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Crossover in the mechanism of ferroelectric phase transition of $\mathrm{Pb}[(\mathrm{Mg}_{1/3}\mathrm{Nb}_{2/3})_{1-x}\mathrm{Ti}_x]\mathrm{O}_3$ single crystals studied by Brillouin light scattering

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The inelastic light scattering spectrum of $\mathrm{Pb}[(\mathrm{Mg}_{1/3}\mathrm{Nb}_{2/3})_{1-x}\mathrm{Ti}_x]\mathrm{O}_3$ (PMN-xPT) single crystals with $x=0-0.55$ due to longitudinal-acoustic (LA) waves was investigated in a wide temperature range by using a Brillouin scattering technique. The acoustic frequency of LA modes of all PMN-xPT crystals showed a significant softening upon cooling in the high-temperature range where the deviation from the high-temperature linearity starts from ~ 750 K. In addition, hypersonic damping exhibited a remarkable increase upon cooling toward the freezing or ferroelectric phase-transition temperature. These acoustic anomalies were attributed to the polarization fluctuations due to the displacive polarization component arising from the condensation of transverse-optic mode, flipping of polar nanoregions, and, for PMN-xPT with large x, correlated polar nanometer-sized regions (PNRs) as ordering units. The application of the modified superparaelectric model to the measured acoustic properties revealed that the activation energy for the flipping of PNRs displayed a sharp increase upon crossing the composition of morphotropic phase boundary (MPB) of PMN-xPT. This change was attributed to the appearance of order-disorder polarization component, i.e., polar clusters in PMN-xPT with large x beyond MPB, which indicated PNRs are correlated and oriented along the same direction. These results may suggest a crossover in the mechanism of phase transition with increasing x: disordered glass state with random directions of PNRs in PMN, comparatively abrupt growth of PNRs at the ferroelectric phase transition without changing the directions of their dipole moments at small x, and order-disorder type ferroelectric transition through alignment of PNRs into single direction via order-disorder mechanism at large x. These results are consistent with broadband dielectric and quasielastic scattering data that show critical slowing down for PMN-xPT with large x.

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I. INTRODUCTION

Relaxor ferroelectrics (RFEs) such as $\mathrm{Pb}(\mathrm{Mg}_{1/3}\mathrm{Nb}_{2/3})\mathrm{O}_3$ (PMN) have been studied intensively during the past decades due to their peculiar dynamic and static characteristics from the viewpoint of fundamental physics, as well as due to their wide applicability in various fields.[1,2] RFEs show a broad dielectric permittivity peak in the temperature window with a strong frequency dispersion. Polar nanometer-sized regions (PNRs) have been considered to play an essential role in the formation of the complex relaxor behaviors.[3] PNRs were first proposed from the study on the optic index of refraction of PMN to appear at the Burns temperature (T_B) which is much larger than the typical dielectric maximum temperature (T_m),[4] and later confirmed by other various experiments.[5] Recently, it was proposed that the dynamic PNRs, which predominantly exist in the disordered matrix, should be differentiated from the static PNRs that reside in the cation-ordered regions in RFEs.[6] Gehring *et al.*[7] furthermore suggested a new $T_B \sim 420$ K at which static PNRs condense, and similar suggestions for additional characteristic temperature have been proposed based on several experiments about the temperature evolution of dynamics of PNRs.[8,9] In spite of all the experimental and theoretical efforts carried out up to date, the exact knowledge of static and dynamic features of PNRs, which is prerequisite to revealing the microscopic origin of the unusual characteristics of RFEs, is far from complete understanding. In this situation, another approach may be to investigate the effect of the addition of ferroelectrically active Ti^{4+} ions to typical relaxors on the dynamics of PNRs and corresponding relaxor properties in more detail.

