Resonance Raman scattering of perovskite-type relaxor ferroelectrics under nonambient conditions

G. de la Flor,^{1,*} M. Wehber,² A. Rohrbeck,² M. I. Aroyo,¹ U. Bismayer,² and B. Mihailova^{2,†}

¹Departamento Física de la Materia Condensada, Universidad del País Vasco (UPV/EHU), Bilbao (Spain)

²Fachbereich Geowissenschaften, Universität Hamburg, Grindelallee 48, 20146 Hamburg, Germany

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Resonance Raman scattering (RRS) of two model perovskite-type (ABO₃) relaxor compounds PbSc_{0.5}Ta_{0.5}O₃ (PST) and PbSc_{0.5}Nb_{0.5}O₃ (PSN) excited with a laser wavelength of 325 nm (3.8 eV) is studied at different temperatures and ambient pressure as well as at high pressures and room temperature (for PST). The origin of the observed RRS is reinspected by applying group-theory analysis of phonons compatible with symmetry-allowed electron transitions in cubic and possible polar and nonpolar rhombohedral ferroic structures. It is shown that the simultaneous enhancement of first- and second-order RRS generated by antisymmetric BO₆ bending and stretching modes under resonance conditions when the photon energy is slightly above the energy gap $E_g \sim 3.2$ eV results exclusively from spatial regions with coherent polar structural distortions. Upon cooling RRS appears in the vicinity of the characteristic temperature T^* , and its total intensity significantly increases upon further temperature decrease. The predominate type of BO₆ polarity changes from related to difference in B-O bonds to related to distorted O-B-O bond angles. At room temperature and high pressures RRS drops in intensity above the critical pressure of development of long-range antiphase octahedral tilting. However it persists up to 8.3 GPa, which is the highest pressure reached in the experiment, indicating that the high-pressure phase is polar due to the slight BO₆ distortions accompanying the tilt order.

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I. INTRODUCTION

Relaxor ferroelectrics or relaxors are mesoscopically inhomogeneous crystals exhibiting a broad frequency dispersive maximum of the dielectric permittivity as a function of the temperature. The majority of relaxors belong to the family of complex perovskites with the general formula ABO₃ (aristotype structure $Pm\bar{3}m$), having at least two different types of cations on the A and/or B sites. The interest in studying the structure and dynamics of relaxors stems from their great importance in technological applications due to the remarkably strong dielectric, electrostrictive, pyroelectric, piezoelectric, and optoelectric responses over a large temperature range [1-4]. Despite the outstanding macroproperties typical of noncentrosymmetrical materials, the average structure remains cubic or subtly deviates from cubic below the temperature of the dielectric-permittivity maximum T_m . Various analytical methods complementary to conventional x-ray/neutron diffraction, including synchrotron x-ray and neutron total elastic scattering, neutron inelastic scattering, phonon spectroscopy, nuclear magnetic resonance spectroscopy, x-ray absorption spectroscopy, electron diffraction etc., have been extensively used over the last decade to better understand the structure-property relation in these materials. The current opinion is that the compositional disorder on the A and/or B site of the perovskite structure promotes the formation of dynamic local polar distortions well above T_m , which upon cooling couple at the so-called Burns temperature $T_B > T_m$ [5] to form small dynamic polar nanoregions (PNRs) and upon further cooling merge into larger PNRs of slower dynamics at T^* ($T_B > T^* > T_m$) [6,7]. The length of coherence of coupled polar distortions, i.e., the size of PNRs, is insufficient to produce a long-range ferroelectric order detectable by x-ray/neutron diffraction, but it is large enough to generate net polarization on the mesoscopic scale (a few unit cells of the aristotype ABO₃ structure), which can be considered as "giant" electric dipoles in comparison to the local dipoles associated with the individual uncoupled polar distortions in the surrounding of PNRs [3]. The existence of such a peculiar structural state has been ascribed for a long time to random local electric fields associated with heterovalent compositional disorder. Recently however, it was shown that homovalent substitution can also significantly influence the relaxor state [8,9]. Furthermore, it was proposed that the relaxor state results from the coexistence of mesoscopicscale ferroelectric and antiferrodistortive order [10-12], which may evolve into the corresponding long-range order at low temperatures [13,14] or high pressures [15]. Hence despite extensive structural studies, the exact mechanism of formation of PNRs as well as the reason for hindering the development of long-range ordered ferroelectric domains is still not completely understood, which calls for the application of further advanced analytical methods to probe the local structure of relaxors.

