Connecting the Multiscale Structure with Macroscopic Response of Relaxor Ferroelectrics

Mojca Otoničar, Andreaž Bradeško, Lovro Fulanović, Tomaz Kos, Hana Uršič, Andreja Benčan, Matthew J. Cabral, Alexandra Henriques, Jacob L. Jones, Lukas Riemer, Dragan Damjanovic, Goran Dražič, Barbara Malič, and Tadej Rojac

Lead-based relaxor ferroelectrics are characterized by outstanding piezoelectric and dielectric properties, making them useful in a wide range of applications. Despite the numerous models proposed to describe the relation between their nanoscale polar structure and the large properties, the multiple contributions to these properties are not yet revealed. Here, by combining atomistic and mesoscopic-scale structural analyses with macroscopic piezoelectric and dielectric measurements across the \((100-x)\text{Pb(Mg}_{1/3}\text{Nb}_{2/3})\text{O}_{3}\text{–xPbTiO}_{3}\text{ (PMN–xPT) phase diagram, a direct link is established between the multiscale structure and the large nonlinear macroscopic response observed in the monoclinic PMN-xPT compositions. The approach reveals a previously unrecognized softening effect, which is common to Pb-based relaxor ferroelectrics and arises from the displacements of low-angle nanodomain walls, facilitated by the nanoscale polar character and lattice strain disorder. This comprehensive comparative study points to the multiple, distinct mechanisms that are responsible for the large piezoelectric response in relaxor ferroelectrics.}

1. Introduction

Lead-based relaxor ferroelectric perovskites, exemplified by the \((100-x)\text{Pb(Mg}_{1/3}\text{Nb}_{2/3})\text{O}_{3}\text{–xPbTiO}_{3}\text{ (PMN–xPT) phase diagram, a direct link is established between the multiscale structure and the large nonlinear macroscopic response observed in the monoclinic PMN-xPT compositions. The approach reveals a previously unrecognized softening effect, which is common to Pb-based relaxor ferroelectrics and arises from the displacements of low-angle nanodomain walls, facilitated by the nanoscale polar character and lattice strain disorder. This comprehensive comparative study points to the multiple, distinct mechanisms that are responsible for the large piezoelectric response in relaxor ferroelectrics.}

Despite a large number of detailed structure–property investigations, alongside highly insightful theoretical studies, an experimental and comprehensive insight into the composition-dependent picture of the multiscale structure of relaxor ferroelectrics and its link to the complex electromechanical response of this class of materials is still lacking.

The prime characteristic of lead-based relaxor ferroelectrics are the nanosized polar entities (most often referred to as the polar nanoregions and polar nanodomain walls) of heterovalent B-site cations (Mg\(^{2+}\), Nb\(^{5+}\), and Ti\(^{4+}\) in PMN–xPT), combined with stereoechemically active lone-pair electrons of Pb\(^{2+}\) ions that hybridize with oxygen. This nanoscale polar structure is believed to strongly contribute to the large dielectric permittivity of relaxor-based materials and is responsible for the characteristic dielectric relaxation. While a number of models have been proposed to explain the structure and role of the nanosized polar entities in the relaxor dielectric signatures, it has recently been suggested, based on phase-field modeling and molecular dynamics simulations, that they also play a key role in the ultrahigh piezoelectricity of PMN–xPT and similar relaxor ferroelectric materials. The recent model by Li et al. for example, assumes a field-induced rotation of the PNRs inside long-range-ordered ferroelectric domains, which assists the rotation of the ferroelectric
polarization. On the other hand, the model by Takenaka et al. predicts a high density of low-angle domain walls in a PND or slush-like polar structure, arising from anisotropically coupled dipoles, ultimately contributing to a greater flexibility for polarization rotation and thus large properties. Coupling between PNRs and ferroelectric polarization was experimentally observed by X-ray and neutron scattering experiments, and the role of PNRs on the large piezoelectricity of relaxor ferroelectrics has also been discussed. Polarization rotation, which was identified as the main mechanism responsible for the property enhancement in relaxor ferroelectrics, was directly evidenced during field application by in situ pair distribution function analysis on PMN–PT.

While the described models explain the effects of PNR dynamics or the presence of high density low-angle domain walls on the lattice response under external fields in terms of the polarization rotation mechanism, it is not clear how this nanoscale structure in relaxor-based materials affects the motion of domain walls and thus the macroscopic piezoelectric response, and whether it can relate to high properties of compositions at different parts of the phase diagram. This is particularly important for the high performance polycrystalline relaxor ferroelectrics where, unlike in domain-engineered single crystals, the nonlinear and hysteretic domain-wall contributions may dominate the total piezoelectric response. In domain engineered single crystals, on the other hand, the best properties are observed in AC-poled crystals where the domain-wall motion does occur during poling even if its contribution is not as obvious as in ceramics.

In this work we present a broad picture of the multi-scale structure of relaxor ferroelectrics, and relate it to the piezoelectric and dielectric nonlinear response by studying polycrystalline PMN–xPT over a wide compositional range, spanning from the relaxor PMN end member (x = 0) to the ferroelectric tetragonal phase region (x = 40). By nonlinear macroscopic measurements we identify three distinct regions in the dynamic electromechanical and dielectric response, which we associate with specific atomic- and mesoscale-structure structures of the PMN–xPT solid solutions. In contrast to the nonlinear response of the morphotropic phase boundary (MPB) and tetragonal PMN–xPT compositions (i.e., x ≥ 35) where polarization rotation dominates, the results reveal additional large hysteretic and anhysteretic nonlinear contributions to the response in a wide range of compositions with monoclinic symmetry (20 ≤ x ≤ 33.5), which are characterized by a complex nanodomain structure and relaxor behavior. Based on the detailed compositional comparison of the atomic and nanoscale structures, we show that this additional nonlinear response in the monoclinic compositions, ascribed to a hitherto unreported softening effect, is related to the nanoscale polar entities and to the A-sublattice strain disorder, which makes the nanodomain walls exceedingly mobile. We thus present here a comprehensive structure–property investigation that enables us to experimentally demonstrate a new softening effect, which originates in the displacement of nanodomain walls, boosting the piezoelectric response of relaxor ferroelectrics. This effect contrasts the widely considered polarization rotation mechanism that dominates the piezoelectric response of PMN–xPT compositions close to the MPB with the tetragonal phase.

