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Specific heat anomalies at 37, 105 and 455 K in $SrTiO_3$:Pr

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Abstract

Strontium titanate modified with praseodymium was investigated by means of a combination of synchrotron x-ray diffraction and thermal analysis at high and low temperatures. The x-ray diffraction data obtained at room temperature revealed a breakdown of the cubic symmetry via the (002)/(200) split peaks. Thus, both the diffuse anomaly in the DTA measurement and the permittivity peak indicate that cubic symmetry is reached at about 455 K. At low temperatures, the specific heat reveals two anomalies at ∼105 and ∼37 K. Both anomalies were sensed for the phonon part of the total specific heat. The soft acoustic phonon modes are responsible for the plateau region in the specific heat at about 105 K, which is slightly larger for undoped samples. Furthermore, a clear anomaly at ∼37 K in the specific heat is sensed by the Pr impurity in the host lattice of $SrTiO_3$ and a minimum in the temperature dependence of the Debye temperature, Θ_D around 30 K is observed. A maximum in the CT^{-3} versus T^2 curve seems to indicate that the low-lying vibrational modes dominate at 37 K.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

$SrTiO_3$ (STO) is a prototype model (ABX_3) of the basic perovskite system that displays a wide range of physical and chemical properties such as incipient ferroelectricity, semiconductivity, superconductivity and catalytic activity [1–4]. The phase transition at about 105 K is very interesting since the structural transformation is dynamical and it is driven by the oxygen rotation around the c axis. The anisotropic fluctuation of the local-order parameter (φ) close to the structural phase transition has been the subject of numerous investigations. Despite the apparent simplicity of the phase transition, a direct and clear analysis in terms of the simplest soft-mode picture is elusive. Müller *et al* [2] evoked that the quantum-mechanical atomic motion is already strong enough at 35.5 K. At this temperature, the reciprocal dielectric constant, $1/\varepsilon(T)$, extrapolates linearly to zero. In the classical picture, this zero reciprocal dielectric extrapolation, which varies as $k_B T/\hbar\omega$, should be identified as the Curie temperature. However, the so-called quantum paraelectric state takes place in STO, where the dielectric reciprocal constant should be proportional to the Bose population factor $n(t)$ of certain acoustic phonons into which the soft optic phonons decay [3]. Also, Bednorz and Müller [4] showed that the upper limit temperature achievable for ferroelectricity was 35 K in Ca doped $SrTiO_3$; that is, T_c increases from zero to 35 K with increasing Ca concentration. Regardless of these early dielectric constant studies, several anomalies at $T < T_c$ stimulated experiments and theoretical studies to explain the 'extra modes' in the Brillouin spectrum. For instance, a novel phase transition was found at about 37 K by EPR measurements where the authors suggest some kind of macroscopic coherence [5]. Hehlen *et al* [6] have interpreted this anomaly as a second sound following the prediction of Gurevich [7]. Based on the ultrasonic data, Scott and Ledbetter [8] proposed that the dispersion at 37 and 65 K arose from the crossing of the optical mode ($A_{2u} + E_u$) with the soft phonon modes (E_g, A_{1g}). Salje *et al* [9] and Balashova *et al* [10] have observed domain-wall

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freeze-out which the latter authors suggest to be the cause of the 37 K anomalies reported in several experiments. Recently, Cheng *et al* [11] have found a set of permittivity peaks around 16, 37 and 65 K ascribed to the defect modes and the mode-crossing phenomena. These experiments have confirmed that these anomalies at low temperatures are not an isolated fact, so that many of these experimental observations are been reproducible and are incompatible with proposed models.

