Intermediate temperature scale T^* in lead-based relaxor systems

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Via a combination of various experimental and theoretical techniques, a peculiar, identical temperature scale T^* is found to exist in all complex lead-based relaxor ferroelectrics studied by us. T^* corresponds to a nanoscale phase transition associated with random fields. Interestingly, T^* also exists in other oxides with extraordinary properties, such as giant magnetoresistivity or superconductivity. By analogy with such latter systems, the giant piezoelectricity related to relaxors might originate from proximity competing states effect.

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I. INTRODUCTION

Lead-based perovskite relaxors $Pb(BB')O_3$ such as $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN), $Pb(Zn_{1/3}Nb_{2/3})O_3$ (PZN), or $Pb(Sc_{1/2}Nb_{1/2})O_3$ (PSN) and related materials have recently attracted a great deal of attention due to the excellent piezoelectric properties of their solid solutions with $PbTiO_3$ (PT) within the morphotropic phase boundary (MPB).[1] In contrast to classical ferroelectric, relaxors display[2] (i) a strong frequency dependence of the dielectric permittivity, (ii) a broad dielectric anomaly around the temperature of the maximum dielectric permittivity, T_m, for a given frequency, and (iii) no structural macroscopic phase transition across T_m. Nowadays it is generally accepted that the strong dielectric relaxation of T_m needs two crucial ingredients. The first one concerns the quenched random electric and strain fields[3] (RFs) arising from chemical disorder and the difference in ionic charges and radii between the different kinds of B cations (in fact, the cations on the B site of the perovskite structure typically deviate from a perfectly random distribution by possessing a short range order at a nanoscale through chemically ordered regions). The second ingredient concerns the dynamical polar nanoregions (PNRs), which nucleate several hundred degrees above T_m at the Burns temperature, T_B.[4] On cooling, the dynamic of the PNRs slows down and freezes out at the freezing temperature, T_f.[5] In case of PMN, T_B, T_m at 1 kHz, and T_f are close to 630, 260, and 220 K respectively.[4,5] Another interpretation of T_f is related to a phase transition into a nanodomain state due to the existence[3] of the RFs.

However, it was also suggested that another intermediate temperature exits. This temperature was first proposed to occur around 400 K in the model relaxor PMN by Viehland *et al.*[6] via dielectric-constant measurement and was considered to be a local Curie temperature. Later by means of diffraction data, Dkhil *et al.*[7] suggested the existence of such intermediate temperature and proposed that it corresponds to a local Heisenberg-Ising-type phase transition associated with an order-disorder transition of the Pb^{2+} cations. Svitelskiy *et al.*[8] also proposed the existence of this temperature (which they called T^*) via an analysis of Raman spectra. Despite some additional studies,[9–12] the existence of T^* is still controversial and therefore requires definite proofs. In this paper, we demonstrate that the temperature scale T^* is a definite signature of complex lead-based $Pb(BB')O_3$ relaxors and corresponds to a local phase transition that gives rise to the appearance of static polar nanoclusters. We demonstrate that T^* is neither dependent on the B(B′) species nor on the amount of doping (with Ti) (within the error bar of our experiments), unlike other critical temperatures (such as the macroscopic Curie and Burns temperatures). Moreover, theoretical calculations show that T^* exists if RFs through chemical disorder are present and, in agreement with our experimental observations, T^* is not significantly affected by the strength of these RFs, unlike the ferroelectric transition. Finally, by analogy with other nanoscale inhomogeneous systems,[13,14] we propose that the giant piezoelectricity observed in relaxor-based systems within their morphotropic phase boundary (MPB) can be explained by phase separation and proximity competing effects. This work brings a microscopic view of relaxors-based materials and insights for a universal picture of materials with colossal effects.

II. RESULTS AND DISCUSSION

Figure 1 displays the acoustic emission (AE) radiation for PMN and PZN from 450 to 750 K. The AE results on PZN have been already published[11] but are plotted here for comparison. There are two acoustic signals (thus associated with a strain release) that can be seen at around 500 and 630 K for PMN versus 500 and 740 K for PZN. 630 and 740 K correspond to the Burns temperature for PMN and PZN, respectively, as consistent with previous works, whereas we propose that 500 K is this T^* temperature. Interestingly, T^* is the same for PMN and PZN, while these two compounds are rather different: PZN displays a macroscopic phase transition at $T_C \sim 400$ K (close to T_f) and has a $T_B \sim 740$ K (Ref. 4) whereas in PMN no phase transition occurs down to 5 K and $T_f \sim 220$ K and $T_B \sim 630$ K (Refs. 4 and 5).