The addition of PbTiO_3 (PT) to PMN results in an interesting phase diagram of $\mathrm{Pb}[(\mathrm{Mg}_{1/3}\mathrm{Nb}_{2/3})_{1-x}\mathrm{Ti}_x]\mathrm{O}_3$ (PMN-xPT) solid solutions, where the morphotropic phase boundary (MPB) separates the rhombohedral (R) and tetragonal (T) regions at low temperatures.[10] The temperature evolution of dynamic PNRs starting at T_B is manifested in many physical properties, one of which being acoustic properties. Thermally excited sound waves are coupled to PNRs since acoustic waves change the off-centered ionic displacements in PNRs. The longitudinal-acoustic (LA) mode begins to be affected by PNRs near T_B via electrostrictive coupling, and its mode frequency exhibits a marked softening upon further cooling.[11] This softening is normally accompanied by substantial increase in the acoustic damping, as well as the appearance of quasielastic central peak.[12] The Brillouin scattering by which acoustic properties of REFs can be studied has been a help to access the relaxational dynamics of PNRs in the gigahertz range that cannot not be easily approached by conventional experiments. However, in spite of previous Brillouin scattering studies on PMN (Refs. 11, 13, and 14) and PMN-xPT with x close to the compositions of MPB,[15,16] more thorough investigation over the full PT concentrations is necessary to find out clear correlation between acoustic anomalies and the dynamics of PNRs which will be affected by the PT content. This paper reports the systematic comparison and analysis of acoustic anomalies of PMN-xPT single crystals over a wide range of PT concentration up to $x=55\%$. The results of this study indicate a crossover in the mechanism of ferroelectric phase transition of the PMN-xPT system.

II. EXPERIMENT

The PMN-xPT single crystals with $x=0$, 0.15, 0.31, 0.35, and 0.55 were grown by the Bridgman method and cut to obtain (100)-oriented platelets.[17] A diode pumped solid-state laser at the wavelength of 532 nm was used as an excitation light source. A micro-Brillouin scattering system with a (3+3) pass Sandercock tandem Fabry-Perot interferometer was used to measure the Brillouin spectra at a backward-scattering geometry with a free spectral range of 75 GHz. The sample was placed inside a cryostate cell (Linkam, THMS600) and the temperature was changed from 873 to 300 or 100 K with a minimum temperature interval of 1 K. Before the measurement, the sample was annealed at the highest temperature for at least half an hour. In the present backward-scattering geometry, only the LA mode can be probed, of which the phonon propagation direction is parallel to the pseudocubic [100] direction. The results of PMN-55%PT shown in this paper were reported in our previous letter.[18]

III. RESULTS AND DISCUSSION

Figure 1 shows the Brillouin frequency shift ν_B and the full width at half maximum (FWHM), denoted as Γ_B, of the LA mode of PMN and PMN-15%PT. Temperature dependences of ν_B and Γ_B of these two crystals are very typical in RFEs. ν_B changes linearly in the high-temperature range above ~750 K, where normal lattice anharmonicity determines the phonon behaviors. This part was fitted by a linear function, which corresponds to the limiting high-frequency sound velocity and is shown in Fig. 1(a) as solid lines. It will be denoted as ν_∞ of which the fitted temperature dependence is tabulated in Table I. Below T_B, ν_B begins to decrease upon cooling, concurrent with increasing damping indicating shorter lifetime of LA phonons. The minimum of ν_B and the maximum of Γ_B appear at almost the same temperature around 300 K, which is close to the low-frequency dielectric maximum temperature. Figure 2 displays the temperature dependence of ν_B and Γ_B of other three PMN-xPT single crystals with $x=0.31$, 0.35, and 0.55. All ν_B's are linear above ~750 K, are fitted by linear functions, which are shown as solid lines in Fig. 2(a). The best-fitted results are included in Table I. Compared to PMN which remains cubic (C) down to the lowest temperature, these samples exhibit well-defined structural phase transitions from C to T long-range ferroelectric phase, for example, at the temperature $T_c \sim 413$ K in case of PMN-31%PT, where a sharp minimum of ν_B occurs. Additional steplike change in ν_B of PMN-31%PT at around 343 K corresponds to another phase transition to R or monoclinic symmetry.