At higher temperatures, the thermoelectric properties of STO are heavily dominated by their oxygen content as well as by donor and acceptor type impurities. It has been demonstrated that rare earth elements are substituted at the A-site as trivalent ions so that charge neutrality is satisfied through the formation of oxygen vacancies acting as effective donors [12, 13]. On the other hand, it is known that there are different ways to induce a polar state in STO, i.e. by application of a sufficiently strong electric field [14], by application of uniaxial stress [15], by using an isotope of the oxygen anion [16] and by substitution of the Sr cation, either iso- or aliovalent cations [4, 17]. Lately, Heani *et al* [18] showed that stressed STO in thin films induces ferroelectricity at room temperature. Dielectric anomalies with remarkable frequency dispersion were obtained for non-isovalent substitution of Sr by rare earth ions [19]. Previous work of the present authors [20] found, on heating, a dielectric anomaly starting at about 455 K (182 °C) with a peak of about 515 K (242 °C) that was taken as an indicative of a ferroelectric–paraelectric transition; however, work in progress seems to indicate that this anomaly might be due to ferroelastic behavior. The effect of Pr on the structural and dielectric response, consequently, needs to be clarified. On the other hand, an open question that needs to be answered is what happens with the ferroelectric transition at low temperature when Pr is doped into STO?

Here, we analyzed the phonon part of the specific heat in STO and $Sr_{0.75}Pr_{0.15}TiO_3$(SPT) at low temperature. When Cp/T versus T for the undoped sample is subtracted from that of the doped sample, the resulting curve reveals two anomalies at 105 and ∼37 K. A plateau is observed around 105 K. It is caused by the condensation of the soft mode at the zone boundary, as stated by Fleury [21]. The second anomaly may be due to the vanishing or hardening of a certain kind of soft phonon mode. The structural analysis at room temperature showed that the cubic symmetry is broken down at room temperature when Pr is introduced in the STO compound. Here, the differential thermal analysis (DTA) reveals that the high cubic symmetry is reached above 455 K (182 °C). The results shown here conclude that specific heat anomalies at low temperature are mainly dominated by the soft phonon mode so that they are independent and of a different nature from that observed at high temperature where the transition is caused by trivalent ion doping.

2. Experimental details

Two samples of the $Sr_{1-x}Pr_xTiO_3$ solid solution with $x = 0$ and 0.15 were prepared by solid state reaction. Details of the synthesis are given elsewhere [21]. X-ray diffraction analysis was performed in beamline 2-1 of the Stanford Synchrotron Radiation Laboratory. The sample was mounted on a zero background holder and data were collected in reflection geometry at 10 keV ($\lambda = 1.239\,852$ Å). The measured interval was $15° < 2\theta < 130°$ for SPT. The scanning step was 0.005° in 2θ. Thus, the structural parameters were determined with good precision using Rietveld refinement analysis [22]. To check the phase transition at low and high temperatures, heat capacity (Cp) and differential thermal analysis (DTA) measurements were carried out. The heat capacity measurements were performed using a relaxation method in a commercial calorimeter (Quantum Design, PPMS-1) and the DTA measurements were performed using Netzsch 409 thermal equipment.

3. Results and discussion

To be able to resolve subtle structural changes we have performed x-ray diffraction at room temperature using synchrotron radiation. Figure 1 shows the experimental and calculated synchrotron XRD profiles for $Sr_{0.75}Pr_{0.15}TiO_3$ (SPT). The important question regarding the lowering of the cubic symmetry, $Pm\bar{3}m$, is investigated via the observation of the (002)/(200) split peaks from the (200) plane family. The results clearly show a splitting of the peaks which is magnified by means of a zoom at about 37.2°. A semi-quantitative agreement was obtained, starting with the $pm\bar{3}m$ space group as Jauch *et al* [23] did for pure $SrTiO_3$. To properly characterize peak splitting, the constraint of centrosymmetric symmetry was removed. The tetragonal *P4mm* space group was tested and a final satisfactory convergence was obtained. Structural information extracted from Rietveld refinement considering both $Pm\bar{3}m$ and *P4mm* space groups for $SrTiO_3$ and $Sr_{0.85}Pr_{0.15}TiO_3$ is listed in table 1.