2. Results and Discussion

2.1. Relaxor Character, Domain Structure, and Atomic-Scale Structure of PMN–xPT

We begin by presenting in Figure 1 the phase composition, the relaxor character, and the domain structure of the analyzed PMN–xPT compositions. Figure 1a shows the phase diagram of the PMN–xPT solid solution system derived from X-ray powder diffraction (XRD) analysis and temperature-dependent permittivity measurements of the PMN–xPT samples (Section S1, Supporting Information) possessing comparable (3–5 μm) average grain sizes (Section S2, Supporting Information). The phase diagram agrees well with the one proposed by Singh et al. The distortion of the perovskite lattice of PMN progressively increases with the increasing PT content, evolving from pseudocubic (Pc) to monoclinic (M) M<sub>B</sub> symmetry (rhombohedral-like M distortion), then to M<sub>C</sub> (tetragonal (T)-like M distortion) and finally to the T phase (P4mm space group) (Figure 1a: Section S1, Supporting Information). M<sub>B</sub> and M<sub>C</sub> notations correspond to the Cm and Pm space groups, respectively (after Vanderbilt and Cohen). Figure 1b illustrates the relaxor character of the samples by plotting the frequency dispersion of the permittivity maximum, defined as ΔT<sub>xmax</sub> = T<sub>xmax</sub> @ 100 kHz – T<sub>xmax</sub> @ 1 kHz, as a function of composition, where T<sub>xmax</sub> @ 100 kHz and T<sub>xmax</sub> @ 1 kHz correspond to the temperature of the permittivity maximum measured at 100 and 1 kHz, respectively. The compositional region in the PMN–xPT phase diagram exhibiting a dispersive permittivity maximum (indicated by orange color in Figure 1a,b) is commonly linked to the presence of nanosized polar entities and short-range ordering, giving rise to the relaxor behavior, as supported by previous diffuse scattering analyses. From the highest frequency dispersion measured in the canonical PMN relaxor (ΔT<sub>xmax</sub> = 10 °C), the dispersion tends to approach zero as the PT content is increased to x = 33.5 and beyond. The trend of the decreasing ΔT<sub>xmax</sub> with increasing PT content reflects the well-known gradual weakening of the relaxor character and the emergence of the long-range ferroelectric order when approaching the T phase.

Next, we investigate the compositional relaxor-to-ferroelectric evolution of pristine samples from the domain structure perspective. Figure 1c–e presents the micro- and nanoscale domain structures of compositions representative of the M (30PT), MPB (35PT), and T (40PT) phase regions. The monoclinic 30PT composition is characterized by a hierarchical arrangement of differently oriented sets of 5–10 nm wide striation-like nanodomains, generally extending along (111) (see Section S3, Supporting Information), separated by irregular wedge-shaped microscale domains (Figure 1c). In the morphotrophic 35PT composition, the hierarchical domain arrangement still persists, however, the nanodomains are embedded in straighter and more regular microscale lamellar domains of up to 300 nm in width (Figure 1d). Finally, in tetragonal 40PT the domain hierarchy is no longer present and the domain structure consists of straight lamellar domains of up to 400 nm in width (Figure 1e). Full transmission electron microscopy (TEM) analysis of the PMN–xPT compositional series, reported in Section S3 of the Supporting Information,
Further confirms the domain-structure development from hierarchical nanodomain arrangement in $20 \leq x \leq 32$, to nanodomains merging at $x = 33.5$ and formation of straight lamellar domains with embedded nanodomains at $x = 35$ (i.e., at the onset of T symmetry), up to the disappearance of the hierarchical domains at $x > 37$. The observed domain-structure evolution with the increasing PT content is consistent with recent theoretical predictions, experimental diffuse scattering measurements in PMN–PT, and previously reported domain evolution in PMN–PT ceramics and single crystals. The presented domain-structure evolution already suggests that the high piezoelectric response present in PMN–xPT over a wide range of compositions cannot have a unique origin (such as polarization rotation alone).

We further note that despite the domain-structure analysis performed on unpoled samples, in the case of the monoclinic 30PT composition we observe qualitatively the same nanoscale features before and after poling, i.e., the nanodomains are also present after poling, but their orientation is changed depending on the direction of the applied external field (see ref. [36]). In the case of the MPB 35PT composition, on the other hand, the microscale lamellar domains become thinner with an applied field and settle in their preferred orientation, partially eliminating the hierarchically arranged nanodomains and likely making the accumulated domain walls of high density harder to move after initial poling, as compared to the monoclinic compositions. As shown later, these observations are consistent with the nonlinear piezoelectric analysis.

From a comparison of the presented results, it becomes clear that the drastic drop of $\Delta T_{\text{max}}$ at $x = 33.5$ (see Figure 1b) coincides with the striation-like nanodomains starting to merge and pattern into more regular lamellar-like domains (Section S3, Supporting Information). Following this observation, it is also evident that the absence of the relaxor character ($\Delta T_{\text{max}} \approx 0$) at $x > 35$ is related to the emergence of the T phase and the disappearance of the hierarchical domain structure. The provided analyses thus confirm an intimate relationship between the average symmetry, relaxor behavior, and the domain structure in PMN–xPT.

