Chemically-induced renormalization phenomena in Pb-based relaxor ferroelectrics under high pressure

Running head: Doped Pb-based relaxors under high pressure

B Mihailova^{1,5}, N Waesermann¹, B J Maier^{1,2}, R J Angel³, T Prüßmann^{1,4}, C Paulmann¹, M Gospodinov⁵ and U Bismayer¹

¹ Fachbereich Geowissenschaften, Universität Hamburg, Grindelallee 48, D-20146 Hamburg, Germany

² Department für Geo- und Umweltwissenschaften, Ludwig-Maximilians Universität München, Theresienstraße 41/II, D-80333 München, Germany

³ Dipartimento di Geoscienze, Università degli studi di Padova, via G. Gradenigo 6, 35131 Padova, Italy

⁴ Institute for Nuclear Waste Disposal, Karlsruhe Institute of Technology, Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Germany

⁵ Institute of Solid State Physics, Bulgarian Academy of Sciences, Blvd. Tzarigradsko Chausse 72, 1784 Sofia, Bulgaria

⁵ Corresponding author: boriana.mihailova@uni-hamburg.de

Abstract

The pressure-induced phase-transition sequence in $\text{PbSc}_{0.5}\text{Ta}_{0.5}\text{O}_3$ (PST) and $\text{PbSc}_{0.5}\text{Nb}_{0.5}\text{O}_3$ (PSN) heavily doped with homo- and heterovalent cations on the A or B site of the perovskite-type structure (ABO_3) was analyzed by in-situ synchrotron x-ray diffraction and Raman spectroscopy up to pressures of 25 GPa. We focussed on the structural phenomena occurring above the first pressure-induced phase transition at p_{c1} from a relaxor state to a non-polar rhombohedral phase with antiphase tilting of the BO_6 octahedra. The samples studied were PST doped with Nb^{5+} and Sn^{4+} on the B site, PST doped with Ba^{2+} and La^{3+} on the A site, and PSN doped with Sr^{2+} and La^{3+} on the A site. All of them exhibit a second pressure-induced phase transition at p_{c2} , similar to pure PST and PSN. The second transition involves the development of either order of antiparallel Pb^{2+} displacements and complementary $a^+b^-b^-$ octahedral tilts, or $a^-b^-b^-$ ($0 \leq a < b$) tilting alone. As in pure PST and PSN, the second phase transition is preceded by the occurrence of unequal octahedral tilts on the local scale. The substitution of Nb^{5+} for Ta^{5+} as well as the coupled substitution of Sn^{4+} for $\text{Sc}^{3+} + \text{Ta}^{5+}$ on the octahedral B sites increases the second critical pressure. The doping by Nb^{5+} also reduces the length of coherence of antipolar Pb^{2+} order developed at p_{c2} . The isovalent substitution of the larger Ba^{2+} for Pb^{2+} on the A site suppresses the antipolar Pb^{2+} order due to the induced local elastic stresses and thus significantly increases p_{c2} . The substitution of smaller cations for Pb^{2+} on the A site generally favours the development of long-range order of antiparallel Pb^{2+} displacements because of the chemically enhanced $a^-a^-a^-$ octahedral tilts. However, this ordering is less when the dopant is aliovalent, due to the charge imbalance on the A site. For all of the relaxors studied here, the dynamic compressibility estimated from the pressure derivative of the wavenumber of the soft mode associated with the first phase transition is larger in the pressure interval between p_{c1} and p_{c2} than above p_{c2} . The dynamic compressibility of the phase above p_{c2} decreases, if the antipolar Pb^{2+} order is disturbed.

PACS: 77.80.Jk, 61.50.Ks, 63.20.-e, 78.30.-j

Keywords: relaxor ferroelectrics, phase transitions, high pressure, synchrotron XRD, Raman scattering

Submitted to: Journal of Physics: Condensed Matter

1. Introduction

Lead-based perovskite-type (ABO_3) relaxors are advanced ferroelectric materials which have been attracting considerable attention due to their extraordinarily high dielectric, electro-elastic and electro-optic response [1,2]. Their superior performance is of great technological importance, for example in nonvolatile memory devices, yet their structure-property relationships are still a matter of debate. It is now well known that the broad frequency-dependent peak of the dielectric permittivity as a function of temperature is related to the existence of dynamic polar nanoregions distributed within a cubic paraelectric matrix [3,4], but it is still not clear which is the most efficient way to tune the relaxor properties via chemically induced changes in the nanoscale structure. High-pressure experiments on pure and doped relaxor compounds are of particular importance for the better understanding of the interplay between the structure and properties, because pressure can stabilise some of the ferroic atomic clusters that are present at ambient conditions but which may be suppressed at lower temperatures.

Recently it has been shown that pressure triggers a continuous phase transition from a relaxor cubic state to a non-polar rhombohedral phase with long-range ordering of antiphase octahedral tilts of equal magnitude in all three cubic $\langle 100 \rangle$ directions ($\bar{a}\bar{a}\bar{a}$ in Glazer's notation [5]) [6,7,8]. The effect of partial substitution of the Pb^{2+} on the A sites by cations with isotropic outermost electron shells depends on whether the ionic radius r_i of the substitution element is larger or smaller than that of Pb^{2+} because this changes the structural tolerance factor $t = \frac{r_i(\text{A-cation}) - r_i(\text{O})}{\sqrt{2}(r_i(\text{B-cation}) - r_i(\text{O}))}$ [9]. The substitution of Pb^{2+} by smaller cations reduces t and hence favours octahedral tilting, which results in a decrease of the critical pressure almost to ambient pressure [10]. The introduction of larger cations into the A site smears out the phase transition over a pressure range [11,12]. The critical pressure may also be changed by B-site substitution even when the tolerance factor remains the same [13]. High-pressure diffraction and Raman scattering studies of stoichiometric $\text{PbSc}_{0.5}\text{Ta}_{0.5}\text{O}_3$ (PST) and $\text{PbSc}_{0.5}\text{Nb}_{0.5}\text{O}_3$ (PSN) up to 30 GPa complemented by DFT calculations [14] revealed that the $\bar{a}\bar{a}\bar{a}$ tilt system becomes metastable upon a further pressure increase, which triggers a phase transition to a structure with unequal antiphase tilts (e.g. $a^0b^+b^-$ as the end member of $\bar{a}b^+b^-$, $a < b$) or with mixed tilts ($a^+b^+b^-$) and long-range order of the Pb^{2+} antiparallel displacements (antipolar Pb^{2+} order). The phase transition pathway depends on the inherent mesoscopic order existing at ambient pressure. The latter is closely related to chemical variations on the A and/or B sites [10, 11, 15-19]. Hence complementary spectroscopic and diffraction studies of doped relaxor compounds at pressures above the first critical pressure p_{c1} can further elucidate the interplay between chemistry and nanoscale ferroic clusters. Thus, the aim of this paper is to compare the high-pressure structural phenomena in pure and doped PST and PSN above p_{c1} and in this way to shed light on the complex physics of relaxor ferroelectrics. For the purpose we have applied single-crystal x-ray diffraction (XRD) with synchrotron radiation and off-beam Raman spectroscopy to PST heavily doped with Nb^{5+} and Sn^{4+} on the B site, PST heavily doped