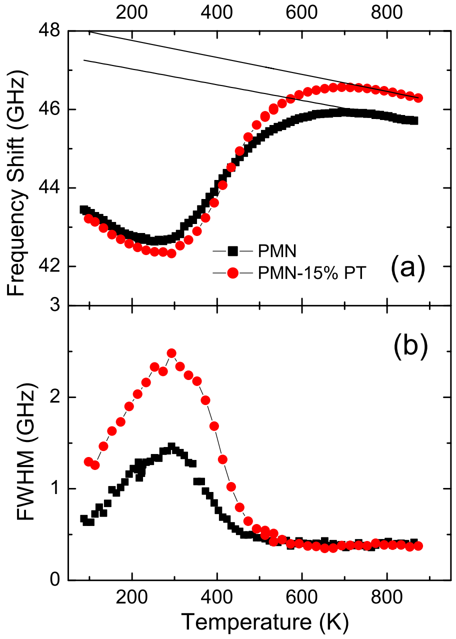

FIG. 1. (Color online) Temperature dependence of (a) the Brillouin shift of the LA mode and (b) the FWHM of the LA mode of PMN and PMN-15%PT. The solid lines denote the limiting high-frequency Brillouin shift.

Figures 1(a) and 2(a) show that softening of LA mode upon cooling (deviation of the Brillouin frequency shift, ν_B, from the high-temperature linear trend) begins at almost the same temperature of ~750 K for all studied compositions x. However, T_B is observed in PMN-PT at 620–650 K, which is about 100 K lower. Similar softening of the LA mode in its temperature dependence was observed recently[19] in normal displacive-type ferroelectrics $BaTiO_3$, where the softening also began at ~750 K (i.e., ~350 K above the Curie point) but the formation of the characteristic relaxor PNRs is not expected. In case of $BaTiO_3$, this anomaly has been attributed to the order-disorder component of the phase transition, more specifically, to the polarization fluctuations related to the hopping of the off-centered Ti ions among eight equivalent ⟨111⟩ directions.[20] Such kinds of the off-centered cations are known to exist in paraelectric phase in many displacive-type perovskite ferroelectrics. In Pb-containing normal ferroelectrics and relaxors the significant permanent off-center displacements are typically observed for Pb cations. In relaxors, their directions are believed to be correlated inside PNRs and random in nonpolar matrix. However, in PMN these displacements exist only below T_B.[21] Furthermore, in PMN-xPT solid solutions with large enough x, the off-centering of Pb cations is absent even at $T < T_B$ as found by x-ray diffraction studies of PMN-40% PT crystals at 603 K.[22] Therefore, the acoustic-mode behavior in PMN-xPT can hardly be related to hopping of the individual (not belonging to PNRs) off-

TABLE I. The limiting high-frequency Brillouin shift, the background acoustic damping, and the best-fitted parameters to Eq. (2) for the PMN-xPT single crystals.

	ν_∞ (GHz)	Γ_∞ (GHz)	E_0/k_B (K)	τ_0 (s)
PMN	$47.43-0.0020\times T$	0.40	2120 ± 160	$(3.9\pm2.0)\times10^{-14}$
PMN-15%PT	$48.19-0.0022\times T$	0.38	2160 ± 100	$(8.6\pm2.8)\times10^{-14}$
PMN-31%PT	$49.41-0.0017\times T$	0.37	3740 ± 120	$(1.0\pm0.3)\times10^{-13}$
PMN-35%PT	$50.43-0.0020\times T$	0.50	5390 ± 150	$(7.5\pm3.1)\times10^{-14}$
PMN-55%PT	$51.48-0.0012\times T$	0.47	5830 ± 130	$(2.0\pm0.7)\times10^{-13}$

centered cations. One possible origin of the acoustic-phonon softening may be related to the displacive-type phase transition, i.e., transverse-optic (TO) mode condensation, in PMN-xPT. The zone-center TO mode in pure PMN and PMN-xPT softens upon cooling when T approaches T_B from above as observed by inelastic neutron scattering[23] and IR experiments.[24] Condensation of TO mode in nanometer-size regions leads to appearance of PNRs below T_B. In other words the formation of the PNR corresponds to local displacive ferroelectric phase transition. Therefore, softening of LA mode from the high-temperature linearity upon cooling below ~750 K may be related to the thermal fluctuations of displacive order parameter. As the paraelectric phase is non-piezoelectric this coupling is quadratic in polarization.[25]