Let us now check if the T_B and T^* temperatures can also be evidenced by x-ray diffraction (XRD), a technique which presents the practical advantage to be applied to powder or single crystal in small amount whereas AE requires a large

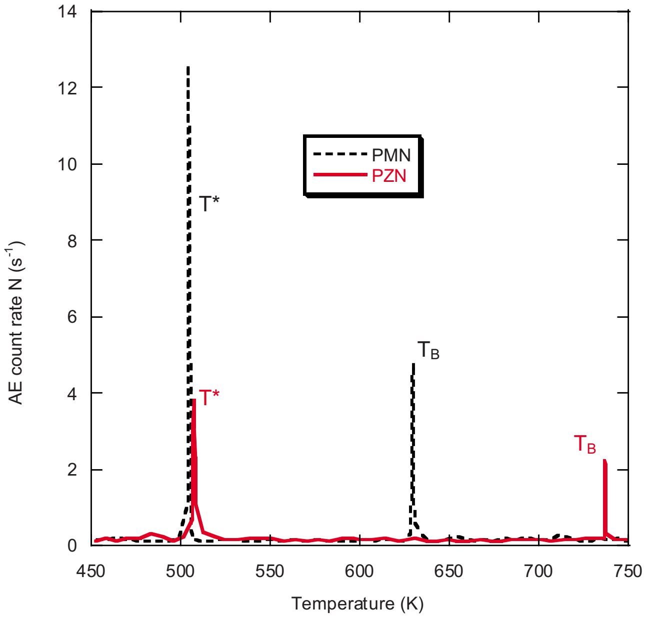

FIG. 1. (Color online) AE activity from 450 to 750 K for PMN (black dashed line) and PZN (red continuous line). A crystal was glued with a silver epoxy to the polished side of an acoustic fused silica waveguide. A lead zirconate titanium (PZT-19) piezoelectric sensor was attached to the rear end of the waveguide. The sensor was electrically coupled to a 500 kHz band pass low noise variable preamplifier (up to 40 dB) connected to an amplifier detector (40 dB). A Cr-Al thermocouple junction was glued to a waveguide near the sample. A sample with the adjacent part of the waveguide was mounted from below in a tube resistance element furnace. The AE count rate ($dN/dt=\dot{N}\ \mathrm{s}^{-1}$) was measured at an average cooling rate of 1–3 K s^{-1}.

enough single crystal. The XRDs were performed on a highly accurate two-axis diffractometer in a Bragg-Brentano geometry using Cu $K\beta$ wavelength issued from a 18 kW rotating anode generator with diffraction angles precision better than 0.002° (2 theta). Each powder was placed inside a furnace from 300 to 850 K (estimated precision of 2 K). Two distinct changes are detected on the lattice parameter above 400 K [Fig. 2(a) for PMN and Fig. 2(b) for PZN]: the most obvious one concerns the appearance of a plateau below T^* whereas T_B is associated with a weak change in slope. Actually, it is not obvious to simply determine T^* based on these data. Indeed T^* can be taken to be equal to ~440 and ~480 K for PMN and PZN, respectively, if one considers the deviation from the horizontal quasiplateau (Fig. 2). However, one can also define T^* as the highest temperature at which there is deviation from the linear slope below T_B (which gives a T^* that is very close to the one determined from AE experiment). Taking into account such differences, one can conclude that T^* is equal to 500 K with a relative error of ±30 K.

Figure 2 also shows the temperature dependence of the lattice parameter for several other Pb(BB′)O$_3$ relaxors. It is remarkable that whereas T_B can differ from one compound to another T^* remains close to 500 K. Figure 2(c) further shows data obtained on partially chemically ordered (order degree of 92%) and disordered PSN, and reveals that T^* and T_B are independent on the B-cation ordering [unlike other critical temperatures such as T_f and T_C (Ref. 15)] within our error bar. Furthermore, Fig. 2(d) reports x-ray data on PMN mixed with PT (PMN-PT) for different amount of mixing. It is obvious that the addition of PT does neither affect T_B nor T^*, while such addition is known to result in both an increase in the Curie phase transition temperature and a change in the low-temperature ground state.[11,12] Such independency of T_B and T^* to PT was also observed in PZN-PT and PSN-PT (not shown here). Moreover, we also studied several other lead-based relaxors with different B cations (size, charge, and proportion). All of them show both a deviation around T_B and T^* [Figs. 2(e) and 2(f)] and once again T^* is the same (within the error bar) among all the investigated compounds.