with Ba^{2+} and La^{3+} on the A site, and to PSN heavily A-site-doped with Sr^{2+} and La^{3+} . The results are interpreted in the light of the high-pressure behaviour of stoichiometric PST and PSN [14].

2. Samples and background information

2.1 Chemistry and ambient-conditions structure

Cube-shaped optically and chemically homogeneous single crystals of stoichiometric and heavily doped PST and PSN were synthesized by the high-temperature solution growth method. The samples studied here are from the same corresponding synthesis batches of the samples that have been already studied at lower pressures [20]. The sample designation and chemical composition determined by electron microprobe analysis are given in table 1. According to powder XRD, at room temperature and ambient pressure the samples are cubic and exhibit no or a very low degree of chemical 1:1 B-site long-range order (see table 1). Powder neutron diffraction however revealed that at ambient conditions La-doped PSN (PLSN) contains non-polar rhombohedral domains with a long-range antiphase tilt order of the BO_6 octahedra [10]. The similarity between single-crystal synchrotron XRD data on PLSN, La-doped PST (PLST) and Sr-doped PSN (PSSN) suggests that PLST and PSSN also possess long-range $a^-a^-a^-$ tilt order at ambient conditions [10], which is consistent with the doping-induced reduction of the tolerance factor (see table 1). At room temperature and ambient pressure all samples show x-ray diffuse scattering along the cubic $\langle 110 \rangle^*$ reciprocal-space directions, which is typical of polar nanoregions [21] and indicates that the samples are in a relaxor state. A temperature-induced paraelectric-to-ferroelectric phase transition was observed only for the stoichiometric samples. In-house powder XRD clearly revealed that the Curie temperature of the PST sample studied here is near 270 K [18], which is typical of chemically disordered PST, while the Curie temperature of PSN, which was expected to be near 378 K [22], was only indirectly detected from the kink in the temperature dependence of the pseudocubic unit-cell parameter [23]. The latter, along with the presence of $\langle 110 \rangle^*$ x-ray diffuse scattering, indicates that at room temperature the predominant structural state of PSN is also relaxor ferroelectric rather than normal (long-range ordered) ferroelectric.

2.2 Pressure-induced structural changes in pure PST and PSN

Both PST and PSN show two characteristic intermediate pressures p_1^* and p_2^* associated with local structural transformations preceding the corresponding macroscopic phase transitions at p_{c1} and p_{c2} ($p_1^* < p_{c1} < p_2^* < p_{c2}$). Overall, the characteristic and critical pressures of PST are smaller than those of PSN [14]; for PST $p_1^* = 1.2$ GPa, $p_{c1} = 1.9$ GPa, $p_2^* = 3.0$ GPa, $p_{c2} \sim 5.5$ GPa, whereas for PSN $p_1^* = 2.5$ GPa, $p_{c1} = 4.1$ GPa, $p_2^* \sim 7\text{-}10$ GPa, p_{c2} is between 13.5 and 16.6 GPa (see also table 2).

According to complementary Raman scattering and neutron diffraction analysis [20], at p_1^* the off-centred Pb^{2+} and B-site cations in polar nanoregions decouple as the B-site cations begin to

move to the octahedral centres. The off-centred displacements of the Pb^{2+} cations become locally ordered and quasi-dynamical long-range antiphase octahedral tilts are developed without breaking the average crystal symmetry. For PST the local coupling between the off-centred Pb^{2+} ions is stronger along the cubic $\langle 111 \rangle$ direction, whereas for PSN it is more pronounced within the perpendicular plane [14, 20]. The continuous phase transition at p_{c1} from a cubic or pseudocubic relaxor to a non-polar rhombohedral state is associated with the development of static long-range order of antiphase octahedral tilts, resulting in the appearance of hkl Bragg peaks with $h, k, l = 2n+1$ in reciprocal-space layers reconstructed from single-crystal synchrotron XRD data (throughout this paper the Miller indices refer to the doubled-perovskite cell with a $\sim 8\text{\AA}$ and $Fm\bar{3}m$ symmetry), a discontinuity of the isothermal bulk modulus K , and the appearance of a Raman-active soft mode [7, 12, 13]. For continuous phase transitions the jump in the bulk modulus at the critical pressure ΔK is indicative of the overall degree of structural alteration, which can be considered as a combined effect of the fraction of material that transforms and the structural difference between the two phases. The corresponding values of ΔK for PST and PSN are 45 GPa and 17 GPa. The degree of structural alteration at p_{c1} also influences the integrated intensity of the soft mode, which is well pronounced in the Raman spectra of PST at p_{c1} . In the case of PSN however, at p_{c1} the soft mode could not be resolved from the adjacent Pb-localized mode near 50 cm^{-1} which generates strong Raman intensity in both relaxor and non-polar rhombohedral states [18, 20, 23]. For PSN the soft mode was resolved only at 7.5 GPa, approximately 3.5 GPa above the first phase transition pressure p_{c1} . Thus the change in $K(p)$ at p_{c1} as well as the weaker intensity of the soft mode indicates that the degree of structural alteration at p_{c1} is considerably lower in PSN than in PST.