On the other hand, the observed acoustic frequency shift below T_B can be attributed to flipping of dipole moments of PNRs and related electrostrictive coupling (quadratic in polarization, linear in strain) in addition to the mutual interaction between TO phonons and LA phonons. According to the thermodynamic Landau theory[25] electrostrictive coupling gives rise to the change in elastic constant proportional to $\langle P\rangle^2$, where $\langle P\rangle$ is the static value of polarization. If there is no static polarization in the paraelectric phase, elastic constant will not show any change in the thermodynamic limit. In reality, softening is observed in the paraelectric phase due to interactions with thermal fluctuation of order parameter (i.e., dynamic effects) which are beyond the scope of the thermodynamic theory. PNRs in ergodic relaxor phase give rise to the existence of local nonzero polarization inside PNRs. Therefore, with decreasing temperature the electrostrictive acoustic-phonon softening appears and grows because the number of PNRs grows. When the acoustic waves propagate in the sample, they induce additional component of polarization in certain direction due to electrostrictive coupling. Microscopically this happens by means of reorientations (or flipping) of PNR dipole moments, i.e., through relaxation mechanism. Upon further cooling across the freezing temperature, the TO mode hardens as observed by inelastic neutron scattering[26] and by IR experiments,[24] and the fluctuation contribution of this displacive polarization component to the Brillouin shift weakens as a result. The contribution related to the PNRs flipping also weakens because of increase in the relaxation time which becomes much larger than the inverse of the acoustic-phonon frequency. Accordingly, these effects should give rise to hardening of acoustic-mode frequency, which is really observed upon cooling at low temperatures.

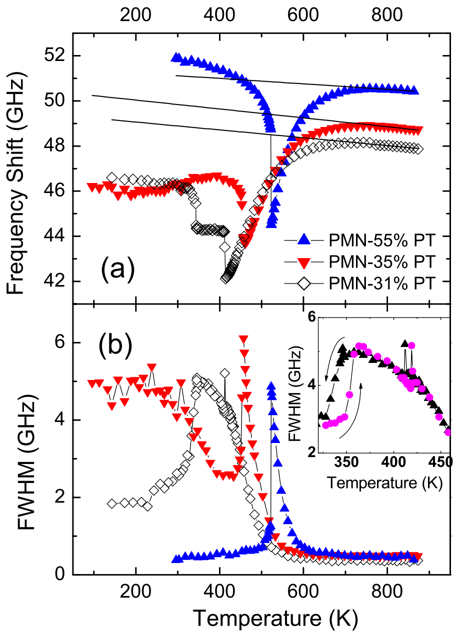

FIG. 2. (Color online) Temperature dependence of (a) the Brillouin shift of the LA mode and (b) the FWHM of the LA mode of PMN-31%PT, PMN-35%PT, and PMN-55%PT. The solid lines denote the limiting high-frequency Brillouin shift. (Inset: the FWHM of PMN-31%PT measured during cooling and subsequent heating processes.)

The dependence of Γ_B on the PT concentration shown in Figs. 1(b) and 2(b) exhibits interesting changes related to the phase transitions. At high temperatures near T_B, both the TO-mode frequency and the flipping frequency of PNRs are much higher than the acoustic-mode frequency. This means that the polarization can follow the acoustic vibrations without any delay and the static regime is valid. This explains why the frequency change near T_B is not accompanied by variation in the hypersonic damping. In contrast to high temperatures, the acoustic behaviors at temperatures lower than T_B are strongly dependent on the PT composition. In the case of PMN-xPT single crystals with x=0, 0.15, and 0.31, Γ_B shows a very broad peak over a wide temperature range, reflecting a strong relaxor nature in these compositions. There is no long-range polar order even at low temperatures in PMN and only the PNRs can be coupled to the LA waves in this sample. The broad damping seen in Fig. 1(b) is thus ascribed to the order-parameter fluctuations due to PNRs.