Let us now examine the Raman signal of several relaxors. Note that it is usually not obvious to deal with the Raman spectra of relaxors because the selection rules are strongly relaxed due to chemical and polar order/disorder. Here, we nevertheless show that this widely used technique is also pertinent to evidence T^*. For convenience, Fig. 3 shows only a selected wave-number region between 180 and 400 cm^{-1} of the Raman spectrum of PMN. When one compares the spectra at different temperatures, it is easy to see that the mode at around 270 cm^{-1} becomes weaker and weaker when the temperature increases. We plotted on Fig. 3(d) the ratio of the intensity of the mode at 270 cm^{-1} (mode D) with respect to that at 240 cm^{-1} (mode C). Interestingly, mode D appears around T^* indicating that a “local” change takes place at this temperature. We also plotted on the same figure the same ratio but for PSN compound, which confirms that T^* is the same for PSN and PMN (as consistent with our previous data). Note that in Ref. 8, T^* was evidenced by the broadening of some specific bands (including ones we investigated in Fig. 3) whereas here we show a clear appearance of a mode, whose origin remains to be elucidated.

Having demonstrated here that this temperature T^* indeed exists, let us look for a fingerprint of T^* in previous works. For instance, such temperature corresponds to the maximum of the transverse acoustic phonon linewidth in Ref. 16, the crossover between low and high temperatures of the transverse optical phonon wavelength in Ref. 17 and the appearance of the “butterflylike” diffuse scattering in Ref. 18. In other words, previous works further confirm the existence of T^* even if they overlooked it.

Now let us turn our attention to the physical reason for the existence of T^*. For that, it is important to emphasize again that our results clearly reveal that T^* is the same (within the error bar) for all lead-based systems studied here, unlike other critical temperatures. T^* is thus not directly linked to the type of B cations. Note that all the compounds we analyzed show B-cations disorder that provides RFs. Therefore by affecting the already existing quenched RFs, no effect (if any) is detected on T^* as the change of slope in the lattice parameter remains the same in any PMN-PT compound and in disordered or partially ordered PSN. Besides, it also appears that T^* should be associated with lead Pb^{2+} cations and/or oxygen network. Pb^{2+} is known to be responsible for the main polarization in lead-based relaxors.[7] The fact that T^* is a local Curie temperature[6] indicates that the nanoclusters becoming static at T^* are polar. It is worth mentioning that