The resonance Raman scattering (RRS) effect can occur when the energy of the exciting laser beam is in the vicinity of the energy of a dipole-allowed electron transition and consists of interaction of photons with both electrons and phonons. Thus resonance Raman spectroscopy has the advantage to selectively enhance the intensity of those phonon modes that couple with the excited electrons. The first RRS experiments were reported back in 1946 [16], and since then resonance Raman spectroscopy has been gaining continuously growing interest among the scientific community [17–20] because it can provide information about both the electron and phonon states. In semiconducting and dielectric solids the phonon-electron coupling is realized through Fröhlich interactions, consisting of electrostatic forces between electrons and the instantaneous

gemma.delaflor@ehu.es

[†]boriana.mihailova@uni-hamburg.de

electric field arising from the dipole moment induced during the atomic vibrations [21]. Fröhlich interactions are hence significant for longitudinal optic (LO) phonons that carry polarity and therefore these phonon modes are enhanced under resonance Raman conditions. Thus the RRS intensities in materials with polar structural distortions should be indicative of the degree of structural polarity, which is beneficial for studying advanced ferroelectrics. Surprisingly however, there are only a few resonance Raman spectroscopic studies of ferroelectric oxides [22-24] which either report RRS of relaxors at ambient conditions [22] or are focused on excitations from point defects in the ferroelectric matrix [23,24]. Furthermore, resonance Raman peaks arising from infrared-active phonon modes are commonly considered as symmetry "forbidden" if these modes are not active in nonresonance Raman scattering. Such phonon modes may in fact be symmetry allowed when coupled with the corresponding electron transition, but studies on selection rules for RRS are scarce.

Thus the main contributions of this study are: (i) the application of group-theory analysis to coupled electronphonon states in order to reinspect the origin of RRS of ABO₃-type relaxors enhanced with photon energy close to the energy gap, and (ii) analysis of the temperature/pressure evolution of the structural polarity in relaxors. For the purpose we have analyzed the RRS of PbSc_{0.5}Ta_{0.5}O₃ (PST) and PbSc_{0.5}Nb_{0.5}O₃ (PSN) single crystals in the temperature range 100-800 K as well as the pressure dependence of RRS of PST up to 8.3 GPa. The resonance Raman spectra were excited with a laser wavelength $\lambda = 325$ nm corresponding to 3.8 eV, which is above the energy gap $E_g \sim 3.2 \text{ eV}$ of the studied compounds [22]. It should be however underlined that E_g has been determined by applying the Tauch equation for direct transition processes to the optical absorption edge, i.e., this experimental value may be slightly below the energy value corresponding to the highest probability of electron interband transitions. Besides, relaxors comprise polar nanoregions surrounded by a nonpolar substance, while on the other hand E_g for classical ferroelectrics such as LiTaO₃ and LiNbO₃ is approximately 15% higher in the ferroelectric state as compared to the paraelectric state [25]. Therefore the mesoscopic-scale structural inhomogeneity typical of relaxors may considerably enlarge the energy distribution of electron transitions. Indeed, previous multiwavelength Raman spectroscopy of PST and PSN revealed that the strongest resonance Raman scattering is observed when the energy of the exciting photon is higher than E_g and it is in the vicinity of the very broad maximum of the optical dielectric permittivity ($\sim 3.6-3.8 \text{ eV}$) [22]. Furthermore, the resonance Raman signal is gradually enhanced when the energy of the incident photon increases from E_g towards the energy of the optical dielectric-permittivity maximum [22], indicating the same nature of electron-phonon coupling processes in this energy range. Hence, a laser wavelength of 325 nm has been chosen to ensure strong resonance Raman scattering due to phonon interactions with electron transitions close to the energy gap. Group theory analysis was performed using the recently developed additional online tools for first- and second-order Raman scattering [26], which were implemented on the Bilbao Crystallographic Server [27] while conducting this study.

II. EXPERIMENTAL DETAILS

Single crystals of PST and PSN from the same synthesis batches as the samples analyzed by synchrotron x-ray and neutron diffraction, conventional Raman spectroscopy, and acoustic-emission and dielectric-permittivity measurements [7,8,28–30] were used in this study. Both compounds exhibit subtle or no chemical B-site order of NaCl-type and develop a long-range ferroelectric order at low temperatures.