The observed acoustic behavior of PMN-15%PT is very similar to the behavior of pure PMN even though the ferroelectric phase appears at $T_c \sim 320$ K in PMN-15%PT.[27] In case of PMN-31%PT, the FWHM exhibits a sudden increase at ~413 K superposed on the broadly increasing damping. This temperature is coincident with the minimum of ν_B, which indicates the ferroelectric phase-transition temperature of this system. Therefore, this additional sharp contribution might be related to the growth and merging of PNRs at this temperature. The hysteresis of the sharp peak of Γ_B, which is reproducible and is shown in the inset of Fig. 2(b), indicates the first-order nature of the $C \rightarrow T$ phase transition in PMN-31%PT. It should be noted that the sharp damping component is superposed on the broadly increasing damping upon cooling. These results may indicate that the ferroelectric order formed in PMN-31%PT below T_c is not macroscopic but mesoscopic coexisting with PNRs, as was observed by piezoresponse force microscopy.[28]

As the PT concentration increases beyond that of MPB, PMN-*x*PT exhibits a well-defined phase transition into the tetragonal long-range ferroelectric phase. The transition temperature T_c is characterized by sharp anomalies in the temperature dependence of both ν_B and Γ_B. However, PMN-*x*PT crystals with $x=0.35$ and 0.55 commonly show substantial softening of ν_B as well as significant damping in the high-temperature phase above T_c, which is different from acoustic behaviors of ideal ferroelectrics. Moreover, quasielastic central peaks centered at zero frequency appear in the same temperature range above T_c where substantial change in Γ_B occurs[18] (which will be reported elsewhere). It was reported that there is no strong diffuse scattering due to the static PNRs in PMN-60%PT (Ref. 29) and that purely dynamic PNRs are suggested to be responsible for the acoustic anomalies and central peaks in PMN-55%PT.[18] The acoustic properties of PMN-35%PT and PMN-55%PT share common anomalies, such as the significant softening of the LA mode, rapid increase in the fluctuation damping upon cooling toward T_c concurrent with growth of central peaks. The rapid increase in Γ_B indicates that the LA phonons are scattered more substantially at high PT concentration, which may be attributed to the increase in size of PNRs as well as to the correlation between PNRs due to the enhanced ferroelectric instability. The appearance of the ferroelectric order-disorder component, i.e., the correlated PNRs finally percolates the whole crystal resulting in the ferroelectric long-range order, which is represented by the sharp Landau-Khalatnikov-type damping at T_c.

The relaxation process of dynamic PNRs manifests itself as the acoustic anomalies in the high-temperature ergodic relaxor phase due to the coupling between the LA mode and PNRs through density fluctuations. It was proposed from Brillouin study on $\mathrm{Pb}[(\mathrm{Zn}_{1/3}\mathrm{Nb}_{2/3})_{1-x}\mathrm{Ti}_x]\mathrm{O}_3$ with $x=7\%$ that the relaxation process coupled to LA waves is closely related to the 180° flipping motions of PNRs not inducing any change in local strains.[30] If potential wells responsible for equilibrium positions of PNR are symmetric (as might be expected based on cubic symmetry of ergodic relaxor phase), the 180° reorientations should not give rise to any coupling because they do not lead to any change in strain. However, due to large static (quenched) chemical disorder, local and global symmetries are different and potential wells can be different from symmetric ones.[2] In this case the 180° reorientations cause change in strain and coupling to acoustic waves can appear. This coupling is expected to be smaller than at non-180° reorientations because the related change in strain is smaller. Based on an assumption of a single-relaxation process coupled to the LA mode, the temperature dependence of the relaxation time of this process, τ_{LA}, can be calculated by using the following equation:[30]

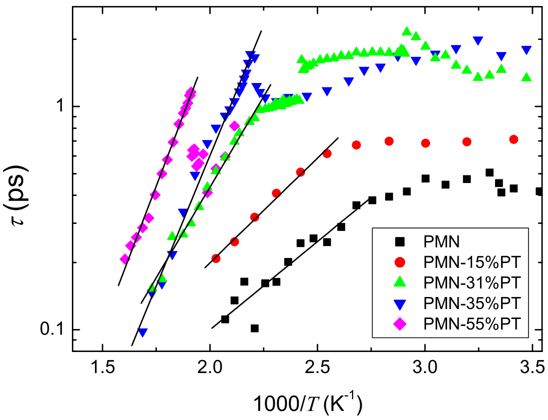

FIG. 3. (Color online) The relaxation time estimated by using Eq. (1) for all PMN-*x*PT single crystals. The solid lines denote the fitted results by using Eq. (2).