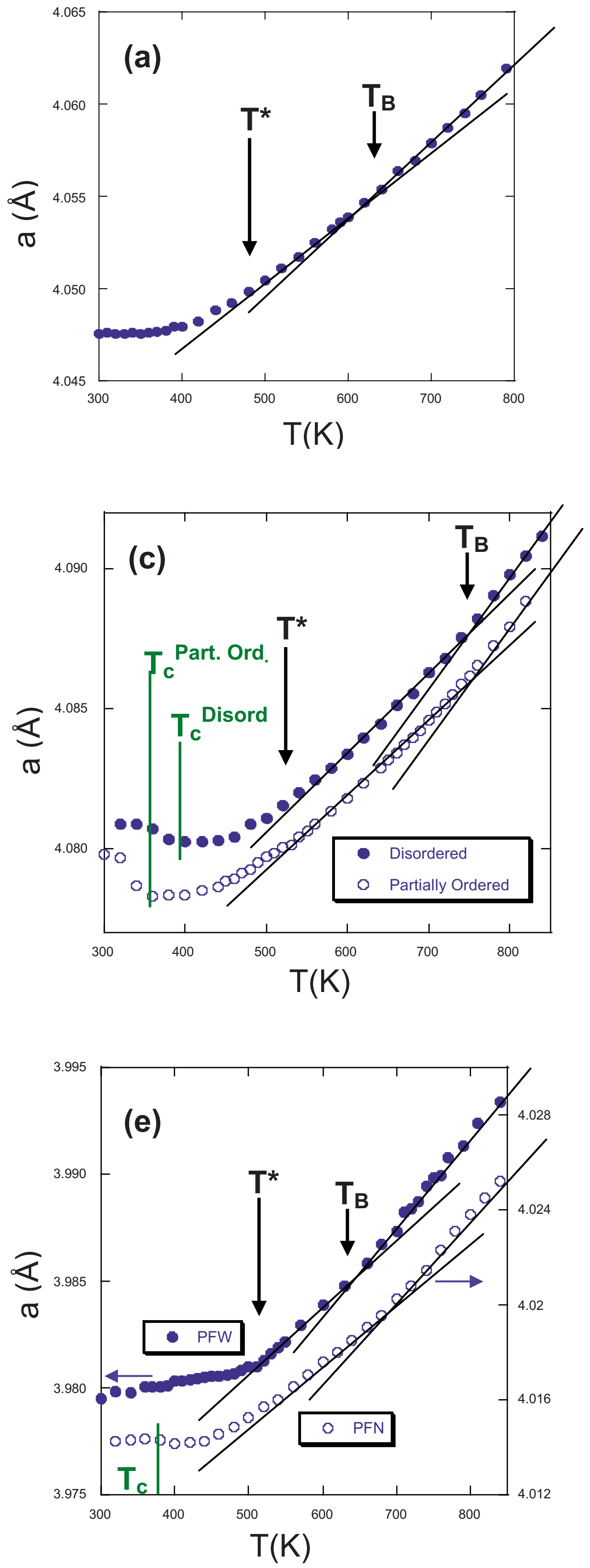

FIG. 2. (Color online) Pseudocubic lattice parameter a as a function of temperature from 300 to 850 K obtained with the (200), (220), and (222) Bragg peaks for (a) PMN, (b) PZN, (c) PSN partially ordered (order degree of 92%) and disordered, (d) $PbMg_{1/3}Nb_{2/3}O_3$-$PbTiO_3$ (PMN-PT) with PT concentration of 0%, 10%, 25%, and 33%, (e) $PbFe_{2/3}W_{1/3}O_3$ and $PbFe_{1/2}Nb_{1/2}O_3$, and (f) $PbMg_{1/3}Ta_{2/3}O_3$ and $PbSc_{1/2}Ta_{1/2}O_3$. The straight lines are guide to the eyes.