In order to elucidate the nature and temperature of the transition in the complete range of temperatures, thermal analysis is performed at high temperatures, 1170–300 K, and specific heat measurements at low temperatures, 300–2 K. In the first case, the structural change was confirmed upon heating since a single endothermic broad anomaly is distinguished at about 455 K, as shown clearly in figure 2(a). In addition, a peak in the permittivity starts to develop at about 455 K with a maximum at about 515 K as seen in figure 2(b). We suspect that the occurrence of this thermal anomaly may be related to the displacive structural contributions providing unambiguous evidence of a diffuse phase transition. Accordingly, the synchrotron results as well as the occurrence of this thermal anomaly and the peak in the permittivity could be related to the following two facts: (i) Displacive contributions as a consequence of structural changes from pseudo-cubic ($P4mm$) to cubic structure ($Pm\bar{3}m$). (ii) Stress relaxation in the structure via re-ordering of the cations and oxygen vacancies which can lead to a ferroelastic transition in the permittivity data. The first one arises from distortion of the TiO_6 octahedron due to the Pr ion, which has a significantly different size from that of the original Sr ion producing more than one off-center position for some Ti^{4+} ions. The latter contribution is explained as a result of the permittivity dependence with the thermal history of the samples. In the second case,

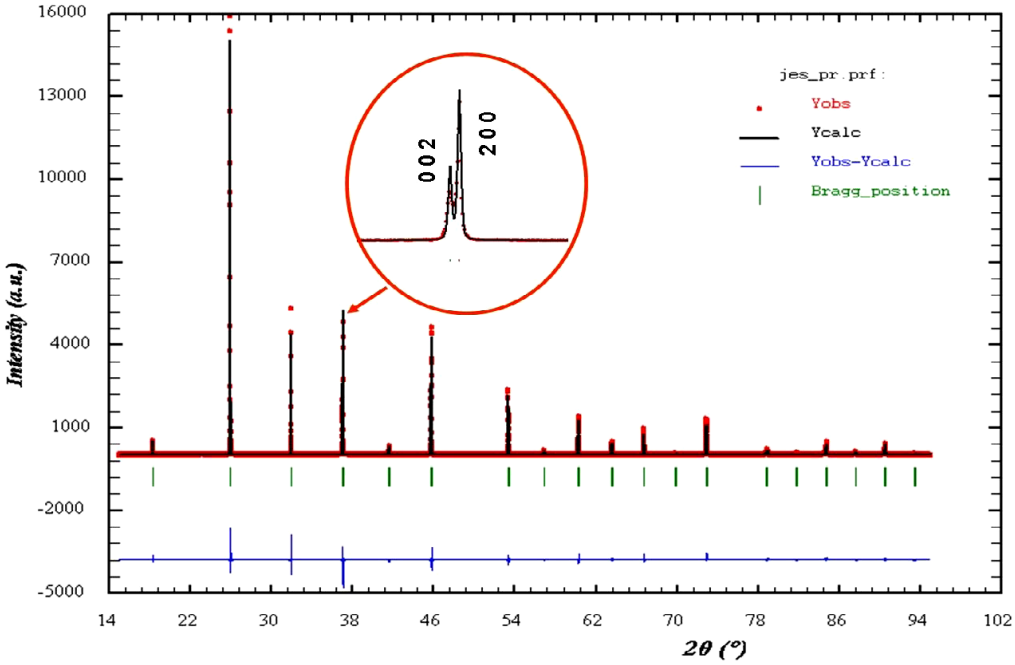

Figure 1. Observed and calculated diffraction patterns for $Sr_{1-x}Pr_xTiO_3$ with $x = 0.15$. The inset represents the zoom of the (002)/(200) doublet in the perovskite cell.

Table 1. Refined structural parameters for $Sr_{0.85}Pr_{0.15}TiO_3$ from XRD synchrotron radiation data at room temperature.