Resonance Raman spectra were measured with a Horiba Jobin-Yvon T64000 triple-grating spectroscopic system equipped with a LN₂-cooled CCD detector Symphony, an Olympus BH41 microscope and optics suitable for UV radiation, including holographic gratings with 2400 grooves/mm and UV objectives (40× for measurements at ambient conditions and $10 \times$ for *in situ* experiments at different temperatures or high pressures). The measurements were conducted using the 325-nm line of a CdHe laser (IK Kimmon Koha Co. LTD) in the spectral range $30-2200 \text{ cm}^{-1}$. The achieved spectral resolution was approximately 4 cm⁻¹. For comparison nonresonance Raman spectra in the same spectral range were collected at ambient condition, using the 514.5-nm line of an Ar⁺ laser (Coherent Innova 90C FreD), 1800-grooves/mm gratings, and a VIS objective $50 \times$. In both resonance and nonresonance Raman experiments parallel polarized $\overline{Z}(XX)Z$ and cross polarized $\overline{Z}(XY)Z$ spectra were collected (Porto's notation), where X, Y, and Z are along the crystallographic [100], [010], and [001] directions, respectively. Experiments at different temperatures were conducted upon cooling from 800 to 100 K with a Linkam THMS-E600 stage. High-pressure resonance Raman spectra were collected in a Boehler-Almax diamond anvil cell and 16:3:1 methanol-ethanol-water mixture as a pressure-transmitting medium, which ensures hydrostaticity up to 10.5 GPa [31]. The pressure was determined from the pressure-induced shift of the R1 photoluminescence line of ruby [32].

The measured spectra were subtracted by a background spectrum measured aside from the sample to eliminate artificial signals and baseline corrected by a polynomial function to take out the electronic contribution. Then the spectra were temperature reduced to account for the Bose-Einstein phonon occupation factor and fitted with pseudo-Voigt functions [PV = qL + (1 - q)G, L and G are Lorentzian and Gaussian functions, q is a weight coefficient] to determine the peak positions, full widths at half maximum (FWHMs), and integrated intensities.

III. RESULTS AND DISCUSSION

A. Resonance Raman scattering at ambient conditions

The resonance Raman spectra of PST and PSN collected with $\lambda = 325$ nm and the nonresonance Raman spectra collected with $\lambda = 514.5$ nm, which corresponds to 2.4 eV < $E_g \sim 3.2$ eV, show a striking difference (see Fig. 1). The spectra measured under nonresonance conditions indicate that the first-order Raman peaks are below 850 cm⁻¹. The resonance Raman spectra however exhibit peaks generated by both first- and second-order inelastic scattering, which are much stronger in parallel polarized $\overline{Z}(XX)Z$ than in cross polarized $\overline{Z}(XY)Z$ scattering geometry. In addition, the



FIG. 1. Parallel polarized $\overline{Z}(XX)Z$ (solid lines) and cross polarized $\overline{Z}(XY)Z$ (dashed lines) resonance (black lines) and nonresonance (gray lines) Raman spectra of PST (upper plot) and PSN (bottom plot) measured at ambient conditions; B and S mark the first-order RRS peaks generated by antisymmetric BO₆ bending and stretching, respectively, whereas 2B, B + S, and 2S mark the corresponding second-order RRS peaks. For clarity the parallel polarized spectra are vertically offset with respect to the cross polarized spectra.

first-order Raman scattering near 435 cm^{-1} and 705 cm^{-1} labeled in Fig. 1 by B and S order is strongly enhanced under resonance conditions. These Raman peaks arise respectively from LO antisymmetric BO₆ bending and stretching modes [33,34] (see Fig. 2), which are both polar and in a cubic ABO₃ structure generate infrared-active T_{1u} phonon modes. It should be noted that the energy gap of perovskite-type ferroelectrics having a d element (e.g. Ti, Nb, Ta) on the B site is formed by the 2p level of O and the d level of the B cation [25,35–37]. Therefore the enhancement of polar internal BO₆ modes in RRS excited with photon energy close to E_g is anticipated. The comparison of the peak positions (see Table I) reveal that the RRS near 865 cm⁻¹ (peak 2B in Fig. 1) results from the overtone of the LO antisymmetric BO₆ bending, the peak near 1405 cm^{-1} (peak 2S) is from the overtone of the LO antisymmetric BO₆ stretching, while the peak near 1135 cm⁻¹ (peak B + S) is a combination mode between the two internal antisymmetric BO₆ modes. The very good accordance between the two-phonon wave numbers ω_{2B} ,

antisymmetric BO_6 bending, T_{44} in a cubic ABO₃ structure antisymmetric BO₆ stretching, T_{1u} in a cubic ABO₃ structure



FIG. 2. (Color online) Sketch of antisymmetric BO_6 bending and stretching modes in a cubic perovskite structure; open circles represent oxygen atoms, smaller and larger filled circles are B-site and A-site cations, respectively. The atomic vector displacements are given only for one BO_6 species (marked in red) in the unit cell and for one set of vibrations of the corresponding triply degenerate mode.

