions inside the non-polar tetragonal phase with their further expansion on cooling. The results were confirmed by dielectric measurements. It was revealed that the PSTx with the lowest Pb concentration \( x = 0.005 \) is close to the quantum critical point (QCP), where the thermal and quantum fluctuations compete.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/cryst11121469/s1, Figure S1: Diffraction pattern and refined model of profile for \( \text{Sr1} - \text{xPbxTiO}_3 \) with \( x = 0.005 \), Figure S2: Diffraction pattern and refined model of profile for \( \text{Sr1} - \text{xPbxTiO}_3 \) with \( x = 0.02 \), Figure S3: Diffraction pattern and refined model of profile for \( \text{Sr1} - \text{xPbxTiO}_3 \) with \( x = 0.04 \), Table S1: Refined lattice parameters from Le Bail fit, maximal strains with anisotropy and reliability factors with all non-excluded points.

Author Contributions: Conceptualization, E.D.L., I.A.L. and A.G.R.; methodology, A.S.M., D.M., A.G.R. and D.R.; formal analysis, E.D.L., S.V.K. and A.G.R.; investigation, E.D.L., D.M., A.S.M. and D.R.; data curation, S.V.K., V.B.S. and A.G.R.; writing—original draft preparation, E.D.L., I.A.L. and A.G.R.; writing—review and editing, I.A.L., V.B.S. and A.G.R.; project administration, A.G.R. and D.R. All authors have read and agreed to the published version of the manuscript.

Funding: This research was financially supported by the Ministry of Science and Higher Education of the Russian Federation, grant agreement number 075-15-2021-953 from 5/10/2021, and by the European Union H2020-MSCA-RISE-MELON action, project number 872631.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data underlying the results presented in this paper are not publicly available at this time but may be obtained from the authors upon reasonable request.

Acknowledgments: D.R. thanks Beatriz Noheda, Groningen University, for the access to the equipment to perform the capacitance vs. temperature measurements and the MELON action for visiting financial support.

Conflicts of Interest: The authors declare no conflict of interest.

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