	$SrTiO_3$ ([20])	$Sr_{0.85}Pr_{0.15}TiO_3$ (This work)
Crystal system	Cubic	Tetragonal
Space group	$Pm\bar{3}m$	$P4mm$
Cell parameters		
a (Å)	3.9056 (5)	3.9018(7)
b (Å)	3.9056 (5)	3.9018(7)
c (Å)	3.9056 (5)	3.9072(7)
Structure refinement		
2θ range/degree	5–90	15–130
Rwp (%)	10.8	13.8
χ^2	1.45	1.39

Atomic coordinates and occupancies of SPT (This work)

Atom	X	Y	Z	Occ.
Sr	0.0000	0.0000	0.0328	1.895(7)
Pr	0.0000	0.0000	0.0328	0.105(7)
Ti	0.5000	0.5000	0.5328	1.000
O(1)	0.5000	0.5000	0.0000	1.000
O(2)	0.5000	0.0000	0.5000	2.000

the total heat capacity for $Sr_{1-x}Pr_xTiO_3$ with $x = 0$ and 0.15 in the range of temperature between 2 and 300 K is shown in figure 3. The difference in the heat capacity for Pr doped and undoped samples becomes very small in the tested temperature range. As shown there, we did not find any evidence of critical behavior, in the form of a peak or a discontinuity in the total Cp, regardless of the low rate of temperature variation around the transition temperature. This fact makes evident that the 'excess' of Cp, probably extra oscillator modes, screens the critical behavior in STO. A plateau is clearly observed at about 95–116 K in the Cp/T versus T representation, in the inset (a) of figure 3 which is more evident and pronounced in magnitude for the $x = 0$ sample. It is well know that in the STO compound, in this narrow region of temperature, one type of soft phonon mode condenses (F_{2u}, Γ_{25}) and a structural phase transition from cubic ($pm3m$) to tetragonal ($I4/mcm$) takes place [26]. The structural transition is related to the small rotation of the oxygen octahedron associated with the development of the so-called incipient ferroelectric state. The plateau in the Cp/T–T curve (arrows in the inset of figure 3) is clear evidence of the competing effect of two kinds of order parameters, one represented by the polarization and the other by the rotation of the oxygen octahedra involving in some way optic and acoustic

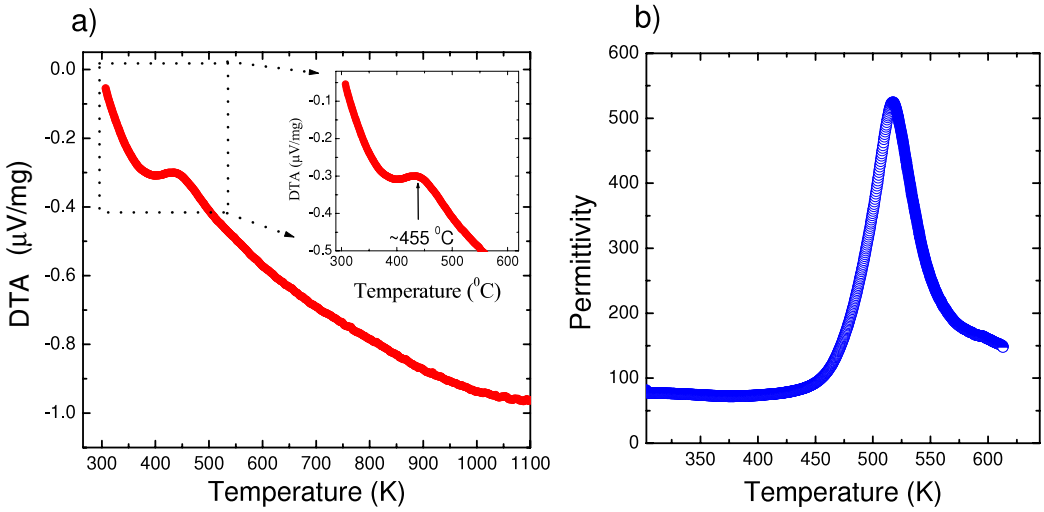

Figure 2. (a) DTA measurement on heating and (b) permittivity versus temperature for the $Sr_{0.85}Pr_{0.15}TiO_3$ sample.