At the second characteristic pressure p_2^* the octahedral tilts around the three $\langle 100 \rangle$ cubic directions become different from each other on the mesoscopic scale as deduced from the splitting of the Raman scattering near 350 cm^{-1} [14], which is related to the silent F_{2u} mode of the prototype cubic structure and arises from Pb-O bond stretching within the Pb-O sheets perpendicular to the cubic body diagonal (see figure 1) [20]. The second phase transition at p_{c2} was revealed by the appearance of additional sets of Bragg reflections and/or splitting of pre-existing Bragg peaks observed by single-crystal synchrotron XRD [14]. The presence of Bragg peaks with $h, k = 2n$ and $l = 2n+1$ accompanied by weaker XRD peaks with $h = 2n$ and $k, l = 2n+1$ indicates antipolar long-range order of Pb^{2+} displacements along cubic $[uv0]$ directions and a mixed a^+b^- tilt system. The splitting of the Bragg peaks with $h = 2n$ and $k, l = 0$ into peaks with different d -spacings, without the appearance of new reflections, reveals a reduction of the rhombohedral symmetry due to a long-range order of unequal antiphase tilts [14]. The latter structural alteration was observed for PSN, while the former for PST. The difference between PST and PSN in the structural state above p_{c2} has been ascribed to the different correlation length of antiferrodistortive Pb-O species existing at ambient pressure, which is most probably due to the different degrees of short-range ordering on the octahedral B sites [14].

2.3. The effect of doping on the phase transition at p_{c1} .

The analysis of PST heavily doped on the B sites with Nb (0.72PST-0.28PSN, PSTN) and Sn (0.78PST-0.22PbSnO₃, PSTS) showed that the isovalent substitution of Nb⁵⁺ for Ta⁵⁺ shifts p_{c1} to 2.5 GPa, which is between the critical pressure of the end members, whereas the aliovalent substitution of Sn⁴⁺ for pairs of Sc³⁺ and Ta⁵⁺ slightly decreases p_{c1} to 1.3 GPa [13]. The latter is related to the disturbance of the intermediate-range order of B-cation off-centre displacements in the polar nanoregions induced by the Sn incorporation, which facilitates the development of antiphase BO₆ tilt order [13]. The bulk modulus change ΔK at p_{c1} is 21 GPa and 11 GPa for PSTN and PSTS, respectively, indicating that both types of B-site doping weaken the phase transition compared to pure PST, with the degree of structural alteration from a relaxor to a non-polar rhombohedral state being less in PSTS than in PSTN.

The partial isovalent substitution of Ba²⁺ for Pb²⁺ generates local elastic fields because of the larger ionic radius of Ba²⁺ and the absence of stereochemically-active electron lone pairs typical of Pb²⁺. Due to the local strains in the vicinity of the individual substituent Ba²⁺ cations, the first pressure-induced phase transition in Ba-doped PST (PBST) is smeared out over a pressure range from 2 to 4 GPa [11, 20]. The change in the bulk modulus between 2 and 4 GPa is 25 GPa [20], which shows that A-site Ba doping also weakens the phase transition at p_{c1} .

The incorporation of Sr²⁺ or La³⁺ on the A-site also disturbs the system of Pb²⁺ lone pairs because both Sr²⁺ and La³⁺ have isotropic outermost electron shells. However, by contrast to the case of Ba²⁺, the ionic radii of Sr²⁺ and La³⁺ are smaller than that of Pb²⁺, which leads to a decrease in the tolerance factor and therefore generally favours the development of octahedral tilting. The partial replacement of Pb²⁺ by La³⁺ additionally generates local electric fields, but the simultaneous structural analysis of La-doped PST (PLST), La-doped PSN (PLSN) and Sr-doped PSN (PSSN) unambiguously proved that the "strain" effects are stronger than the "charge" effects and independent of the dopant valence. As a consequence, the substitution of small-radius cations on the A site results in chemically induced antiphase BO₆ tilt order at ambient conditions, i.e. the first critical pressure p_{c1} in at the vicinity of ambient pressure [10].

3. Experimental details

Plate-like specimens parallel to the cubic {100} planes with a size of approximately 60×60×30 μm³ were loaded in diamond-anvil cells of the Boehler-Almax design [24] equipped with diamonds with a culet diameter 500 or 600 μm. The sample size was restricted by the requirement to have a large enough specimen to produce satisfactory intensities in both XRD and Raman experiments and at the same time, the specimen had to be small enough not to touch the rim of the gasket hole or the diamond culets up to 25 GPa in order to avoid undesired strain in the sample. The actual pressure values were

determined by the ruby photoluminescence method [25]. Helium was used as a pressure-transmitting medium, which remains hydrostatic up to 20 GPa and between 20 and 30 GPa shows negligible non-hydrostaticity [26].

Synchrotron single-crystal XRD experiments were conducted at the F1 beamline of HASYLAB/DESY, using a radiation of wavelength $\lambda = 0.5000 \text{ \AA}$ and a MarCCD 165 detector. Data were collected at a sample-to-detector distance of 100 mm with a step width of 0.5° and an exposure time of 120 s per frame.

Raman spectra were measured from the same specimens in between two successive synchrotron XRD measurements, using a Horiba Jobin-Yvon T64000 triple grating spectrometer equipped with a Symphony CCD detector, an Olympus BH41 microscope and a $50\times$ long-working distance objective. Spectra were collected in backscattering geometry, using the 514.5-nm line of an Ar^+ laser, with a spectral resolution of 2 cm^{-1} . All spectra were collected with the polarization of the incident light parallel to one of the cubic $\langle 100 \rangle$ directions, without analyzer on the scattered light. The conduction of precise polarized HP spectroscopic measurements is in general hindered by the partial depolarization of light from the diamond anvils and changes in the optical properties of strained diamond at high mechanical loads. At each pressure spectra from several different areas of the sample were measured to check the structural homogeneity. The measured spectra were corrected by subtracting a background spectrum collected from alongside the crystal in the sample chamber. Spectra were subsequently temperature-reduced by the Bose Einstein occupation factor and fitted with Lorentzian functions. Measurements conducted during decompression of the sample verified the reversibility of the observed structural changes.