 ω_{B+S} , ω_{2S} and the corresponding sums of the one-phonon wave numbers $\omega_B + \omega_B$, $\omega_B + \omega_S$, $\omega_S + \omega_S$ (less than 0.007 relative difference) implies that phonons mainly from the Brillouin-zone center participate in the two-phonon RRS [17]. This assumption is also consistent with the dispersion of Fröhlich interactions, which significantly weaken for large wave-vector phonons [17,21].

B. Group-theory analysis

At ambient conditions the average structure of the studied PST and PSN is cubic with space group $Fm\bar{3}m$ (double-perovskite) and $Pm\bar{3}m$ (single-perovskite), respectively [38,39]. The doubling of the structure is related to the presence of chemical 1:1 B-site order. It should, however, be underlined that on the length scale of sensitivity of Raman spectroscopy, Pb-based B-site complex relaxors always exhibit a double-perovskite structure due to the existence of local chemical B-site order, and in addition, they exhibit intermediate-range polar as well as antiferrodistortive ferroic order [7,8,10,28]. For PST and PSN the former evolves into long-range ferroelectric order of rhombohedral symmetry (R3m for single-perovskite or R3 for double-perovskite structure) [13,14], while the latter transforms into a long-range order under high pressure ($R\bar{3}c$ for single-perovskite or $R\bar{3}$ for double-perovskite structure) [38,39]. Hence, to clarify the origin of RRS in PST and PSN we have applied group-theory analysis to all six above specified space groups [26].

Generally, to derive the selection rules for resonance Raman scattering one has to first check if the corresponding electron dipole transitions are symmetrically allowed or not.

TABLE I. Peak positions in cm^{-1} of first-order RRS generated by antisymmetric BO₆ bending (B) and antisymmetric BO₆ stretching (S) as well as the corresponding second-order RRS: 2B, B + S, and 2S for PST and PSN at ambient conditions.

	В	S	2B	B + S	28
PST PSN	$\begin{array}{c} 435\pm1\\ 439\pm1\end{array}$	707 ± 1 706 ± 1	$\begin{array}{c} 865\pm2\\ 871\pm6\end{array}$	1135 ± 1 1137 ± 1	$1408 \pm 1 \\ 1403 \pm 1$

An electron transition is symmetry allowed if the following condition is satisfied:

$$\Gamma_{e^f} \otimes \Gamma_V \otimes \Gamma_{e^i} \subset A,\tag{1}$$

where Γ_{e^i} , Γ_{e^f} , Γ_V , and A represent the initial electron state, the final electron state, the vectorial representation, and the totally symmetric irreducible representation, respectively.

For symmetry-allowed electron transitions one can calculate the RRS selection rules, i.e., one can obtain the phonon modes compatible with the symmetry-allowed electron transition using the following expression [40]:

$$\Gamma_{e^i} \otimes \Gamma_{v^i} \otimes \Gamma_{e^f} \otimes \Gamma_{v^f} \cap \Gamma_{[V^2]} \neq 0, \tag{2}$$

where Γ_{v^i} and Γ_{v^f} are the initial and final phonon states and $\Gamma_{[V^2]}$ is the symmetrized square of the vector representation. Generally, the initial phonon state is the ground state $\Gamma_{v^i} = A$ and therefore Eq. (2) can be written as

$$\Gamma_{e^i} \otimes \Gamma_{e^f} \otimes \Gamma_{v^f} \cap \Gamma_{[V^2]} \neq 0. \tag{3}$$

Therefore, if the intersection between the symmetrized square of the vector representation and the direct product of the initial electron state, the final electron state, and the final vibration state is different from zero, the final vibration state is symmetry allowed under resonance Raman conditions.

The above described procedure has been applied to derive selection rules for RRS of ABO₃-type relaxors with space groups $Pm\bar{3}m$, $Fm\bar{3}m$, R3, R3, R3c, and $R\bar{3}$. For conciseness here we present the results only for double-perovskite cubic $(Fm\bar{3}m)$ and double-perovskite rhombohedral polar (R3) structures.