$$\tau_{\mathrm{LA}} = \frac{\Gamma_B - \Gamma_\infty}{2\pi[\nu_\infty^2 - \nu_B^2]}. \tag{1}$$

In this equation, Γ_∞ is the background damping and is estimated to be the average FWHM of the flat region at high temperatures in Figs. 1(b) and 2(b). The obtained relaxation times are shown in the Arrhenius plot in Fig. 3. The relaxation times shown in this figure are on the order of picosecond. In the high-temperature phase above T_c or T_m τ_{LA} increases upon cooling reflecting the slowing down process of the dynamic PNRs. The onset of the relaxation process is located at higher temperature as the PT concentration increases. The high-temperature part of τ_{LA} above T_c or T_m exhibits a linear behavior suggesting thermal activation process of PNRs between equivalent polarization states. However, the application of the simple Arrhenius law of $\tau_{\mathrm{LA}} = \tau_0 \exp(E/k_B T)$, where τ_0 and k_B are the attempted relaxation time and the Boltzmann constant, respectively, results in unphysical values for τ_0. For example, the high-temperature τ_{LA} data of PMN-35%PT may be fitted by the Arrhenius law, which gives $\tau_0 = 1.3 \times 10^{-17}$ s. This indicates that the assumption of the temperature-independent activation energy is not suitable for describing the dynamics of PNRs since their size will grow upon cooling and affect the activation barrier.

In this respect, it is more appropriate to consider temperature-dependent activation energy in the Arrhenius law, which was indeed included in the modified superparaelectric model.[15] According to this model, the activation energy E is considered to change as $E_0(T_B - T)/T_B$, where E_0

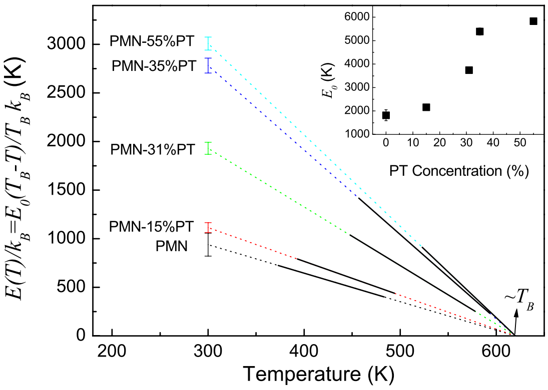

FIG. 4. (Color online) The temperature dependence of the activation barrier E estimated by using Eq. (2) for all PMN-xPT single crystals. (Inset: the dependence of E_0 on the PT concentration.)

is the energy barrier extrapolated to 0 K. The relaxation time τ_{LA} can thus be restated as follows:

$$\tau_{\mathrm{LA}} = \tau_0 \exp\left[\frac{E_0}{k_B}\left(\frac{1}{T} - \frac{1}{T_B}\right)\right]. \tag{2}$$

This formula suggests that the activation barrier separating different polarization states of PNRs is proportional to the volume of PNRs which grows upon cooling. The high-temperature linear part of τ_{LA} in Fig. 3 was fitted using this equation, and the fitting results are shown as solid lines in the same figure. T_B was fixed to 620 K, the well-known Burns temperature of PMN. It was suggested that the addition of PT does not have substantial effect on T_B.[31] For example, T_B of PMN-55%PT was estimated to be about 610 K,[17] very similar to that of PMN. It should be pointed out that the choice of T_B for the fitting procedure does not affect the activation barrier while it changes τ_0 slightly. The best-fitted parameters are tabulated in Table I. The attempted frequencies $\nu_0(=1/2\pi\tau_0)$ are in the range of $10^{11}-10^{13}$ Hz for all examined samples, which are the order of typical Debye frequencies and justify the fitting procedure based on the modified superparaelectric model. The temperature-dependent activation energy is shown in Fig. 4 for each composition. The dotted lines depict the extrapolated data while the solid lines correspond to the activation energy in those temperature ranges where the fitting procedure was applied to the measured data. The inset of Fig. 4 exhibits the dependence of E_0 on the PT concentration.