4. Results and Discussion

High-pressure Raman spectra and reciprocal-space layers reconstructed from synchrotron XRD of each of the samples are shown in figures 2-7. The Raman spectra of all doped compounds show the same behaviour as those of pure PST and PSN: pressure suppresses the peaks near 140 and 240 cm^{-1} arising from off-centre cations in polar nanoregions and strongly enhances the Raman scattering near 350 cm^{-1} arising from Pb-O bond stretching vibrations. For all compounds a low-energy soft mode appears at or above p_{c1} (table 2), depending on the overall degree of structural transformation at p_{c1} , as discussed above. The difference between p_{c1} determined from XRD data and the first pressure at which the soft mode could be resolved is largest for PBST, which actually exhibits a diffuse phase transition over a pressure range. A strong enhancement and a splitting of the peak near 350 cm^{-1} was observed for all compounds, indicating the development of a BO_6 octahedral tilt pattern with unequal tilts around the cubic $[100]$, $[010]$, and $[001]$ directions. The second intermediate pressure p_2^* determined from the splitting of this Raman peak is given in table 2. For the compounds with no substitution disorder on the A site the dependence of p_2^* on chemistry follows that of p_{c1} . For

the A-site doped compounds there is no apparent trend of p_2^* with the dopant content x or the tolerance factor t , most probably due to the direct impact of the substituent atoms on the Pb-O bond stretching vibrations within planes perpendicular to the cubic body diagonal. However, for aliovalent small-cation substitution on the A site (the case of La^{3+}) p_2^* is higher than for the isovalent substitution (Sr^{2+}) and one might speculate that the charge imbalance on the A site somehow hinders the development of local structural changes preceding p_{c2} .

The wavenumber of the soft mode ω_{SM} as a function of pressure clearly shows non-linear behaviour for all compounds (see figure 8). If this were a classic soft-mode phase transition, the soft mode frequency of each compound should exhibit power-law behaviour of the form $\omega = \omega_0(p - p_0)^{n/2}$, in which p_0 is the transition pressure [27]. Unconstrained fits of this equation to the soft-mode frequencies of each sample gave rather unrealistic values for p_0 and systematic misfits to the individual data points. The failure of the classical power function to describe the measured frequencies of the soft mode underlines the complexity of structural transformations that occur in relaxors under pressure and the significant contribution of order-disorder phenomena. On the other hand, for all compounds the soft mode frequencies below and above p_{c2} can be fitted with two separate linear functions $\omega = \omega_0 + \omega' p$ (figure 8). For pure PST and PSN the crossing point of the two linear fits matches very well the second critical pressure p_{c2} determined by diffraction analysis (see table 2). Therefore, one can suggest that for all relaxor compounds the kink in the soft-mode frequency with pressure is indicative of the occurrence of a second pressure-induced phase transition, since a change of $d\omega/dp$ for the soft mode reflects the change in the compressibility of the whole system. Indeed, for all doped compounds studied here the critical pressure p_{c2} determined from the kink in the soft mode frequency is in very good agreement with the synchrotron XRD data (see table 2).

According to XRD data the critical pressure p_{c2} for PSTN should be between 10.5 and 12.3 GPa because additional sets of diffraction peaks are seen at the latter pressure but not at the former pressure (figure 2). The change in the slope of the soft mode indeed indicates $p_{c2} = 11.3$ GPa (figure 8). Likewise, the XRD data suggest that p_{c2} for PSTS is between 8.1 and 11.3 GPa (figure 3), while the pressure dependence of the soft-mode wavenumber indicates a critical pressure at 11.1 GPa (figure 8). For both B-site doped compounds the second pressure-induced phase transition involves antipolar ordering of the Pb^{2+} cations and a development of a mixed $a^+b^-b^-$ octahedral-tilt system. However, while PSTS and PST exhibit sharp even-even-odd Bragg peaks in their diffraction patterns above p_{c2} , the diffraction pattern of PSTN has streak-like $\langle 100 \rangle^*$ diffuse diffraction features even at 19.6 GPa, which is more than 8 GPa above p_{c2} . This indicates that the correlation length of ordered Pb^{2+} antiparallel displacements for PSTN is considerably shorter than that for PSTS. This fact cannot be explained by the difference in the degree of chemical B-site order because PSTN possesses chemically ordered domains detectable by XRD, while PSTS exhibits none, i.e. the correlation length of chemical order is larger for PSTN rather than for PSTS. The well-developed antipolar Pb^{2+} order above p_{c2} in

PSTS is most probably related to the impact of Sn doping on the local-scale polar coupling at ambient conditions, which in turn facilitates the octahedral tilt ordering and slightly shifts p_{c1} towards lower pressures [13]. The second critical pressure for PSTS is however higher than that for pure PST, indicating that the Sn doping disturbs the antipolar Pb^{2+} order to a certain extent. This can be attributed to the enhanced substitutional disorder in the B-cation surroundings of the Pb^{2+} cations. Therefore, the delicate balance between the mesoscopic polar and antiferrodistortive order can be chemically tuned by appropriate aliovalent B-site doping even if such doping does not change the tolerance factor. It should be mentioned that PSTS also exhibits odd-odd-odd Bragg peaks just above the p_{c1} determined from p - V data, similar to all other Pb-based perovskite relaxors; the previously reported absence of such Bragg peaks between 1.5 and 3.5 GPa [13] was due to the compromised chemistry of the particular specimen analyzed by synchrotron XRD up to 6.1 GPa.

Up to 22.4 GPa no additional sets of Bragg peaks were detected for PBST. Hence, doping with Ba^{2+} suppresses the antipolar long-range order of Pb^{2+} cations and consequently the BO_6 -tilt pattern does not change to a mixed inphase/antiphase or a pure inphase tilt system. The length of coherence of B-site chemical order in PST-Ba is approximately 5 times larger than that in PST (see table 1), which would be expected to facilitate antipolar Pb^{2+} cation ordering. Therefore, the local elastic fields induced by the incorporation of Ba^{2+} have a stronger impact on the second pressure-induced phase transition than the B-site chemical order. At 22.4 GPa a well resolved d -spacing splitting of the $0k0$ reflection with k even is observed (see figure 4), which unambiguously reveals that the symmetry is lower than rhombohedral. Accordingly, the wavenumber of the soft mode at this pressure deviates from the linear trend (see figure 8). Hence, the second pressure-induced phase transition in PBST involves only a change in the BO_6 tilt pattern from antiphase tilts with equal magnitudes along the three cubic $\langle 100 \rangle$ directions ($a^-a^-a^-$) to a system of unequal antiphase tilts. For all compounds structure refinements to the collected synchrotron XRD data to determine the exact tilt pattern were not possible because of the oversaturation of the strong even-even-even Bragg peaks under the experimental conditions necessary for the detection of the pressure-induced diffraction features. However, DFT calculations on pure PST and PSN revealed that among the tilt configurations containing only antiphase tilts, $a^-b^0b^0$ is the most energetically unfavourable at high pressures while $a^0b^-b^-$ is the most energetically favourable [14]. In addition DFT calculations show that $a^-b^-b^-$ systems relax to $a^0b^-b^-$, indicating that $a^-b^-b^-$ tilt patterns with $0 \leq a < b$ are energetically more stable than those with $a > b$ [14]. Hence, we suggest that the second pressure-induced phase transition in PBST resembles that in PSN [14] and consists of alteration of the tilt pattern from $a^-a^-a^-$ to $a^0b^-b^-$ or $a^-b^-b^-$ with $a < b$. It should be emphasized that the doping of PST with Ba^{2+} not only changes the phase transition pattern but also substantially shifts the second critical pressure p_{c2} from ~ 5.5 GPa to ~ 22 GPa.