As mentioned above, the electron band structure of perovskite-type ferroelectric has a common feature: The energy gap is formed from the oxygen *p*-electron states, which dominate the top of the valence band, and the B-cation *d*-electron states, which dominate the bottom of the conduction band. In a cubic structure with point group $m\bar{3}m$ the *p*-electron state transforms as a triply (t_{1u}) degenerate representation, while the *d*-electron state transforms as triply (t_{2g}) and doubly (e_g) degenerate representations. Therefore, the initial electron state is t_{1u} and the final electron state is t_{2g} or e_g , resulting in two possible electron transitions (see Fig. 3).

Using the multiplication table of irreducible representations of the point group $m\bar{3}m$ [41] and by applying Eq. (1) with $\Gamma_V = t_{1u}$, we obtain

$$t_{2g} \otimes t_{1u} \otimes t_{1u} \subset a_{1g}$$

$$e_{g} \otimes t_{1u} \otimes t_{1u} \subset a_{1g}.$$
(4)

Therefore, both electron transitions, $t_{1u} \longrightarrow t_{2g}$ and $t_{1u} \longrightarrow e_g$, are symmetrically allowed.

TABLE II. Mechanical representation for the double perovskite structure with space group $Fm\bar{3}m$; WP stands for Wyckoff position; r, ir, and in denote Raman-active, infrared-active, and inactive modes, respectively. Only infrared-active modes carry polarity.

	WP	Mechanical representation
A	8c	$T_{2g}(\mathbf{r})$
\mathbf{B}'	4a	$T_{1u}(ir)$
$\mathbf{B}^{\prime\prime}$	4b	$T_{1u}(\mathrm{ir})$
0	24e	$A_{1g}(\mathbf{r}) + E_g(\mathbf{r}) + 2T_{1u}(\mathbf{ir}) + T_{2u}(\mathbf{in}) + T_{1g}(\mathbf{in}) + T_{2g}(\mathbf{r})$

Then, we can calculate the selection rules for first-order RRS by applying Eq. (3) for both electron transitions and all symmetry-allowed phonons in $Fm\bar{3}m$ (see Table II) with $\Gamma_{[V^2]} = A_{1g} + E_g + T_{2g}$. As can be seen in Table III, only T_{1u} and T_{2u} phonons of PST and PSN are symmetry allowed in RRS excited with photon energy corresponding to the $O(2p) \longrightarrow B$ -cation (d) electron transition. However, T_{2u} phonons do not carry polarity (see Table II) and therefore cannot participate in Fröhlich interactions. The selection rules for second-order RRS can also be obtained using Eq. (3) with Γ_{v^f} equal to the possible products of fundamental phonon modes (see Table III). The results reveal that in cubic PST and PSN overtones are not allowed in RRS for any of the electron transitions. In particular $(T_{1u} \otimes T_{1u}) \otimes (t_{1u} \otimes e_g)$ and $(T_{1u} \otimes T_{1u}) \otimes (t_{1u} \otimes t_{2g})$ are forbidden, which correspond to overtones of antisymmetric BO₆ bending and stretching in a cubic structure. A combination mode of these two fundamental modes is also not allowed. The only symmetryallowed combination modes are those with mixed parities, e.g., $(A_{1g} \otimes A_{2u}) \otimes (t_{1u} \otimes e_g)$ and $(A_{1g} \otimes A_{2u}) \otimes (t_{1u} \otimes t_{2g})$.

Therefore group-theoretical arguments prohibit the simultaneous coexistence of first- and second-order RRS from the internal antisymmetric BO₆ modes in cubic symmetry $(m\bar{3}m)$. Similar considerations revealed that for nonpolar rhombohedral symmetries ($\overline{3}$ and $\overline{3}m$) first- and second-order RRS from internal antisymmetric BO₆ modes are also not simultaneously allowed, if the electron transition goes from the p-electron state of oxygen to the d-electron state of the B cation (see Fig. 3). The T_{1u} mode of $m\bar{3}m$ splits into A_u and $\{{}^{1}E_{u} + {}^{2}E_{u}\}$ for $\bar{3}$ symmetry ($\{{}^{1}E_{u} + {}^{2}E_{u}\}$ is the so-called physical irreducible representation formed by the direct sum of the complex conjugated irreducible representations ${}^{1}E_{u}$ and ${}^{2}E_{u}$). The low-symmetry modes A_{u} and $\{{}^{1}E_{u} + {}^{2}E_{u}\}$ are symmetry allowed in RRS processes but their second harmonics and their combination modes are not allowed under resonance conditions. Using similar arguments one can also discard the $\bar{3}m$ symmetry.