We next present in Figure 2 the analysis of the three representative compositions at the atomic scale by high-angle annular dark field imaging with scanning transmission electron microscopy (HAADF-STEM; original HAADF images are shown in Section S4, Supporting Information). Motivated by theoretical studies, which predict a strong effect of localized Pb displacements from their average position, as well as the
influence of Ti-concentration in PMN–xPT on both the correlated B-site and localized Pb displacements, we base our analysis on the B-atom off-center displacements within its Pb-cage (Figure 2a–c) and on the A-sublattice distortions arising from the Pb positional disorder (Figure 2d–f).

As shown in Figure 2a, the 30PT M composition is characterized by small B-atom displacements (represented by the arrows) with island-like patches of a few-unit-cell semiuniform displacements of up to ≈20 pm in magnitude (darker yellow regions). In between these patches the displacements are smaller than ≈14 pm and appear as uncorrelated, randomly pointing in all directions (see the polar plot underneath Figure 2a), which illustrates an average picture of the displacements. By contrast, the morphotropic 35PT shows much larger and more correlated B-atom displacements of ≈30 pm on average, displaced roughly along [011] direction, but slightly tilted toward [001] (which in the (100) projection corresponds to the distortion of an M cell away from [111] and toward [001]—see arrow in the polar plot underneath Figure 2b; all indexing is given in pseudocubic perovskite setting). Homogeneous areas of stronger distortions are connected into patches that extend along [01-1], i.e., perpendicular to the direction of the displacements (dark red areas in Figure 2b). These regions likely correspond to the striped nanodomains within microscale lamellar domains, as observed in Figure 1d. Finally, Figure 2c shows the tetragonal 40PT composition with the strongest, up to ≈60 pm B-atom displacements and the largest regions of uniform displacements. The average B-atom displacements along [001] direction coincide with the expected T distortion (see polar plot underneath Figure 2c), and the regions of larger displacements

Figure 2. Atomic-position analysis from HAADF-STEM for 30PT, 35PT, and 40PT compositions, marked by red circles on the PMN–PT phase diagram in Figure 1. a–c) B-atom displacements from the center of four neighboring A-atoms of the perovskite unit cell (see schematics on the left). Arrows and colors represent the direction of displacements and their magnitude, respectively. Below the B-atom displacement maps are the corresponding polar plots with arrows indicating the average displacement direction, while the circle in 30PT plot illustrates uncorrelated displacements (centrosymmetric on average). d–f) A-sublattice positional disorder maps for 30PT, 35PT, and 40PT, represented by the distortion angle $\Phi_{\text{Pb}}$ marking the positional deviation of each next Pb atom away from the equatorial line of its neighboring Pb atom (see schematics on the left-hand side); below the maps are normal distribution curves of $\Phi_{\text{Pb}}$ with the mean distortion-angle values and standard deviations; circles in (d) indicate larger $\Phi_{\text{Pb}}$ distortions in the 30PT, while arrows in the distribution curves below panel (e) and (f) are drawn to contrast the width of the distribution peaks in 30PT and 35PT.
with similar orientation extend along [011] (see extension of the reddish areas in Figure 2c), as expected for T domain walls. The yellow intermediate region with nearly no displacements, also extending along [011], is suggested to correspond to a 90° T domain (with the T distortion oriented normal to the imaging plane; see polar plot in Figure 2c showing strongly dispersed points from a combination of in-plane and out-of-plane polarization due to the scanned area crossing adjacent domains). We also note that the strongest displacements in the 40PT composition (up to 60 pm) suggest largest c/a ratio of the unit cell (see also the largest 002/200 peak splitting in the XRD pattern of the Section S1, Supporting Information), and thus strongest intrinsic polarization in this PT-rich composition.

Figure 2d–f shows the positional disorder of the Pb atoms, derived from the same HAADF images as those used for analysis in Figure 2a–c, and determined by the distortion angle $\Phi_{\text{Pb}}$, which is defined as the angle of displacement of each next Pb atom from the equatorial plane of the previous Pb in the horizontal direction (see schematics on the left-hand side and detailed description in the Experimental Section). This lattice distortion reflects the localized nature of Pb off-center displacements, believed to play the key role in the nanoscale polar structure and the relaxor nature of PMN.$^{[3,4,8,13,33,38]}$ We note that imaging was performed at room temperature, thus below the corresponding maximum in the permittivity and freezing temperature $T_f$ of the samples (see $T_f$ values in Section S1, Supporting Information), meaning that the off-center atom displacements are temporally and spatially frozen.$^{[13,38]}$ making the visualization of the associated average Pb-sublattice positional disorder on the atomic scale possible. This disorder is observed in all the representative compositions (see colored contour maps in Figure 2d–f); however, the average distortion angle and its lateral fluctuation are clearly larger in the M composition ($\overline{\Phi_{\text{Pb}}} = 0.96° \pm 0.73°$), as compared to the MPB ($\overline{\Phi_{\text{Pb}}} = 0.67° \pm 0.50°$) and the T composition ($\overline{\Phi_{\text{Pb}}} = 0.68° \pm 0.54°$). Furthermore, the largest local Pb distortions with highest $\Phi_{\text{Pb}}$ angles are observed in the 30PT M composition (red-circled spots in Figure 2d); see also the broader proximities of zero field amplitude, confirming that the hysteresis is indeed field-induced. In ferroelectrics, this behavior is commonly attributed to the contribution from irreversible displacements of non-180° domain walls$^{[27,40–42]}$ or other types of dynamic interfaces$^{[43]}$ (see Section S5, Supporting Information). Close inspection of the data reveals a transition in the nonlinear behavior between $x = 33.5$ and $x = 32$ (arrow in Figure 3a).

For compositions $x \geq 33.5$, the $d_{33}'$ versus field curves show a slightly descending (sublinear) trend, while for $x < 33.5$ these curves change to a strongly ascending (superlinear) trend. This transition is accompanied by an anomalous increase in the field dependence of $\tan \delta_{\text{P}}$, occurring at the same compositional point (see arrow in Figure 3b). The same two nonlinear regimes, observed in the piezoelectric coefficient (Figure 3a), along with the anomaly in the phase angle (Figure 3b), were also identified in the field-dependent permittivity response (see Figure S7 in Section S6, Supporting Information), and are additionally highlighted in the schematic in Figure 3c. We note that the crossover between the two regimes coincides with the ferroelectric ordering. The atomic analysis provided here experimentally confirms these theoretical predictions and illustrates the compositionally induced relaxor-to-ferroelectric crossover in PMN–xPT at the atomic level.