Sections of the reciprocal-space layers of PLST are shown in figure 5. At 8.1 GPa very weak streaks and diffuse spots with even-even-odd Miller indices were detected in the $hk0$ and $hk1$ layers,

respectively, indicating the development of medium-range order of antiparallel Pb^{2+} off-centre shifts. The even-even-odd spots are much sharper and better resolved at 10.8 GPa, demonstrating that antipolar order of Pb^{2+} displacements is developed on the long-range scale. The change in the slope of $\omega_{\text{SM}}(p)$ is also at 10.8 GPa (see figure 8) and therefore we propose that this is the second critical pressure p_{c2} for PLST. Subtle even-odd-odd Bragg peaks, revealing the change of the BO_6 tilt order from $a^-a^-a^-$ to $a^+b^-b^-$, could be seen in the $hk2$ layer only at 15.6 GPa. This suggests that the degree of in-phase BO_6 tilting is considerably lower than that for pure and B-site doped PST, for which even-odd-odd Bragg peaks occurred along with the antipolar Pb^{2+} order.

If PLST is compared to pure PST, it appears that the existence of chemically-induced antiphase tilting is not sufficient alone to favour the development of antipolar Pb^{2+} order. However, the shift of p_{c2} to higher pressures upon A-site doping with smaller-radius cations may be due to the dilution of the Pb^{2+} system or it may also result from the slightly less abundant B'-O-B'' atomic linkages, since the degree of chemical order is 0.05 and 0.13 for PLST and PST, respectively [20]. The analysis of the structural changes in PLSN and PSSN has clarified this issue because both compounds as well as pure PSN are entirely B-site chemically disordered within the sensitivity of powder XRD. For PLSN no sharp even-even-odd or even-odd-odd diffraction peaks were observed in the entire pressure range up to 25.4 GPa. Yet at 12.0 GPa weak diffuse streak-like diffraction features corresponding to even-even-odd Miller indices appeared in hkl layers with l even, without evolving into Bragg peaks upon further pressure increase (see figure 6). The pressure dependence of the wavenumber of the soft mode suggests a phase transition near $p_{c2} = 14.9$ GPa but synchrotron XRD data did not reveal a formation of long-range antipolar Pb^{2+} order or any evidence for change in the BO_6 tilt pattern. On the other hand, the diffraction analysis of PSSN clearly shows that the partial substitution of Sr^{2+} for Pb^{2+} leads to the development of long-range antipolar Pb^{2+} order and a mixed tilt system (figure 7). Subtle diffuse spots in the reconstructed reciprocal-space layers of PSSN can be detected at 7.4 GPa and are clearly seen as sharp diffraction peaks at 9.6 GPa, while the change in the slope of the soft mode frequency with pressure indicates that $p_{c2} = 8.4$ GPa. Note that for pure PSN $p_{c2} = 16.6$ GPa and the phase transition consists only of a change in the magnitudes of the tilts. Above 14.5 GPa the even-even-odd diffraction peaks for PSSN become as strong as the odd-odd-odd peaks indicative of antiphase BO_6 tilts, revealing the abundance of material that develops a long-range order of antiparallel Pb^{2+} displacements. Therefore, the chemically enhanced antiphase BO_6 -tilt long-range order resulting from the reduction of the tolerance factor in general favours the development of antipolar Pb^{2+} long-range order. However, the local electric fields induced by the aliovalent A-site substitution oppose the development of Pb^{2+} antipolar ordering and the compatible mixed tilt system. Raman scattering experiments suggest that this is related to the fact that the local electric fields induced by aliovalent A-site doping (La^{3+} , Bi^{3+}) reduces the pressure-induced suppression of off-centred B-cations because the Raman scattering near 240 cm^{-1} generated by off-centred B-site cations persists to higher pressures as compared to the pure or isovalent doped compounds [10, 12, 14]. Thus

the substitution of La^{3+} for Pb^{2+} has two competing effects on the second pressure-induced phase transition; on one hand, it favours the antiferrodistortive order in the Pb sublattice because of the abundance of preexisting antiphase octahedral tilts, on the other hand the associated randomly-distributed local fields slightly interfere with the antipolar ordering of Pb^{2+} displacements along the cubic $[uv0]$ directions. Depending on the degree of aliovalent substitution on the A-site, the overall antipolar Pb^{2+} ordering may be enhanced at least on the mesoscopic scale as in the case of PLSN ($x = 0.23$) or slightly disturbed as in the case of PLST ($x = 0.08$), leading to a shift of p_{c2} to higher pressures. It is worth noting that for the three compounds that we studied with small cations doped on to the A site, the value of p_{c2} correlates well with the second characteristic pressure p_2^* .

The normalized pressure derivatives of $\omega_{\text{SM}}(p)$, $\eta = \omega' / \omega_0$, for pure and doped PST and PSN calculated from the linear fits of $\omega = \omega_0 + \omega' p$ below and above p_{c2} are compared in figure 9. The parameter η represents the dynamic compressibility of the structure. The dynamic compressibility $\eta_{<p_{c2}}$ of the phase existing between p_{c1} and p_{c2} is the same for PST and PSN as well as for the solid solution PSTN. The value of $\eta_{<p_{c2}}$ of PSTS is also the same as that of pure PST, within the mutual uncertainties. However for all A-site doped compounds $\eta_{<p_{c2}}$ is clearly lower than that of pure PST and PSN and it decreases with the decrease in the tolerance factor. The latter trend is the same as the trend of the ‘static’ compressibility of three of these samples previously determined in the same pressure range by p - V measurements: PBST, PLST and PLSN, exhibiting zero-pressure bulk modulus $K_0 = 103 \pm 11$ GPa, 114.2 ± 1.6 GPa and 130.4 ± 0.7 GPa, respectively. This is the behaviour expected for perovskites with relatively rigid framework octahedra, in which the compressional behaviour is dominated by the compression of the A site [28].