FIG. 3. (Color online) Possible electron transitions between O 2p and B-site-cation *d* levels in a cubic ABO₃ as well as rhombohedral ABO₃ structures with different symmetries; the corresponding point-group symmetries are specified in the plot.

TABLE III. Selection rules for first- and second-order RRS for point group $m\bar{3}m$; the symmetry-allowed RRS processes are designated by check marks. The irreducible representations labeled in lowercase and uppercase denote the electron and phonon states, respectively.

	$t_{1u}\otimes e_g$	$t_{1u}\otimes t_{2s}$
$\overline{A_{1g}}$		
E_g		
T_{1g}		
T_{2g}		
T_{1u}	\checkmark	\checkmark
T_{2u}	\checkmark	\checkmark
$A_{1g} \otimes T_{1u}$	\checkmark	\checkmark
$A_{1u} \otimes T_{1u}$		
$A_{2g} \otimes T_{1u}$	\checkmark	\checkmark
$A_{2u} \otimes T_{1u}$		
$E_g \otimes T_{1u}$	\checkmark	\checkmark
$E_u \otimes T_{1u}$		
$T_{1g} \otimes T_{1u}$	\checkmark	\checkmark
$T_{1u}\otimes T_{1u}$		
$T_{2g} \otimes T_{1u}$	\checkmark	\checkmark
$T_{2u} \otimes T_{1u}$		

Group-theory analysis indicates that among the plausible ferroic phases, first- and second-order RRS of antisymmetric BO₆ are simultaneously allowed only for polar structures. For example, in the case of R3 the triply degenerate electron states of the prototype structure split into nondegenerate a and doubly degenerate $\{^{1}e + {}^{2}e\}$ electron states (see Fig. 3). As a result, there are four different possible electron transitions: $a \rightarrow a$, $a \longrightarrow \{^1e + ^2e\}, \{^1e + ^2e\} \longrightarrow a, \text{ and } \{^1e + ^2e\} \longrightarrow \{^1e + ^2e\} \longrightarrow$ ²e}. According to Eq. (1) with $\Gamma_V = A + \{{}^{1}E + {}^{2}E\}$, all these electron transitions are symmetry allowed. The fundamental phonon modes in ABO₃ with space group R3 are of symmetry A and $\{{}^{1}E + {}^{2}E\}$ and they all carry polarity. By applying Eq. (3) with $\Gamma_{[V^2]} = 2A + 2\{{}^{1}E + {}^{2}E\}$ we can obtain the resonance Raman selection rules for R3 (see Table IV). As can be seen, all fundamental phonon modes as well as all overtones and combination modes are Raman active under resonance conditions.

Therefore, the group-theory analysis indicates that the intense RRS peaks near 435, 705, 865, 1135, and 1405 cm⁻¹ arise from antisymmetric internal BO₆ modes in *polar* structures. It should be mentioned that the peak near 865 cm⁻¹ was previously assigned to the A(LO) mode in polar nanoregions related to the symmetric BO₆ stretching, which in a cubic phase

TABLE IV. Selection rules for first- and second-order RRS for point group 3; the symmetry-allowed RRS processes are designated by check marks. The irreducible representations labeled in lowercase and uppercase denote the electron and phonon states, respectively.

	$a \otimes a$	$a \otimes \{^1 e + ^2 e\}$	${}^{1}e+{}^{2}e \otimes {}^{1}e+{}^{2}e \}$
A	\checkmark	\checkmark	\checkmark
${^{1}E+^{2}E}$	\checkmark	\checkmark	\checkmark
$A \otimes A$	\checkmark	\checkmark	\checkmark
$A \otimes {{}^{1}E+{}^{2}E}$	\checkmark	\checkmark	\checkmark
${}^{1}E+{}^{2}E \otimes {}^{1}E+{}^{2}E $	\checkmark	\checkmark	\checkmark

appears as A_g mode [22]. This phonon mode might contribute to the RRS at 865 cm⁻¹, but the good accordance between the positions of the peaks labeled in Fig. 1 as B and 2B implies that the dominant RRS near 865 cm⁻¹ results from the overtone of the antisymmetric BO₆ bending in polar nanoregions.