As can be seen from Fig. 4, the activation barrier for the flipping of PNRs changes with PT concentrations. It is worth pointing out that the activation barrier for the relevant relaxation process is similar when PMN-xPT crystals are located on either the R side or the T side of the phase diagram. For example, there is no difference in E_0, which determines the slope of $E(T)$ in the temperature window, between PMN-15%PT and PMN within the experimental uncertainty. The difference in E is only ~7% between PMN-55%PT and PMN-35%PT. However, it changes drastically at the PT composition near MPB as can be seen from the steplike change in E_0 at $x \sim 0.31$ described in the inset of Fig. 4.

An assumption of a single-relaxation process is a reasonable approximation for high temperatures because dielectric data show that distribution of relaxation times is narrow at high temperatures.[32] This is because the concentration of PNRs and interactions between them are small. The superparaelectric model (which implies the absence of interactions among relaxation dipoles) works well in this temperature range with the modification which takes into account the growth of PNRs size and consequently the activation energy upon cooling. Below about 370 K the interactions between PNRs become important and superparaelectric model is not able to describe the relaxation. It is known that in pure PMN the interactions are frustrated and lead to formation of glassy state at low temperatures.[1] Due to these interactions the relaxation spectrum broadens on cooling dramatically and the characteristic (mean) dielectric relaxation time follows the Vogel-Fulcher (VF) law as confirmed by dielectric experiments.[32,33] Different model instead of superparaelectric model is needed to describe the behavior in this case, e.g., spherical random-bond-random-field model.[34] The most part of the spectrum at low temperatures is in the low-frequency limit where PNR reorientations are too slow to follow acoustic vibrations and cannot contribute to acoustic-mode softening. The main contribution to the measured hypersonic damping at low temperatures comes from the high-frequency part of the relaxation spectrum. Breathing mode of PNRs instead of flipping mode may be the major part of this high-frequency component coupled to the acoustic waves.[32,35]

Note that in the VF law typically expressed as $\tau = \tau_0 \exp[E_a/(T-T_0)]$ the parameter E_a has the meaning of activation energy of PNR flipping in assumption that frustrated interactions between them are negligible while the parameter T_0 describes the effect of interactions leading to glassy freezing at T_0. The value of the VF parameter $E_a \sim 800$ K extracted from analysis of dielectric data in PMN at around 300 K (Refs. 32 and 33) is in a good agreement with the extrapolation to this temperature range of the modified superparaelectric model trend as can be seen from Fig. 4. The pre-exponential factor (reciprocal attempt frequency), τ_0, extracted at different temperature ranges from VF law and from Brillouin data are also practically the same (2.8×10^{-14} s and $3.9 \pm 2.0 \times 10^{-14}$ s, respectively).[32] This confirms the applicability of the modified superparaelectric model for description of PNRs in high-temperature range of ergodic relaxor phase in PMN. The observed acoustic behavior of PMN-15%PT is very similar to the behavior of pure PMN in spite of the fact that in the latter case the ferroelectric phase appears at $T_c \sim 320$ K.[27] This suggests that in the ergodic relaxor phase the same evolution of PNRs occurs upon cooling in both cases, namely, from noninteracting PNR (described by superparaelectric model) to PNRs with frustrated interactions. The ferroelectric phase transition in PMN-15%PT is the kinetic effect corresponding to sudden growth or PNR size at T_c so that PNRs transform into mesoscopic/macroscopic ferroelectric domains.[27] Growth and merging of PNRs can be considered as percolation transition and can probably be responsible for small sudden peak of damping at T_c in PMN-31%PT.