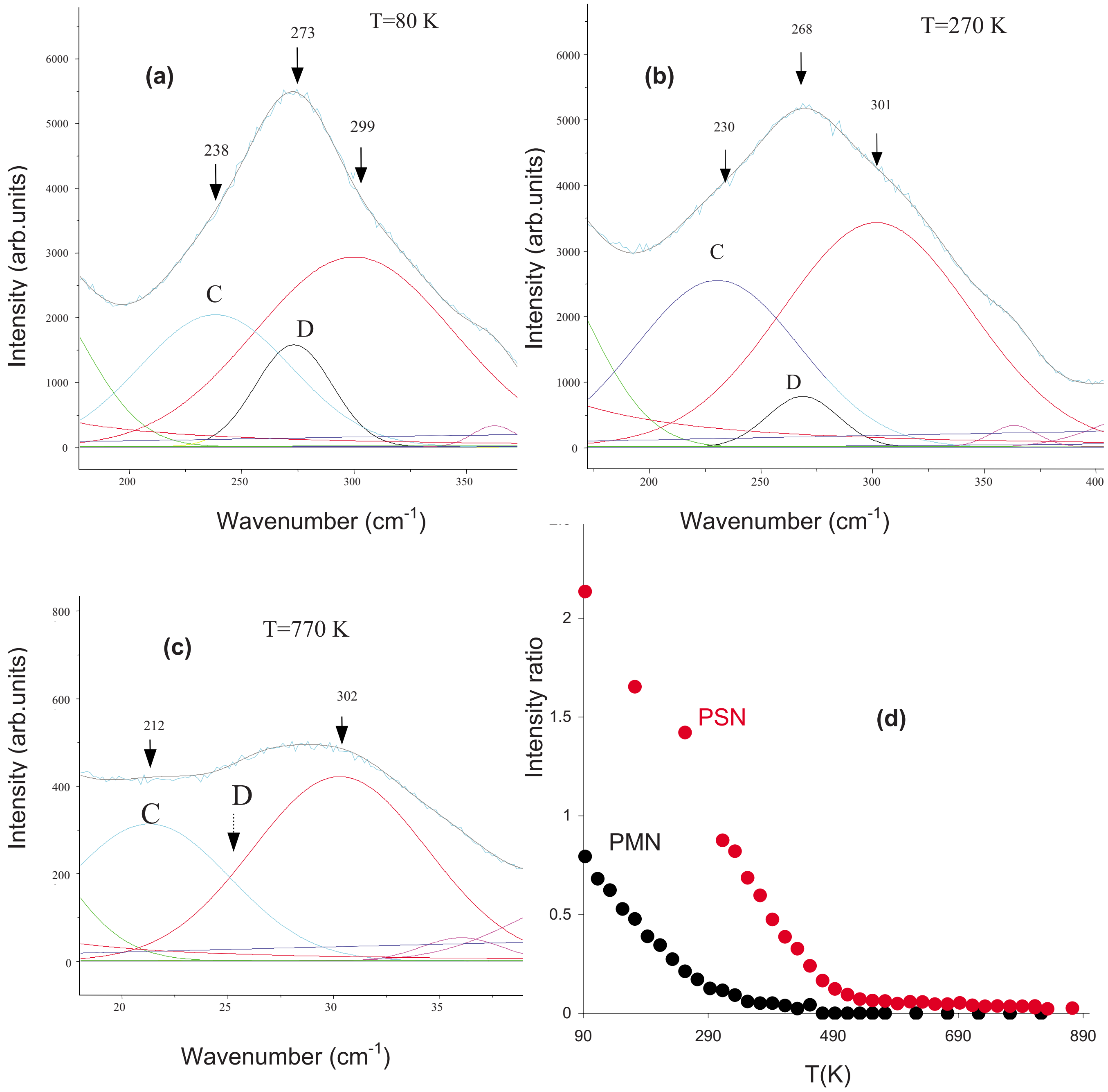

FIG. 3. (Color online) Selected wavelength Raman spectra between 180 and 400 cm^{-1} at (a) 80, (b) 270, and (c) 770 K with representative Lorentzian-shape deconvolution of the spectra. Panel (d) represents the ratio between the intensities of mode C (around 240 cm^{-1}) and mode D (around 270 cm^{-1}). The Raman measurements were performed in backscattering geometry using the 514,5 nm excitation line from an Ar^{+} laser focused to a spot of about 5 μm in diameter. The scattered light was analyzed using a Labram spectrometer (Jobin Yvon) equipped with a single-grating monochromator with a resolution of 1 cm^{-1}. We checked that the laser power did not produce significant heating or damage of the sample. The temperature measurements were carried out within a range from 80 to 770 K, using a commercial cell (Linkam THLS 600).

the term polar nanoregions can be misleading. Usually, the Burns temperature T_B is considered as the temperature of appearance of polar nanoregions.[2] However, such entities are mainly dynamic and are supposed to be related to off centring of Pb^{2+} ions (see references herein Ref. 2). We believe that it is only at T^* that the PNRs acquire a static component, that is, they become static clusters at a nanoscale (the average sample symmetry remaining cubic), leading to all the anomalies we previously evidenced. Still at T^*, as we already mentioned, Pb^{2+} ions appear to play a key role. We suggest that T^* marks the beginning of their static correlation (Ref. 7) but additional investigations (that go beyond the scope of this manuscript) are needed to definitely confirm this assumption.

The polar character is also confirmed by recent calculations results.[19,20] As a matter of fact, calculations done by

Iniguez and Bellaiche[19] showed that contrary to the normal ferroelectric piezoelectric transducer (PZT) compound, the relaxor-disordered PSN displays local polarization appearing far above the ferroelectric transition because of the existing RFs related to the *B*-cation disorder. Interestingly, they found that such polarization appears at $T/T_{\max}=1.2$ (where $T_{\max}$ is the temperature at which the static dielectric response is maximum), which experimentally corresponds to $T=480$ K in PSN and which is thus very close to the measured T^*. Such theoretical work brings an additional support for the existence of T^* and confirms that it is related to the existence of the quenched RFs. Interestingly when the RFs are strongly perturbed by removing a fair amount of Pb atoms,[20] it results in an increased broadening of the static dielectric constant and a shift toward a lower temperature for the maximum of the static dielectric constant. However, the highest temperature at which the local polarization starts to develop nearly remained the same, that is, T^*. To confirm these results, we used the same calculations tool—that is, a first-principles-based effective Hamiltonian scheme—to investigate disordered PSN (Sc and Nb are randomly distributed) and completely ordered PSN, planes of Sc atoms alternate with planes of Nb atoms along the [111] direction. Practically, periodic supercells with lateral size of 48 Å along any pseudocubic $\langle 001\rangle$ direction are used in these simulations. Such nanometric cells can be thought as representing a single polar nanocluster with specific RFs in the case of disordered PSN, while no RFs exist inside the ordered PSN supercell (due to the *B*-cation arrangement). Figure 4 shows the local modes (that are directly proportional to the local polarization) as a function of $T/T_{\max}$ for both disordered and completely ordered PSN supercells. As one can see, the local polarization is much broader in disordered, than in ordered, PSN. In particular, such local polarization starts to develop around $T/T_{\max}=1.2$ in the disordered PSN, while it is "only" significant for much lower ratio in ordered PSN. We interpret such difference as indicative of the fact that T^* disappears when the RFs do not exist.