The observed stronger Pb-positional disorder (Figure 2d), which is believed to be the source of the relaxor nature of the M phases of PMN–xPT (Figure 1b), further influences the diffraction contrast in TEM, enabling visualization of the nanodomains (Figure 1c). These nanodomains were previously defined as an assembly of low-angle and low-energy domain walls$^{[7,39]}$ and were predicted to arise from nanoscale variations in polar displacements with weak correlations across the nanodomains. Therefore, we suggest that the observed local Pb distortions, characteristic for the relaxor ferroelectric PMN–xPT compositions, strongly influence the domain-wall mobility and thus the piezoelectric and dielectric response of these compositions.

### 2.2. Field-Dependent Piezoelectric and Dielectric Response

To confirm our hypothesis of the influence of local Pb distortions on the domain-wall mobility, we analyzed the converse piezoelectric response of the PMN–xPT compositional series ($20 \leq x \leq 40$) as a function of electric-field amplitude. It is assumed that the weak-field dynamic nonlinearity and the phase lag in the response are sensitive to the interaction of the domain walls with the identified atomic and nanoscale structural characteristics of the relaxor-ferroelectric (M) compositions. A common approach to represent the response is to use the complex longitudinal piezoelectric coefficients, i.e., the real $d_{33}'$ coefficient along with the tangent of the piezoelectric phase angle $\tan \delta_{\text{P}}$, defined as the ratio between the imaginary $d_{33}''$ and real $d_{33}'$ coefficient ($\tan \delta_{\text{P}} = d_{33}''/d_{33}'$.$^{[40]}$

Figure 3a presents the field-dependent $d_{33}'$ data, from which we assess the nonlinearity (i.e., field-dependence of $d_{33}'$), while Figure 3b shows the field-dependent $\tan \delta_{\text{P}}$ correlated to the piezoelectric hysteresis. All the compositions exhibit increasing $d_{33}'$ and $\tan \delta_{\text{P}}$ values as a function of the field amplitude. In addition, $\tan \delta_{\text{P}}$ of all compositions approaches zero in the proximity of zero field amplitude, confirming that the hysteresis is indeed field-induced.
compositional point (i.e., 33.5PT) where $\Delta T_{\text{trans}}$ drops to almost zero (Figure 1b), providing a direct link between the superlinear field dependence and the relaxor nature of the PMN–$x$PT compositions ($x < 33.5$).

In the next step we quantify the data shown in Figure 3a by determining the reversible ($d_{33}^\text{init}$) and irreversible ($\alpha^*$) coefficients following the Rayleigh law approach [41] (all the details on the Rayleigh formalism are provided in Section S5, Supporting Information)

$$d_{33}'(E_0) = d_{33}^\text{init} + \alpha^* \cdot E_0$$

where $d_{33}'(E_0)$ is the total, field-dependent longitudinal piezoelectric coefficient (data shown in Figure 3a), and $E_0$ is the field amplitude. The two coefficients extracted from the analysis, $d_{33}^\text{init}$ and $\alpha^*$, represent the zero-field intercept and the field-dependent slope of the $d_{33}'-E_0$ curves, respectively. In order to compare the PMN–$x$PT compositions exhibiting different coercive fields (Section S7, Supporting Information), the irreversible $\alpha^*$ coefficient is calculated for the electric field corresponding to 30% of the coercive field ($E/E_C = 0.3$). The differently colored regions in the two graphs mark the monoclinic (M$_B$ – red, M$_C$ – blue) and tetragonal (T – green) phase regions. A steep and correlated increase of $\alpha^*$ and $\tan \delta_p$ is observed when entering the monoclinic M$_B$ region as indicated with red curved arrows in (d) and (e). Insets of panel (e) show the piezoelectric loops measured with increasing field amplitude of two representative compositions, M and MPB.

Figure 3. Field-dependent converse piezoelectric response of PMN–$x$PT. a) Piezoelectric $d_{33}'$ coefficient and b) piezoelectric phase angle ($\tan \delta_p$) as a function of electric-field amplitude for PMN–$x$PT with $20 \leq x \leq 40$. c) Schematic of the sub- and superlinear field dependence of the piezoelectric and dielectric coefficients observed in monoclinic (red curve) and near tetragonal (black curve) compositions (see Section S6 of the Supporting Information for dielectric data). The transition between these two nonlinear regimes (between 33.5PT and 32PT; see arrow in (a)) is accompanied by an anomaly in the field dependent $\tan \delta_p$ (arrow in (b)). Bottom graphs show the analysis of hysteresis and deconvoluted reversible and irreversible coefficients of the converse piezoelectric response of PMN–$x$PT: d) reversible ($d_{33}^\text{init}$) and irreversible ($\alpha^*$) coefficients and e) $\tan \delta_p$ as a function of the PT content. $\alpha^*$ and $\tan \delta_p$ are shown for fields corresponding to 30% of the coercive field ($E/E_C = 0.3$). The differently colored regions in the two graphs mark the monoclinic (M$_B$ – red, M$_C$ – blue) and tetragonal (T – green) phase regions. A steep and correlated increase of $\alpha^*$ and $\tan \delta_p$ is observed when entering the monoclinic M$_B$ region as indicated with red curved arrows in (d) and (e). Insets of panel (e) show the piezoelectric loops measured with increasing field amplitude of two representative compositions, M and MPB.
The evolution of representative MB and MPB samples shown in the hysteresis (also illustrated by the different piezoelectric hysteresis characterized by an enhancement of both nonlinearity and hysteresis of $P_{33}$) under similar driving conditions (in the range of magnitude higher than that reported for morphotropic “soft” Pb(Zr,Ti)O$_3$ (PZT) compositions, dependent on a particular combination of $P^*$ and $P'$ types of responses, derived from the corresponding signs of $P^*$ and $P'$ along with the third-harmonic phase angle $\delta$ (Figure 4c), which is defined as $\tan \delta = \frac{P''_3}{P'_3}$. Based on these measurements among the PMN–xPT compositional series and with reference to the expected third-harmonic response from the Rayleigh model (see Section S5, Supporting Information), we can identify three qualitatively different nonlinear responses, which are color-coded in Figure 4 and denoted as relaxor – RE (gray), relaxor ferroelectric – RE-FE (red), and ferroelectric – FE (blue).