The jump in the composition dependence of E_0 observed at $x \sim 0.3$ near MPB may signify the change in relaxation mechanism related to the fact that at high x the ergodic relaxor phase transforms upon cooling to ferroelectric phase via the sharp phase transition while in pure PMN the freezing into glassy (nonergodic relaxor) phase is observed instead of ferroelectric transition. In crystals with small x the ferroelectric transition is diffused and found only in the outer layer (50 μm thick) of the crystal.[27,36] Apparently, the rapid increase in the activation barrier at high x is attributable to the fast growth of PNRs since the activation barrier is assumed to be proportional to the volume of PNRs in this model. However, ferroelectric interactions among PNRs may appear below T_B due to increased ferroelectric instability at high PT composition so that the superparaelectric model (which implies negligible interactions) is not suitable for large-x crystals. The remarkable change in the activation energy at MPB can thus be due to crossover from frustrated interactions between PNRs (resulting in glassy phase with randomly directed PNPs) to ferroelectric interactions between PNRs giving rise to the long-range ferroelectric phase where dipole moments of all PNRs are aligned along the same direction. Therefore, at large x the new order parameter seems to appear, namely, polarization component related to the order-disorder type ferroelectric transition where PNRs serve as ordering units. Significant contribution to acoustic-mode softening and damping at $T > T_c$ can appear because of electrostrictive coupling of acoustic mode to the polarization fluctuations of this new order-disorder type ferroelectric order parameter. Formal application of the superparaelectric model to PMN-xPT gives dramatically increased values of E_0 as shown in Fig. 4.

We consider, therefore, coexistence of two microscopically different ferroelectric order parameters in PMN-xPT with large x, namely, displacive one which is related to mutual displacement of cations and anions and is nonzero inside PNRs, and order-disorder component which is related to ordering of PNRs and is nonzero inside the correlated precursor clusters including several PNRs. Accordingly, two different damping contributions are expected, one from flipping of PNRs inside precursor cluster and the other one from coherent ion displacements inside these PNRs. The appearance of order-disorder type order parameter at high x may induce changes in the dynamics of PNRs since correlation between PNRs is expected to result in the formation of precursor polar clusters. Order-disorder nature of ferroelectric phase transition often presents itself via critical slowing down of the relevant relaxation process. This was indeed observed in both dielectric and Brillouin measurements of PMN-xPT at high x. For example, Bovtun *et al.*[35] carried out broadband dielectric investigation on PMN-35%PT and found that the temperature dependence of the high-temperature relaxation frequency could be explained by using combination of critical slowing down and VF law. In addition, the temperature dependence of the relaxation time derived from the quasielastic central peaks was found to follow the critical slowing down in PMN-55%PT.[18] On the other hand, the temperature dependence of the relaxation time derived from the quasielastic central peak of ferroelectric relaxors such as potassium lithium niobate is usually deviated from the critical slowing down behavior.[37] These results strongly suggest PNRs are correlated and aligned into single directions in polar clusters at high temperatures and order-disorder type phase transition is realized in high-x PMN-PT.

IV. CONCLUSION

In this study, the LA modes of PMN-xPT single crystals with $x=0-0.55$ were investigated over a wide temperature range including T_B, T_c, or T_m. The acoustic-mode frequency showed a linear behavior above ~750 K and then a substantial softening upon cooling in all examined PMN-xPT. The onset of softening was explained based on possible coupling between the soft TO mode and the LA mode. The softening became more remarkable concomitant with the increase in the hypersonic damping on approaching T_c or T_m, which was attributed to the interaction between the acoustic waves and the relaxational dynamics of independently flipping PNRs and correlated PNRs for low-x and high-x PMN-xPT's, respectively. The characteristic relaxation time of the relaxation process related to this coupling was obtained, which increased rapidly upon cooling in the high-temperature phase. The activation energy for the flipping of PNRs obtained from the application of the modified superparaelectric model to the Brillouin data exhibited a sharp increase when x crosses the MPB concentration. These results suggest a crossover in the mechanism of ferroelectric phase transition with increasing x. The ferroelectric phase transition of PMN is frustrated due to random interactions and quenched random fields and induces broad acoustic anomaly in a wide temperature range. In PMN-xPT on the R side, the ferroelectric phase transition may be realized due to comparatively abrupt growth of PNRs at T_c without any change in the directions of their dipole moments that may be responsible for sharp acoustic damping as was observed from PMN-31%PT. At large x the ferroelectric transition takes place through alignment of PNRs dipole moment into single direction via order-disorder mechanism, resulting in the critical slowing down behaviors of PMN-35%PT and PMN-55%PT probed by dielectric and Brillouin experiments, respectively.

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