The dependence of the dynamic compressibility on chemistry for the phase above p_{c2} is different from that of the phase below p_{c2} . For relaxors with no A-site doping $\eta_{>p_{c2}}(\text{PST}) \approx \eta_{>p_{c2}}(\text{PSTS}) > \eta_{>p_{c2}}(\text{PSN}) \approx \eta_{>p_{c2}}(\text{PSTN})$, i.e. the compounds with well-developed long-range order of Pb^{2+} antiparallel displacements show higher dynamic compressibility than the compounds with no or only intermediate-range antipolar Pb^{2+} order. The situation is similar for the A-site doped compounds: $\eta_{>p_{c2}}$ is highest for PSSN, smaller for PLST and smallest for PLSN, following the degree of antipolar Pb order. Besides, within the uncertainties $\eta_{>p_{c2}}(\text{PSSN}) \approx \eta_{>p_{c2}}(\text{PST}) \approx \eta_{>p_{c2}}(\text{PSTS})$. Apparently, the dynamic compressibility above p_{c2} is related to the abundance and length of coherence of spatial regions with ordered antiparallel Pb^{2+} displacements along cubic $[uv0]$ directions.

The experimental results presented here clearly demonstrate the interplay between the chemical disorder on both A and B sites and lattice antiferrodistortive instabilities of perovskite-type relaxors. The doping-induced renormalizations of the critical pressures suggest that due to the specific

chemically induced local strains heterovalent B-site cation substitution as well as homovalent smaller-size A-site cation substitution may stabilize both the antiphase BO_6 tilting and the antipolar Pb^{2+} order, homovalent larger-size A-site cation substitution enhances the antiferrodistortive instabilities, while heterovalent smaller-size A-site cation substitution stabilizes the antiphase BO_6 tilting but has different effect on the antipolar Pb^{2+} order, depending on the degree of doping. The role of crystal chemistry and the mesoscopic-scale compositional order/disorder phenomena to suppress or enhance certain ferroic lattice instability (ferroelectric, antiferroelectric, ferrielectric) has been theoretically modelled using different approaches [29-32]. Our study does not provide a quantitative picture of the influence of dopant concentration on the antiferrodistortive lattice instabilities due to the absence of appropriate series of single-crystal samples but we hope that it would inspire further theoretical calculations to clarify the relation between various types of substitution elements and ferroic instabilities in complex perovskite-type materials.

5. Conclusions

Similar to the pure compounds, all of the doped relaxors that we have studied exhibit a second pressure-induced phase transition at p_{c2} from a non-polar rhombohedral phase with $a^-a^-a^-$ octahedral tilt order to a lower-symmetry phase with either antipolar ordering of the Pb^{2+} displacements and a complementary $a^+b^-b^-$ pattern of the octahedral tilts, or $a^-b^-b^-$ ($0 \leq a < b$) tilting alone. The second phase transition is preceded by the occurrence of unequal octahedral tilts on the local scale at a second characteristic pressure p_2^* , determined from the splitting of the Raman scattering near 350 cm^{-1} . The critical pressure p_{c2} was determined from the change in the diffraction pattern obtained by single-crystal synchrotron XRD as well as from the change in the pressure derivative of the wavenumber of the soft mode associated with the first pressure-induced phase transition at p_{c1} . Additionally, the dynamic compressibility of the phase below and above p_{c2} was estimated from the normalized pressure derivative of this soft mode.

The change in the value of p_2^* in B-site doped materials follows that of p_{c1} , at which long-range $a^-a^-a^-$ tilt order occurs. Both the isovalent (Nb^{5+} for Ta^{5+}) and aliovalent (Sn^{4+} for a pair of ($\text{Sc}^{3+}, \text{Ta}^{5+}$)) substitutions shift the second critical pressure towards higher pressures but Nb doping also considerably reduces the length of coherence of antipolar Pb order occurring at p_{c2} .

The substitution of an isovalent large cation on the A-site (Ba^{2+} for Pb^{2+}) also shifts p_{c2} significantly towards higher pressures and completely suppresses the development of antipolar Pb order and complementary mixed BO_6 tilts, and the second pressure-induced phase transition is only associated with a change in the antiphase tilt system of the octahedra from $a^-a^-a^-$ to $a^-b^-b^-$ with $0 \leq a < b$. In contrast, substitution of a smaller isovalent cation on the A-site (Sr^{2+} for Pb^{2+}) strengthens the antiphase octahedral tilting, and thus supports the development of long-range antipolar Pb^{2+} order. The transition pressure p_{c2} is therefore reduced. The ordering of antiparallel Pb^{2+} displacements is also promoted by substitution of the smaller La^{3+} for Pb^{2+} , but in this case the local

electric fields in the vicinity of substitution cations partially disrupts the Pb ordering. Therefore, depending on the degree of doping, p_{c2} may be shifted towards higher pressures or the length of coherence of Pb^{2+} antipolar order may be considerably reduced.

The dynamic compressibility in the pressure range between p_{c1} and p_{c2} is in general larger than that above p_{c2} . The phase between p_{c1} and p_{c2} is stiffer if the chemical doping favours the formation of antiphase tilting and/or it disturbs the mesoscopic polar coupling at ambient pressure. For A-site doped compounds the compressibility of this phase is smaller for compounds with smaller tolerance factor, most probably because such compounds have the affinity to develop $a^-a^-a^-$ tilts at ambient pressure and hence, there is less room for the structure to adopt to high pressures via increasing the degree of antiphase tilting. For the phase above p_{c2} the dynamic compressibility is smaller if the chemical composition or degree of short-range chemical order disturbs the formation of antipolar Pb^{2+} order.

Acknowledgements

Financial support by the Deutsche Forschungsgemeinschaft (MI 1127/2-2 and INST 152/526-1) is gratefully acknowledged. The authors thank Björn Winkler, Goethe-Universität Frankfurt, for the opportunity to use the gas-loader available in his lab and Johannes Bauer for help with the He-gas loading.