Consistent with the compositional evolution in the nonlinearity ($\alpha^*$), a similar trend with PT content is revealed in $\tan \delta$ (see red arrow in Figure 3e), with large phase angle values (up to $\tan \delta = 0.31$) confined to the MB phase region. The analysis therefore suggests that the piezoelectric response in the MB phases is characterized by an enhancement of both nonlinearity and hysteresis (also illustrated by the different piezoelectric hysteresis evolution of representative MB and MPB samples shown in the insets of Figure 3e). Note that the compositional trends shown in Figure 3 for the converse piezoelectric response are consistently observed also in the direct piezoelectric and dielectric response (Sections S6 and S8, Supporting Information). This supports the hypothesis that the enhanced nonlinearity and hysteresis in poled MB compositions are likely dominated by the displacements of ferroelectric/ferroelastic non-180° domain walls.

To complement the analysis of the first-harmonic response, we next show the results of the weak-field third-harmonic polarization measurements, which are highly sensitive to nonlinear domain-wall dynamics.[46] Here, we analyze the dependence of $P_{33}''$ (Figure 4a) and $P_{33}'$ (Figure 4b) on the electric-field amplitude, where $P_{33}''$ and $P_{33}'$ are the amplitudes of the out-of-phase and in-phase polarization of the third harmonic, respectively, along with the third-harmonic phase angle $\delta$ (Figure 4c), which is defined as $\tan \delta = \frac{P_{33}''}{P_{33}'}$. Based on these measurements among the PMN–xPT compositional series and with reference to the expected third-harmonic response from the Rayleigh model (see Section S5, Supporting Information), we can identify three qualitatively different nonlinear responses, which are color-coded in Figure 4 and denoted as relaxor – RE (gray), relaxor ferroelectric – RE-FE (red), and ferroelectric – FE (blue).

![Figure 4](image)

**Figure 4.** Third-harmonic nonlinear polarization response of PMN–xPT. a) Out-of-phase ($P_{33}'$) and b) in-phase ($P_{33}'$) polarization amplitude, and c) phase angle ($\delta$) of the third-harmonic polarization response of PMN–xPT as a function of electric-field amplitude. The power exponents of the field dependence of $P_{33}''$ for two sets of compositions denoted with blue and red color are indicated in (a). d) PMN–xPT phase diagram showing color–indicated regions of the three identified third-harmonic responses (relaxor – RE (gray), relaxor ferroelectric – RE-FE (red), and ferroelectric – FE (blue)). The inset above shows the frequency dispersion of the maximum permittivity (\(\Delta \varepsilon_{\text{max}}\)), reproduced from Figure 1b; middle red dashed line links the drop in \(\Delta \varepsilon_{\text{max}}\) at 32PT and the transition between the RE-FE and FE regions. In the middle are schematics of the hysteresis loops characteristic for these three types of responses, derived from the corresponding signs of $P_{33}'$ and $P_{33}''$, and the $\delta$ value or range (see color bands in (a–c)). Loop deformations due to the third-harmonic contribution are indicated by arrows. Right-most inset of (d) shows the $P_{33}'$–$P_{33}''$ phasor diagram with the hysteresis-loop deformations, dependent on a particular combination of $\pm P_{33}''$ and $\pm P_{33}'$. The diagram presents the phasors (colored arrows) related to the three identified third-harmonic responses (curved gray arrow indicates the $\delta$ transition observed in RE response; curved red arrow indicates the transition from FE to RE-FE-type nonlinear response with decreasing PT content). The red and blue shaded triangles surrounding the colored arrows indicate the span of the $\delta$ values identified at the high-field end of the RE-FE and FE response (see colored bands in (c)).

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type of response (see phase diagram in Figure 4d) with the adjacent schematic loop deformations by the third-harmonic response for these three types of responses).

The FE-type response, approximately confined to the region \(33.5 \leq x \leq 40\), is characterized by three features (follow blue-shaded regions in Figure 4a–c): i) a negative \(P'_{33}\) evolving with field with a power exponent close to 2, ii) \(P'_{33}\) settling around zero in the whole field range, and iii) \(\delta_{33}\) varying with field in between extremes of \(-105^\circ\) and \(-75^\circ\), averaging around \(-90^\circ\). These three features of the third-harmonic response are close to those predicted by the Rayleigh relations (Section S5, Supporting Information), thus suggesting a Rayleigh-like response (see also blue loop schematic and the blue arrow in the phasor diagram in Figure 4d). This kind of response was previously reported for “soft” PZT compositions \([27,40,41,46,47]\), and is illustrated with the characteristic third-harmonic polarization response for a Nb-doped morphotropic PZT in Section S9 of the Supporting Information.

The nonlinear response in the RE-FE region \((20 \leq x \leq 32)\) is distinctly different from that in the FE region, and it is identified by (follow red-shaded regions in Figure 4a–c): i) a stronger negative \(P'_{33}\) evolving with field with a power exponent of \(\approx 2.5\), ii) a field-induced negative \(P'_{33}\), and iii) \(\delta_{33}\) that still varies with field, however, around a mean value of \(-125^\circ\) (see red arrow in the phasor diagram in Figure 4d). The RE-FE response clearly deviates from the Rayleigh predictions. We note that the strong field-induced third-harmonic contribution \(-P'_{33}\), which is hysteretic in nature, is consistent with the large first-harmonic field-induced third-harmonic contribution \(3P'_{33}\). These three features of the total polarization amplitude, as indicated with arrows in the red loop schematics in Figure 4d.