C. Resonance Raman scattering at different temperatures

Polarized resonance Raman spectra of PST and PSN measured at different temperatures in the range 100-800 K are shown in Figs. 4 and 5, respectively. No RRS was detected at 800 K, which for both compounds is above $T_B \sim 650-700$ K of nucleation of dynamic PNRs [7,8]. This indicates that the contribution from symmetry-allowed cubic T_{1u} to the RRS is below the experimental detection limit due to the negligibly small strength of electron-phonon coupling in a cubic structure. This observation confirms the conclusion based on group-theory analysis that RRS of PST and PSN arises exclusively from polar structural species. It should be noted that the strength of electron-phonon coupling in polar regions in relaxors depends on the polarity of the individual polar deformation as well as on the correlation length of coherent polar distortions, i.e., the size of PNRs, because the mesoscopic-scale polarization associated with PNR should enhance the electrostatic interactions between the excited electron and the excited polar phonon mode. Nonresonance Raman spectroscopy reveals the existence of uncoupled ferroic distortions even above T_B [7,8], but apparently their polarity, if any, is insufficient to produce detectable RRS. Moreover, for both compounds RRS was first detected near the characteristic temperature T^* , at which the preexisting small PNRs merge into larger PNRs of slower flipping dynamics [7,8], and upon further cooling the intensity drastically grows (see Fig. 6). This also emphasizes that RRS of PST and PSN is generated by coherent polar distortions with a sufficiently large correlation length.

It is worth noting that in general the disappearance of RRS at high temperatures might be due to strong changes in the electron band structure driving the system away from resonance conditions. However the expected redshift of the direct-transition energy gap in ferroelectric perovskitelike oxides upon temperature increase by 400 K is approximately 0.1 eV [42–44], which would hardly affect the electron-phonon coupling to the extent that RRS of relaxors would completely disappear.

At low temperatures the RRS spectra depolarize (see Figs. 4 and 5) due to the development of submicrometer-sized long-range-ordered ferroelectric domains of rhombohedral symmetry; note that X, Y, and Z are along the cubic crystallographic axes. A similar effect was observed in nonresonance Raman spectra [7,8], and it is more pronounced for PST than for PSN due to the larger fraction of ferroelectric domains. We assume that the latter is also the reason for the observed kink near T_c in the RRS intensity for PST (Fig. 6).

Figure 7 shows the temperature evolution of the intensity ratio between the first-order RRS from antisymmetric BO₆ stretching and bending I(S)/I(B). Since these are internal modes of the same structural species, the effect of the PNR/domain size on the electron-phonon coupling should be the same. Hence the ratio I(S)/I(B) should be indicative of



FIG. 4. (Color online) Polarized resonance Raman spectra of PST measured at different temperatures and ambient pressure. The spectra are vertically offset for clarity.

the polarity of BO₆ octahedra due to difference in B-O bond lengths with respect to the polarity of BO₆ species due to distorted O-B-O bond angles. As can be seen in Fig. 7, near T^* I(S)/I(B) < 1, i.e., the BO₆ polarity related to different bond lengths is weaker than that related to distorted O-B-O bond angles. Upon cooling the former initially gains in strength, but at a certain temperature it begins weakening on account of BO₆ polarity due to distorted O-B-O bond angles. The turnover temperature is near 325 K for PST and between 200 and 300 K for PSN. For PST this value coincides with the temperature at which the PNRs formed at T^* start merging with each other to further evolve into long-range ferroelectric order with space group R3 at $T_c \sim 270$ K [7]. The maximum of I(S)/I(B) versus temperature suggests that a similar process occurs in PSN between 200 and 300 K. This assumption is supported by the fact that upon cooling the vanishing of x-ray diffuse scattering from PNRs and the simultaneous appearance of Bragg reflections related to R3 take place at 180 K [8], although the ferroelectric $Pm\bar{3}m$ -to-R3m phase transition is near 360 K [14].

D. Resonance Raman scattering at high pressures

The RRS spectra of PST measured under high pressure at room temperature are shown in Fig. 8(a). Unfortunately the scattering above 1250 cm^{-1} was strongly interfered by



FIG. 5. (Color online) Polarized resonance Raman spectra of PSN measured at different temperatures and ambient pressure. The spectra are vertically offset for clarity.