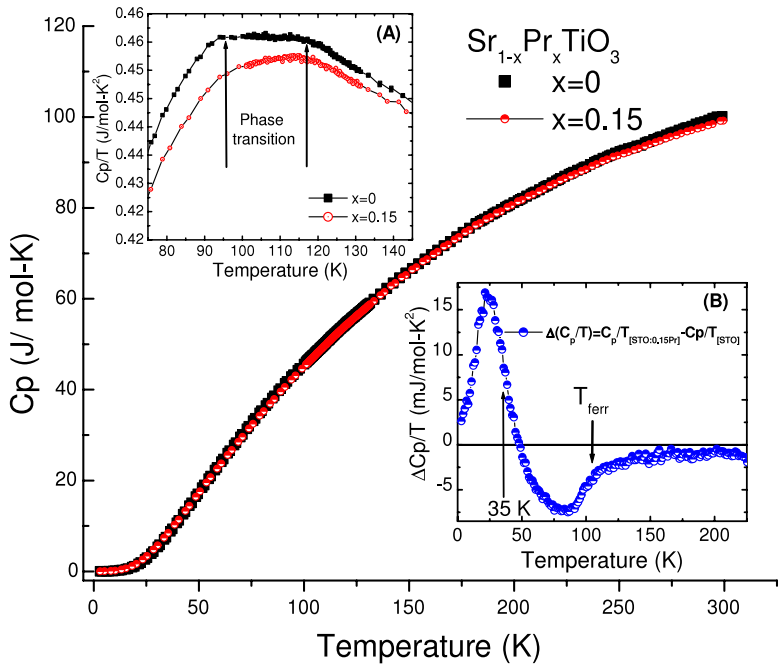

Figure 3. Temperature dependence of specific heat of $SrTiO_3$ and $Sr_{0.85}Pr_{0.15}TiO_3$ from 300 to 2 K. Inset (A) shows the Cp/T–T data in the region of the structural transition. Inset (B) plots the subtraction of the STO from STO:0.15Pr data. The arrows in both insets show the phase transition.

soft phonon modes with some of them becoming Raman-active phonons [15, 27]. It is worthwhile mentioning that the anomaly in Cp/T–T displayed as a broad peak at moderately high temperature has been related to the phononic excitations in many borocarbide superconductors [28], where Einstein modes are superimposed upon the Debye spectrum giving rise to changes in the Debye temperature in a narrow range of temperature and playing an important role in the electron–phonon interaction at lower temperatures. Here, we believe that the second-order transition gives rise to the development of strong coupling between polarization modes and the softening of the acoustic phonon modes, having a marked influence on the Debye temperature. To enable the phonon contribution through the Debye temperature for both samples, we estimated the lattice contribution fitting the Cp data in figure 3 to $Cp = AT + BT^3$. Here, the lattice coefficient B is related to the Debye temperature, Θ_D, by $B = 1944N\Theta_D^{-3}$, where B is in units of J mol^{-1} K^{-4} and N is the number of atoms by unit weight. We found that this simple approach did not reproduce the entire $Cp(T)$ curve as we compared experimental data with the tabulated $D(\Theta_D/T)$ values [24]. The fitting was performed by steps in the whole temperature range in order to determine the temperature dependence of Θ_D. The behavior of this physical quantity is plotted in figure 4. Several features