Finally, for a thorough comparison, we show a third type of response confined to close-to-PMN region, denoted as RE-type (see phase diagram in Figure 4d). This response is characterized by (follow gray-shaded regions in Figure 4a–c): i) a nearly zero \(P'_{33}\), ii) a field induced positive \(P'_{33}\), and iii) \(\delta_{33}\) showing a clear transition with field from \(-180^\circ\) to \(0^\circ\) (see gray curved arrow in the phasor diagram in Figure 4d). This transition between two anhysteretic responses with polarization divergence at weak and saturation at high fields (see gray loop schematics in Figure 4d) was previously suggested to arise from evolving dynamics of PNRs with field \([48,49]\).

Considering that the bridging RE-FE-type response qualitatively deviates from both the RE-type and FE-type, as illustrated in the phasor diagram in Figure 4d, the presented data suggest that this response cannot be simply assigned to the PNR dynamics, nor to the classical Rayleigh-like dynamics. While the underlying mechanisms may be complex, our data provide the key link between this particular nonlinear behavior and the relaxor nature of the MB compositions, which is evidenced by two observations. First, the transition from the FE-FE to the FE-type response (see overlapping red/blue area in the phase diagram in Figure 4d) and the corresponding anomaly in the first-harmonic piezoelectric response (arrows in Figure 3a,b) occur close to \(x = 32\). This is the compositional point above which the dispersion of permittivity maximum \(\Delta T_{max}\) drops to nearly zero (see inset linked to the phase diagram in Figure 4d), and where the nanodomains begin to merge into regular and larger T-like lamellar domains (Section S3, Supporting Information). Therefore, the RE-FE-type response is confined to the monoclinic compositions that demonstrate relaxor characteristics. Second, a qualitatively similar response to that of the RE-FE-type was measured in the relaxor-ferroelectric phase of PMN below the freezing point (see Section S10, Supporting Information), supporting the idea that the observed RE-FE response is likely dominated by PMN, i.e., the relaxor end-member of the PMN–xPT solid solution. In support to this claim is the large nonlinearity and hysteresis measured in PMN–7PT under DC bias.\([50]\). Additionally, the RE-FE-type characteristics are also measured in two other lead-based relaxor-ferroelectric materials, i.e., \(\text{Pb(Fe}_{0.4}\text{Nb}_{0.6})\text{O}_3\) (PFN) and \(\text{Pb(S}_{0.5}\text{Nb}_{0.5})\text{O}_3\) (PSN) (Section S9, Supporting Information).

Figure 5 presents a comparison of different Pb-based perovskites, showing a clear qualitative and quantitative difference in the \(d'_{33}\)-versus-driving field trends between the RE-FE-type materials (i.e., PMN–30PT, PFN, and PSN) and MPB compositions with Rayleigh-like FE-type response, exemplified by PMN–35PT and “soft” \(\text{PbZr}_{0.5}\text{Ti}_{0.5}\text{O}_3\). We observe up to \(\approx 200\%\) increase of the piezoelectric coefficient in the relaxor ferroelectrics, while the “classical” ferroelectric compositions achieve merely an \(\approx 80\%\) increase. This clearly points to the quantitative importance of the observed nonlinear response in relaxor ferroelectrics. The comparison also demonstrates that the relaxor-induced softening effect is, in relative terms, much stronger than that induced in “soft” PZT by the donor dopant (in this case Nb), which is widely exploited in current applications.

**Figure 5.** Comparison of the normalized \(d'_{33}\) responses to electric field magnitude for different types of relaxor/ferroelectric materials. In contrast to the moderate (sublinear) increase in the piezoelectric coefficient (\(\approx 80\%\) relative) in “classical” MPB ferroelectric compositions (PMN–35PT and “soft” PZT), an exceedingly large relative (superlinear) increase in \(d'_{33}\) with field (up to \(\approx 200\%\) in PMN–30PT) is observed in relaxor ferroelectric compositions with characteristic RE-FE-type response (PMN–30PT, and non-MPB PSN and PFN). The relative \(d'_{33}\) was calculated by normalizing the \(d'_{33}\) values to that measured at the lowest electric field amplitude of 0.1 kV cm\(^{-1}\).
2.3. Link between Nanoscale Domains and Atomic Structure

The macroscopic piezoelectric data strongly suggest that the observed large increase in the $d_{33}'$ with field amplitude in monoclinic PMN–xPT and similar relaxor-ferroelectric compositions (see Figure 5) has its origin in the domain-wall dynamics. To further explore the characteristic nano- and atomic-scale structural environment of these domain walls, we next show a combined TEM and STEM analysis on the representative monoclinic 30PT composition. Figure 6a shows a TEM image of the striation-like nanodomains in the 30PT sample. This image was processed for its pixel intensities, which reflect differences in diffraction contrast due to lattice distortion, to obtain the 3D intensity map given in Figure 6b. To compare these nanoscale features with those on the atomic scale, we captured an integrated differential phase contrast (iDPC) STEM image, shown in Figure 6c, which allows detection of the positions of all atoms including those of the oxygen (see Figure 6c–e). The analysis of the iDPC image enabled us to measure the displacements of Pb atoms from the center of their oxygen cage, obtaining information about the local polar structure. We observe that stronger Pb displacements, creating clusters of strong uniform polar distortion, are coherent only within a few nm (Figure 6d), which corresponds to the width of nanodomains (see the indicated scale relation between Figures 6b,e). Similar clusters are observed for B-site displacements from their oxygen cage, with slightly smaller magnitudes but of the same direction as those of Pb (this analysis is presented in Section S11, Supporting Information), confirming the unique nanoscale polar order. The angles between the dipoles in subsequent unit cells vary rather smoothly (see neighboring arrows in Figure 6d), which is in line with what was previously defined as low-angle domain walls.\(^{[7,8]}\) From the atomic-to-nanoscale structural comparison it is now clear that 1) there are no straight domain walls, nor can their thickness be unambiguously defined, 2) clustering of larger polar displacements into nanodomains obeys crystallographic orientation (i.e., extending along $⟨111⟩$ directions; see Figure S5 in Section S3, Supporting Information), and 3) there are no sharp boundaries at the edges of polar clusters, indicating a continuously varying polarization across different polar-cluster regions. This atomic-to-nanoscale comparison indicates that the nanoscale clusters of stronger polarity are directly linked to the observed nanodomains and, as suggested by the macroscopic data (Figures 3 and 4), are greatly affected by external fields, causing easy movement of the nanodomain walls.