FIG. 6. (Color online) Temperature dependence of the $\overline{Z}(XX)Z$ intensity of total resonance Raman scattering in the range 30-2200 cm⁻¹ for PST (circles) and PSN (squares).

the Raman signal from the diamond anvils and the peak 2S could not be detected. However the RRS peaks B, S, 2B, and B + S were clearly observed up to 8.3 GPa, which was the highest pressure reached in the experiment. Under pressure PST undergoes two displacive phase transitions: at $p_{c1} = 1.9$ GPa, from a relaxor cubic to nonpolar rhombohedral $R\bar{3}$ state characterized by antiphase BO₆ tilt order, and at $p_{c2} \sim 5.5$ GPa to a lower-symmetry phase comprising antiparallel Pb²⁺ displacements and mixed in-phase/antiphase BO_6 tilts [28,38,45,46]. The latter phase was anticipated to be also nonpolar (space group $P2_1/c$), although densityfunction-theory calculations indicated that the polar and nonpolar counterparts of the same tilt configurations are energetically indistinguishable at high pressures [28]. Grouptheory considerations reveal that only first-order RRS arising from internal antisymmetric BO₆ modes is allowed in these two nonpolar groups, whereas the corresponding second-order RRS is symmetry forbidden [26]. Experimentally, the total RRS intensity of PST rapidly decreases above p_{c1} [see Fig. 8(b)], but it does not vanish and both the first- and second-order RRS persist up to 8.3 GPa. The resonance Raman selection rules discussed above explicitly indicate that this can



FIG. 7. (Color online) Temperature dependence of the intensity ratio of the first-order $\overline{Z}(XX)Z$ RRS generated by the antisymmetric BO₆ stretching (S) and bending (B) mode for PST (circles) and PSN (squares).



FIG. 8. (Color online) Resonance Raman spectra of PST measured in $\overline{Z}(XX)Z$ scattering geometry at different pressures and room temperature (a) and pressure dependence of the total resonance Raman intensity (b). The spectra in (a) are vertically offset for clarity. Note that the spectrum at ambient pressure was collected after decompression. The dashed line in (b) is a linear fit to the data points above 1.2 GPa. The arrows in (b) mark the critical pressures determined by combined synchrotron x-ray diffraction, neutron diffraction, and nonresonance Raman scattering (Refs. [28,38,45,46]).

Pressure (GPa)

8 9

7

0

0

2 3 4 5 6

be observed only if the structure is noncentrosymmetric. On the other hand, neither $R\bar{3}$ nor $P2_1/c$ contain a subgroup which is simultaneously noncentrosymmetric and nonpolar, i.e., further noncentrosymmetric lowering of the structural symmetry is possible only if the crystal class of the resultant structure is polar. Therefore the coexistence of first- and second-order RRS up to 8.3 GPa indicates that the high-pressure state is actually polar. This is a rather unexpected result because pressure strongly suppresses the off-centering of B-site cations as well as the x-ray diffuse scattering arising from PNRs [15]. Apparently the sensitivity of RRS to polarity in solids is very high, emphasizing the great potential of the method to study advanced ferroelectrics at nonambient conditions. It is worth noting that pressure may enhance ferroelectricity due to the change in the electron density of states rather than structural distortions [47], but this phenomenon is expected to occur at pressures much higher than the pressures reached in our experiment. Thus we suggest that the simultaneous observation of first- and second-order RRS from the internal antisymmetric BO_6 modes is due to structural polarity. The high-pressure polarity is however much weaker than the low-temperature polarity and should be related to slight BO_6 deformations accompanying the long-range octahedral tilt order, in contrast to the large off-centering of B-site cations at low temperatures.

IV. CONCLUSION

Two main conclusions can be drawn from this study: First, the resonance Raman scattering of Pb-based ABO₆relaxors excited with photon energy slightly above the energy gap results exclusively from coherent polar distortions. This follows from the derived selection rules as well as from the fact that no RRS is observed at temperatures above T_B . With the temperature decrease the total RRS intensity drastically increases due to the development of long-range ferroelectric order. The intensity ratio between the first-order RRS from antisymmetric BO₆ stretching and BO₆ bending has a maximum near the temperature at which the large polar

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nanoregions formed at T^* begin to merge, indicating that this process is accompanied by a change in the predominant type of BO₆ polarity from related to difference in B-O bond lengths to related to distorted O-B-O bond angles.

Second, the high-pressure structure of Pb-based ABO_6 relaxors is *polar*. Under pressure the intensity of RRS significantly decreases above the first critical pressure at which long-range BO₆ tilt order is developed but it persists up to 8.3 GPa, indicating structural polarity due to the slight BO₆ distortions accompanying the long-range tilt order.

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