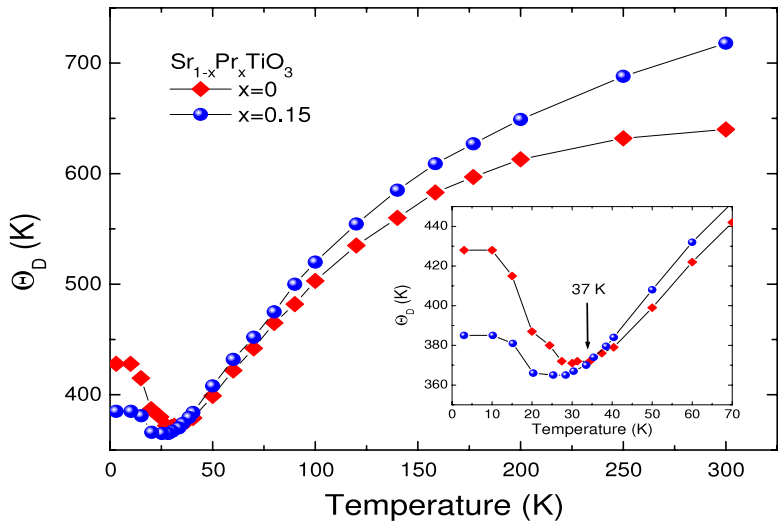

Figure 4. Temperature dependence of the Debye temperature calculated from the molar specific heat Cp for STO and SPT. The inset shows an expanded scale at low temperature where the crossing of both curves takes place.

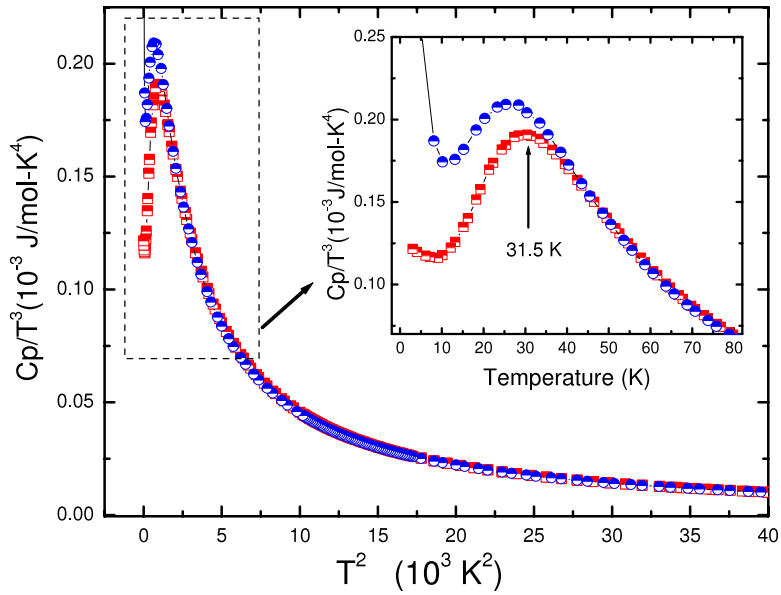

Figure 5. The Debye term (Cp/T^3) as a function of square temperature (T^2) for the $x = 0, 0.15$ sample. The inset is an expanded scale of the low temperature region.

are observed in the plot; a minimum at around 30 K and an independent temperature region at the lowest temperatures are observed in both samples. For the $x = 0$ sample, Θ_D takes values of ∼428 K from about 10 down to 2 K. This value is in good agreement with that reported by Lawless [25]. When the sample is doped with 15% of praseodymium a decrease of Θ_D to about 385 K is observed in the same range of temperature. Note that at ∼37 K (arrow in the inset of figure 4), there is a crossing of the $\Theta_D(T)$ curves, and the deep minimum is shifted from ∼35 for STO to 25 K for SPT. These facts indicate that the behavior described above is related to an intrinsic mechanism, probably low-lying modes, as well as to impurity doping.

Additionally, to isolate the anomalies associated with Pr doping at low temperature, the Cp/T for $x = 0$ was subtracted from the Cp/T for $x = 0.15$, $\Delta Cp = Cp/T_{[STO:Pr]} - Cp/T_{[STO]}$. By means of this operation we obtained additional information about the scattering sensed by the impurity due to the phonon or lattice dynamics associated with STO. Inset (B) of figure 3 shows the behavior of Cp from 250 K down to 2 K. The anomaly at about 100 K (arrow in the inset) related to a phase transition is evident but a rather surprising result is that from about 95 K down to ∼30 K: ΔCp increases steadily, decreasing afterward at lower temperatures. Axe *et al* [29] experimentally demonstrated, by inelastic neutron scattering, the strong dependence of the optical and transverse modes with temperature in centrosymmetric crystals. Here, we can infer that the decrease of ΔCp is due to the vanishing of soft phonon modes within the phonon spectrum involved in the Debye term which becomes unstable from ∼30 to ∼10 K. Furthermore, Lawless [30] has proved that many displacive ferroelectrics,