By combining the compositional evolution of the sub-switching electrical and electromechanical response of PMN–xPT (Figures 3–5) with the meso-to-atomic-scale structural evolution (Figures 1, 2, and 6), we can now propose a link across these different scales, identifying the characteristic response types for each group of materials (i.e., relaxor, relaxor ferroelectric, and ferroelectric). Furthermore, the large nonlinear piezoelectric and dielectric response of the monoclinic PMN–xPT compositions can now be explained. We suggest that the large RE-FE-type response arises from the displacements of the low-angle nanodomain walls, which are mirroring the atomic-scale disorder, i.e., the short-range Pb-sublattice positional disorder (Figure 2d) and the nanoscale regions of stronger polar distortion (Figure 6d,e). This relaxor-specific nanoscale structure is responsible for the increased mobility of the nanodomain walls,\(^{[36,54]}\) representing thus a new type of electromechanical softening, distinctly different from those reported earlier in the frame of the adaptive phase theory\(^{[19]}\) or MPB-related polarization rotation mechanism assisted by rotation of PNRs.\(^{[12]}\) The key role of the low-angle domain walls has been discussed by Takenaka et al.,\(^{[7]}\) however, theoretical modeling in that study describes the mechanism on the lattice scale, pointing to an easy rotation of polar vectors, and is hindered from detecting the domain-wall-motion contribution and the associated softening effect. Despite previous studies identifying the nanodomain structure in PMN–PT, our work provides insights into the relationship between these nanoscale features and the ultrahigh response, revealing multiple contribution to the functional properties. Furthermore, our analysis made it possible to clearly separate the low-angle domain wall dynamics from the polarization rotation mechanism that underpins the response at the MPB with the T phase. Thus, there are more mechanisms contributing to a large piezoelectric response in a given relaxor ferroelectric system, and the dominant mechanism evolves with the composition.

3. Conclusion

In summary, we show here three distinct regions in the dynamic electromechanical response of the polycrystalline PMN–xPT, i.e., the RE, RE-FE, and FE states. We identified a large nonlinear dielectric and piezoelectric response that is confined to a wide monoclinic compositional range of the PMN–xPT ($20 ≤ x ≤ 32$), representing a new type of softening of the electromechanical response, also observed in other Pb-based relaxor ferroelectrics beyond PMN–PT. We further suggest a link between this macroscopic response and the nano- and atomic-scale structure of relaxor ferroelectrics, revealing a softening effect that is different from the usually assumed enhanced polarization rotation at MPBs. Furthermore, the herein observed Pb-positional disorder and the nanoscale polar clusters forming highly mobile low-angle nanodomain walls are suggested to be the key features leading to the exceedingly large nonlinear piezoelectric and dielectric response of the monoclinic PMN–xPT and similar Pb-based relaxor ferroelectrics.
4. Experimental Section

Sample Preparation, Structural, Microstructural, and Domain-Structure Characterization: Polycrystalline ceramic samples of various (100–x)Pb(Mg1/3Nb2/3)O3–xPbTiO3 (PMN–xPT) compositions, i.e., x = 0, 5, 10, 20, 27, 30, 32, 33.5, 35, 37, and 40, were synthesized via a mechanochemical activation route. Details on the synthesis procedure can be found elsewhere.\(^5\) The activated powders were uniaxially...
pressed into pellets at 50 MPa, isostatically pressed at 300 MPa, and then sintered in closed alumina crucibles buried into a packing powder consisting of the same composition as the pellet. The same sintering procedure, i.e., 1200 °C for 16 h with a heating/cooling rate of 2 °C min⁻¹ was employed for all compositions to ensure comparable microstructures (see Section S2, Supporting Information).

The phase composition of the sintered samples was determined by XRD analysis, using PANalytical X’Pert Pro diffractometer with Cu Kα1 radiation (λ = 1.54056 Å) and X’Celerator detector. Room-temperature XRD patterns of the powders, obtained by crushing the pellets, were collected over the range of 2θ = 20°–120° with a step size of 0.008°.

Microstructural features were observed using a field-emission scanning electron microscope (SEM; JSM-7600, Jeol Ltd., Tokyo, Japan) on samples that were ground, polished, and thermally etched at 900 °C for 15 min. Average grain size of the samples was estimated from the SEM images. The density was measured in accordance with the Archimedes’ principle.

TEM (JEM-2100, Jeol Ltd., Tokyo, Japan) operated at 200 kV with a beryllium double-tilt specimen holder was used to determine the domain structure of the samples. TEM samples were prepared by cutting disks, mechanical thinning, and dimpling, then cold-stage Ar-ion milling until perforation (RES 010, Bal-Tec AC, Balzers, Liechtenstein).

All structural, microstructural, and atomic-scale investigations were performed on pristine samples, thus in their unpoloed state.