References:

- [1] Cross L E, Relaxors Ferroelectrics, in Piezoelectricity. Evolution and Future of a Technology, Springer Series in Materials Science, **114**, Eds: W. Heywang, K. Lubitz, W. Wersing (Springer-Verlag Berlin Heidelberg, 2008). pp.131
- [2] Park S E and Shrout T R 1997 *J. Appl. Phys.* **82** 1804
- [3] Bokov A A and Ye Z-G 2006 *J. Mater. Sci.* **41** 31
- [4] Cowley R A, Gvasaliya S N, Lushnikov S G, Roessli B and Rotaru G M 2010 *Adv. Phys.* **60** 229
- [5] Glazer A M, 1972 *Acta Cryst. B.* **28** 3384
- [6] Janolin P E, Dkhil B, Bouvier P, Kreisel J and Thomas P A 2006 *Phys. Rev. B* **73** 094128
- [7] Mihailova B, Angel R J, Welsch A-M, Zhao J, Engel J, Paulmann C, Gospodinov M, Ahsbahs H, Stosch R, Güttler B and Bismayer U 2008 *Phys. Rev. Lett.* **101** 017602
- [8] Waeselmann N, Maier B J, Mihailova B, Angel R J, Zhao J, Gospodinov M, Paulmann C, Ross N, and Bismayer U, 2012 *Phys. Rev. B* **85** 014106
- [9] Bhalla A S, Guo R, Roy R 2000 *Mat. Res. Innovat.* **4** 3
- [10] Maier B J, Welsch A-M, Mihailova B, Angel R J, Zhao J, Paulmann C, Engel J M, Marshall W G, Gospodinov M, Petrova D and Bismayer U 2011 *Phys. Rev. B* **83** 134106
- [11] Welsch A-M, Maier B J, Engel J M, Mihailova B, Angel R J, Paulmann C, Gospodinov M, Friedrich A, Stosch R, Güttler B, Petrova D and Bismayer U 2009 *Phys. Rev. B* **80** 104118

- [12] Maier B J, Welsch A-M, Angel R J, Mihailova B, Zhao J, Engel J M, Schmitt L A, Paulmann C, Gospodinov M, Friedrich A and Bismayer U 2010 *Phys. Rev. B* **81** 174116
- [13] Welsch A-M, Maier B J, Mihailova B, Angel R J, Zhao J, Paulmann C, Engel J M, Gospodinov M, Marinova V and Bismayer U 2011 *Z. Kristall.* **226** 126
- [14] Maier B J, Waesermann N, Mihailova B, Angel R J, Ederer C, Paulmann C, Gospodinov M, Friedrich A, Bismayer U 2011 *Phys. Rev. B* **84** 174104
- [15] Zhao X, Qu W, Tan X, Bokov A. A., and Ye Z-G 2009 *Phys. Rev. B* **79** 144101
- [16] Zhang Y, Li X, Liu D, Zhang Q, Wang W, Ren B, Lin D, Zhao X and Luo H 2011 *J. Cryst. Growth* **318** 890
- [17] Bussmann-Holder A, Bishop A R and Egami T 2005 *Europhys. Lett.* **71** 249
- [18] Mihailova B, Maier, B J, Paulmann, C, Malcherek T, Ihringer J, Gospodinov M, Stosch R, Güttler B and Bismayer U 2008 *Phys. Rev. B* **77** 174106
- [19] Scholz T, Mihailova B, Schneider G A, Malcherek T, Marinova V, Gospodinov M, Pagels N, Heck J and Bismayer U 2009 *J. Appl. Phys.* **106** 074108
- [20] Mihailova B, Angel R J, Maier B J, Welsch A-M, Zhao J, Gospodinov M and Bismayer U 2011 *IEEE Trans. Ultrason. Ferroelectr. Freq. Control* **58** 1905
- [21] Paściak M and Welberry R 2011 *Z. Kristallogr.* **226** 113
- [22] Perrin C, Menguy N, Suard E, Mueller C, Caranoni C and Stepanov A 2000 *J. Phys.: Condens. Matter* **12** 7523
- [23] Maier B, Mihailova B, Paulmann C, Ihringer J, Gospodinov M, Stosch R, Güttler B and Bismayer U 2009 *Phys. Rev. B* **79** 224108
- [24] Boehler R 2006 *Rev. Sci. Instrum.* **77** 115103
- [25] Munro R G, Piermarini G J, Block S and Holzapfel W B 1985 *J. Appl. Phys.* **57** 165
- [26] Klotz S, Chervin J-C, Munsch P and Le Marchand G 2009 *J. Phys. D: Appl. Phys.* **42** 075413
- [27] Blinc R and Žekš B 1974 *Soft modes in ferroelectrics and antiferroelectrics*. Amsterdam-Oxford-North Holland
- [28] Angel R J, Zhao J and Ross N L 2005 *Phys. Rev. Lett.* **95** 025503
- [29] Bussmann-Holder A Bishop A R 2004 *Phys. Rev. B* **70** 184303.
- [30] Kim L, Kim J, Waghmare U V, Jung D and Lee J 2005 *Integr. Ferroelectr.* **73** 3.
- [31] Zhandun V S, Zamkova N G and Zienko V I 2008 *J. Exp. Theor. Phys.* **106** 1109.
- [32] Ohwada K and Tomita Y 2010 *J. Phys. Soc. Japan* **79** 011012.

Table 1. Sample nomenclature and characterization.

	Chemical composition	Tolerance factor	Unit cell parameter ^a [Å]
PST	PbSc _{0.5} Ta _{0.5} O ₃	0.977	8.154(4), $Fm\bar{3}m$
PSN	PbSc _{0.5} Nb _{0.5} O ₃	0.977	4.0863(3), $Pm\bar{3}m$
PSTN	PbSc _{0.5} (Ta _{0.72} Nb _{0.28}) _{0.5} O ₃	0.977	8.158(4), $Fm\bar{3}m$
PSTS	Pb(Sc _{0.5} Ta _{0.5}) _{0.78} Sn _{0.22} O ₃	0.977	4.0733(4), $Pm\bar{3}m$
PBST	Pb _{0.78} Ba _{0.22} Sc _{0.5} Ta _{0.5} O ₃	0.985	8.1637(6), $Fm\bar{3}m$
PLST	Pb _{1-x} La _x Sc _{(1+x)/2} Ta _{(1-x)/2} O ₃ , $x = 0.08$ ^b	0.971	8.1284(6), $Fm\bar{3}m$
PLSN	Pb _{1-x} La _x Sc _{(1+x)/2} Nb _{(1-x)/2} O ₃ , $x = 0.23$ ^b	0.961	4.0603(2), $Pm\bar{3}m$
PSSN	Pb _{0.66} Sr _{0.34} Sc _{0.5} Ta _{0.5} O ₃	0.971	4.0649(1), $Pm\bar{3}m$

^a from powder XRD at ambient conditions, assuming a cubic metric; the degree of long-range chemical B-site order for PST, PSTN, PBST, and PLST was close to 0.1, with a mean size of the chemically ordered domains 6.4, 4.6, 32.8, and 45 nm, respectively [20].