paraelectrics and antiferroelectrics display a broad peak in Cp/T^3 versus T^2 if $T \ll \Theta_D$, due mainly to the Einstein frequency of the optical modes in which such maximum in Cp/T^3 should give the approximate relation at $T_{max} \approx \upsilon_E/3$, where υ_E is the Einstein frequency in cm^{-1}.

Figure 5 shows the Cp/T^3–T^2 data for doped and undoped samples. As can be seen, a gradual increase in Cp/T^3 is observed starting from 200 K, being more pronounced at about 110 K, and reaching a peak at about 35 K. For clarity, an expanded (linear) scale from 80 down to 2 K is shown in the inset of figure 5. There, it is observed that the peak is shifted from 31.5 K to ∼21.5 K, and specific heat is increased for the $x = 0.15$ sample. Earlier studies [15] point out that the thermal properties can be markedly affected by the presence, development and/or vanishing of the soft-mode phonon at low temperature. It is obvious that this marked increase of Cp/T^3, observed as a peak in the inset of figure 5 (also inset (B) of figures 3 and 4), is due to the coupling or vanishing of a soft optic phonon mode (F_{2u}) developing around the phase transition (103 K). This phonon mode reaches a maximum at about 31.5 K for STO and 25 K for SPT samples and then decreases in intensity at lower temperatures. Another important aspect is that the linearity of the Curie–Weiss behavior in the inverse permittivity data is extended down to 35.5 K in the study reported by Müller *et al* [2]. This fact is closely related to the increase of the phonon spectrum mode (optic and acoustic coupling mode) from about 103 K down to 31.5 K observed in the Cp/T^3 data. One plausible explanation could be that the soft phonon mode $F_{2u} \rightarrow E_g + A_{1g}$ developed by the phase transition screens the ferroelectric mode F_{1u} in the ∼103 to ∼31.5 K temperature interval, after that, the soft phonon mode F_{2u} decreases or vanishes at lower temperatures and the ferroelectric mode dominates so that the deviation from the Curie–Weiss behavior takes place. On the other hand, from ∼10 down to 2 K a tail in the Cp/T^3 peak develops with larger values for the doped sample. The increase of the tail with decreasing temperature has been attributed to the freeze-out of the Einstein term of the optical modes as was reported by Lawless and Burns [30, 31] in $SrTiO_3$, $BaTiO_3$ and $LiTaO_3$ ferroelectric materials. The increase of Cp/T^3 in the lower range of temperature has been related to the domain-wall contribution. In particular, the higher values of the tail of the peak for the doped sample imply that the Pr ion enables the domain-wall contribution below ∼7 K. However, a careful analysis in the mK range of temperatures is necessary to elucidate this last fact. It is important to mention that the role of the soft optical mode dispersion and freeze-out for $T < 105$ K is not completely understood, and remains an open problem.

4. Conclusion

We have performed thermal measurements on STO and SPT over a wide temperature range between 1100 down to 2 K and found specific heat anomalies at ∼37, ∼105 and ∼455 K. The combination of synchrotron radiation and thermal analysis at high temperature indicates that the lowered symmetry at room temperature achieves a higher (cubic) symmetry at about ∼455 K when Pr is doped in STO. When the excess of specific heat of the undoped samples $Cp_{[STO]}$ is subtracted from that of the Pr doped sample, $Cp_{[SPT]}$, two clear anomalies are found at about 105 and 37 K. The first one is due to the softening of the acoustic phonon mode, and the second one is probably due to the decoupling between ferroelectric and low-lying acoustic modes.

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