**STEM and Microanalysis:** Samples for STEM analysis were produced by wedge polishing using a Multiprep polishing system (Allied High Tech Product Inc., Compton, USA) and cold-stage low-energy Ar-ion milling (model 3050 TEM MILL, Fischione Instruments, Corporate Circle, USA), and final carbon-coating (PECS system, Gatan Inc., Pleasanton, USA) to prevent charging.

For atomic-resolution imaging a probe-corrected STEM (Titan G2, FEI, Hillsboro, USA) was used, equipped with a Schottky field emission gun operated at 200 kV, with the beam current of 30 pA and a convergence semiangle of 19.6 mrad. For HAADF imaging the annular dark-field inner collection semiangle was 28–150 mrad. Integrated differential phase contrast (dPC) STEM imaging was performed simultaneously with annular dark field imaging at the collection semiangle of 7–28 mrad, using a 4-quadrant segmented detector.[64] Analysis of the HAADF (Section S4, Supporting Information) and dPC images (Section S11, Supporting Information) were measured using a commercial aixACCT TF 2000 analyzer at 1 Hz of sinusoidal driving frequency and 60 kV cm⁻¹ of high voltage. The samples were immersed in silicone oil to prevent charging. The large-signal P–E hysteresis loops and third-harmonic polarization response below room temperature (Section S10, Supporting Information) were measured as described above using a commercial aixACCT low-temperature sample holder.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Author Contributions
T.R. and M.O. conceptualized the research, designed the experiments and analyzed the data. L.F. and T.K. designed and built the hardware and software for harmonic measurements. T.R. and M.O. performed the electrical and electromechanical measurements, assisted by A.B. and L.R. M.O. and M.C. performed the microscopy measurements. A.B. and C.D. assisted in the microscopy data analysis, while H.U. helped in the interpretation of the data. M.O. performed the XRD analyses. A.H. and J.LJ. helped in the evaluation of the XRD data. D.D. suggested interpretations of the results and helped in conceptualizing the work. B.M. led the work on the preparation of samples for analysis. T.R. and M.O. wrote the manuscript. All the authors reviewed and edited the manuscript.

Keywords
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[1] F. Li, S. Zhang, D. Damjanovic, L. Q. Chen, T. R. Shrout, Adv. Funct. Mater. 2018, 28, 1801504.
[2] S. Zhang, T. R. Shrout, IEEE Trans. Ultrason. Ferroelectr. Freq. Control 2010, 57, 2138.
[3] R. Blinc, V. Laguta, B. Zalar, Phys. Rev. Lett. 2003, 91, 24.
[4] J. K. Jeong, T. W. Darling, J. K. Lee, T. Proffen, R. H. Heffner, J. S. Park, K. S. Hong, W. Dmowski, T. Egami, Phys. Rev. Lett. 2005, 94, 147602.
[5] T. R. Welberry, D. J. Goossens, M. J. Gutmann, Phys. Rev. B: Condens. Matter Mater. Phys. 2006, 74, 224108.
[6] H. Takenaka, I. Grinberg, A. M. Rappe, Phys. Rev. Lett. 2013, 110, 147602.
[7] H. Takenaka, I. Grinberg, S. Liu, A. M. Rappe, Nature 2017, 546, 391.
[8] M. Eremenko, V. Krayzman, A. Bosak, H. Y. Playford, K. W. Chapman, J. C. Woicik, B. Ravel, I. Levin, Nat. Commun. 2019, 10, 2728.
[9] D. Viehland, S. J. Jang, L. E. Cross, M. Wuttig, J. Appl. Phys. 1990, 68, 2916.
[10] A. J. Bell, J. Phys. Condens. Matter 1993, 5, 8773.
[11] A. A. Bokov, Z. G. Ye, J. Mater. Res. 2006, 21, 31.
[12] F. Li, S. Zhang, T. Yang, Z. Xu, N. Zhang, G. Liu, J. Wang, J. Wang, Z. Cheng, Z. G. Ye, J. Luo, T. R. Shrout, L. Q. Chen, Nat. Commun. 2016, 7, 13807.
[13] A. Al-Barakaty, S. Prosandeev, D. Wang, B. Dhkil, L. Bellaiche, Phys. Rev. B: Condens. Matter Mater. Phys. 2015, 91, 214117.
[14] M. Pasicia, M. Woltczyz, A. Pietraszko, Phys. Rev. B: Condens. Matter Mater. Phys. 2007, 76, 014117.
[15] A. Bosak, D. Chernyshov, S. Vakhurshev, M. Kirsch, Acta Crystallogr., Sect. A: Found. Crystallogr. 2012, 68, 117.
[16] L. Eric Cross, Ferroelectrics 1987, 76, 241.
[17] J. Hlinka, J. Adv. Dielectr. 2012, 2, 1241006.
[18] R. Piric, R. Blinc, Phys. Rev. B: Condens. Matter Mater. Phys. 1999, 60, 13470.
[53] J. Rödel, W. Jo, K. T. P. Seifert, E. M. Anton, T. Granzow, D. Damjanovic, J. Am. Ceram. Soc. 2009, 92, 1153.
[54] Y. Sato, T. Hirayama, Y. Ikuhara, Appl. Phys. Lett. 2012, 100, 172902.
[55] M. Dragomir, M. Otoničar, M. Vrabelj, L. Fulanović, S. Drnovšek, T. Rojac, B. Malič, J. Eur. Ceram. Soc. 2019, 39, 1837.

[56] I. Lazić, E. G. T. Bosch, S. Lazar, Ultramicroscopy 2016, 160, 265.
[57] T. Rojac, H. Ursic, A. Bencan, B. Malič, D. Damjanovic, Adv. Funct. Mater. 2015, 25, 2099.
[58] M. I. Morozov, D. Damjanovic, J. Appl. Phys. 2008, 104, 034107.
[59] A. Barzegar, D. Damjanovic, N. Setter, IEEE Trans. Ultrason. Ferroelectr. Freq. Control 2004, 51, 262.