^b approximate formula, in which for simplicity the presence of vacancies is neglected; the exact stoichiometry of PLST and PLSN is Pb_{0.86}La_{0.08}Sc_{0.53}Ta_{0.47}O_{2.93} and Pb_{0.70}La_{0.23}Sc_{0.62}Nb_{0.38}O_{2.93}, respectively [10].

Table 2. Characteristic and critical pressures (in GPa) for pure and doped PST and PSN.

	p_{c1} via XRD	Soft mode detected at	p_2^* from the split of the Raman peak $\sim 350 \text{ cm}^{-1}$	p_{c2} via synchrotron XRD, type of change	p_{c2} from the kink in $\omega(p)$ of the soft mode
PST	1.9 GPa	1.9 GPa	3.0 GPa	~ 5.5 GPa, antipolar Pb^{2+} order & $a^+b^-b^-$	5.2 GPa
PSN	4.1 GPa	7.5 GPa	7.4 – 10.1 GPa ^a	between 13.5 and 16.6 GPa, $a^-b^-b^-$ with $0 \leq a < b$	14.5 GPa
PSTN	2.5 GPa	2.5 GPa	4.4 GPa	between 10.5 and 12.3 GPa, antipolar Pb^{2+} order with short length of coherence & subtle $a^+b^-b^-$	11.3 GPa
PSTS	1.3 GPa	1.6 GPa ^b	1.6 – 3.0 GPa ^a	between 8.1 and 11.3 GPa, antipolar Pb^{2+} order & $a^+b^-b^-$	11.1 GPa
PBST	diffuse, in the range 2.0 - 4.0 GPa	13.4 GPa	splitting at ambient pressure due to Ba-induced local stress	between 19.8 GPa and 22.4, $a^-b^-b^-$ with $0 \leq a < b$	between 19.8 and 22.4 GPa ^c
PLST	≤ 0.64	1.7 GPa	5.0 GPa	between 8.1 GPa and 10.8 GPa, antipolar Pb^{2+} order; at 15.6 GPa, subtle $a^+b^-b^-$	10.8 GPa
PLSN	≤ 0.67	2.9 GPa	8.0 GPa	~ 12.0 GPa, antipolar Pb^{2+} medium-range order, no detectable $a^+b^-b^-$	14.9 GPa
PSSN	≤ 0.6	≤ 0.1 GPa	3.0 GPa	7.4 GPa, subtle antipolar Pb^{2+} order & $a^+b^-b^-$, clearly seen at 9.6 GPa	8.4 GPa

^a Raman peak profile at the lower pressure value equally well fitted with one or two components.

^b no Raman data collected exactly at 1.3 GPa.

^c only one point collected above 20 GPa due to time and sample-size restrictions.

Figure 1: Sketch of the Pb-O bond stretching vibrations within planes perpendicular to the cubic body diagonal, which in the prototype cubic structure (point group symmetry $m\bar{3}m$) form the silent F_{2u} phonon mode. The large circles represent the A-positioned Pb^{2+} cations, while the small darker and brighter circles stand for the B-site cations and oxygen anions, respectively. For clarity only two out of six Pb-O-Pb linkages within a single plane perpendicular to the cubic body diagonal are shown.

Figure 2: Raman scattering and reciprocal-space layers (reconstructed in $Fm\bar{3}m$) of PSTN at different pressures. The even-even-odd XRD peaks are systematically stronger than the even-odd-odd XRD peaks, indicating long-range order of antiparallel A-cation displacements and mixed BO_6 tilting [14]. The arrows point to odd-even-even diffuse streaks in hkl layers with l even.

Figure 3: Raman scattering and reciprocal-space layers (reconstructed in $Fm\bar{3}m$) of PSTS at different pressures. The even-even-odd XRD peaks are systematically stronger than the even-odd-odd XRD peaks, indicating long-range order of antiparallel A-cation displacements and mixed BO_6 tilting [14].

Figure 4: Raman scattering and reciprocal-space layers (reconstructed in $Fm\bar{3}m$) of PBST at different pressures. The inset in the corresponding $hk0$ layer shows the 0 10 0 peak profile along the d -spacing direction indicated by the double arrow. The inset in the upper plot shows on an enlarged scale the low-wavenumber Raman scattering at 13.4 GPa, at which pressure the soft mode was first detected.

Figure 5. Raman scattering and reciprocal-space layers (reconstructed in $Fm\bar{3}m$) of PLST at different pressures. The even-even-odd XRD peaks are systematically stronger than the even-odd-odd XRD peaks, indicating long-range order of antiparallel A-cation displacements and mixed BO_6 tilting [14].

Figure 6: Raman scattering and reciprocal-space layers (reconstructed in $Fm\bar{3}m$) of PLSN at different pressures; the arrows trace the sets of diffuse streaks corresponding to $(2k0)$, $(4k0)$, $(6k0)$ with $k = -3, -1, 1, 3, 5$.

Figure 7: Raman scattering and reciprocal-space layers (reconstructed in $Fm\bar{3}m$) of PSSN at different pressures. The even-even-odd XRD peaks are systematically stronger than the even-odd-odd XRD peaks, indicating long-range order of antiparallel A-cation displacements and mixed BO_6 tilting [14].

Figure 8: Pressure dependence of the wavenumber ω_{SM} of the soft mode associated with the first pressure-induced phase transition from a relaxor to a non-polar rhombohedral state with equal antiphase BO_6 tilts. Straight lines represent linear fits to low-pressure and high-pressure data points. The arrows mark the kinks in the dependence of $\omega_{\text{SM}}(p)$ on pressure, which should be indicative of the second pressure-induced phase transition consisting of a change of the tilt pattern from $\bar{a}\bar{a}\bar{a}$ to $a^+b^-b^-$ accompanied with antipolar ordering of the A-site cations or to $\bar{a}^-b^-b^-$ with $0 \leq a < b$.

Figure 9: Normalized pressure derivative $\eta = \omega'/\omega_0$ of $\omega_{SM}(p)$ calculated from linear fits $\omega = \omega_0 + \omega' p$ to data points below (squares) and above (circles) p_{c2} .