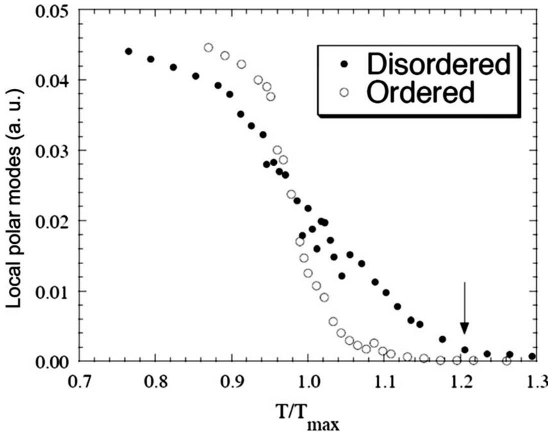

FIG. 4. Local polar modes (i.e., quantity directly related to polarization) as a function of $T/T_{\max}$ for disordered PSN (full circles) and fully ordered PSN (open circles). The effective Hamiltonian used has the following degrees of freedom: the local soft modes (defined in each 5 atom cell and proportional to the local dipoles), the components of the homogeneous strain tensor and the inhomogeneous strain variables. It contains a local mode self-energy (expanded in even-order terms up to fourth order of the phonon local soft modes), a long-range dipole-dipole interaction, a short-range interaction between soft modes (quadratic order of the soft modes), an elastic energy (expanded to second order of the strain variables), an interaction between the local modes and local strain (second order of the soft modes and linear order in strain), and an energy term describing the effects of the atomic configuration on the local strain variables and the phonon local soft modes. This latter energetic term then gathers RFs effects. This alloy effective Hamiltonian is solved by the Monte Carlo technique, using $4.8\times4.8\times4.8$ nm^3 supercells and up to 40 millions Monte Carlo sweeps.

III. CONCLUDING REMARKS

Our experimental and theoretical results thus show that T^* is the temperature at which static polar nanoregions appear if RFs exist (and independently of the strength of the RFs above a certain, significant value). It is now of interest to confront our results for the relaxor systems to other nanoscale inhomogeneous systems with, e.g., colossal magnetoresistance or high-temperature superconductivity and for which several evidences of existence of a peculiar temperature, T^*, were reported.[13,14,21,22] It was suggested that T^* is the result of the introduction of quenched disorder within several competing states and thus T^* is a reminiscence of the clean limit transition between these ordering states. The temperature dependence was then schematically described in electronic systems as following. At high temperature, uncorrelated polarons appear at T_{pol}. These individual polarons start to correlate at T^* becoming correlated nanoclusters. Thus at T^* both uncorrelated and correlated polarons coexist. By decreasing temperature, the number and/or size of the correlated polarons increases and becomes maximum at T_c. This scheme can be exactly applied to relaxors by replacing T_{pol} by T_{Burns}. It is also interesting to underline that in such strongly correlated electronic systems, colossal or proximity effect[13,14,21,23–25] was reported and that doping[14,21] does not affect T^* whereas it affects T_c. Interestingly and as we have shown, in case of relaxor, T^* is also not affected by the doping. Moreover relaxors also display a colossal effect that is the giant piezoelectricity.

By analogy with the electronic systems, it may be advocated that the giant piezoelectric response observed at the MPB of relaxors[26–30] is related to the competition between ordered states at a nanoscale in presence of disorder (that gives rise to RFs) and to the fact that any weak stress or electric field strongly affects such competition. It is well known that in ferroelectric perovskites one may consider several kinds of competitions between different symmetries (rhombohedral, tetragonal, monoclinic, …), different polar states (ferroelectric, antiferroelectric, and paraelectric), different distortions (oxygen tilting, cation displacement), or different dynamics (order-disorder, displacive motions). Thus all the ingredients, i.e., competing phases and quenched disorder, are present in relaxors. Such result provides a way to consider relaxors, that is, as a member of a wide family of materials possessing nanoscale inhomogeneous states and exhibiting different colossal properties but all having common features as a function of temperature.

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