Dielectric and piezoelectric nonlinear properties of slightly textured lead barium niobate ceramics

Diego A. Ochoa,1 Jorge A. Casals,1,2 Michel Venet,3 Jean-Claude M’Peko,4 and Jose E. García1, a)

1) Department of Physics, Universitat Politècnica de Catalunya – BarcelonaTech, 08034 Barcelona, Spain
2) Department of Natural Science, Health & Wellness, Miami-Dade College, Wolfson Campus, Miami, FL 33132, USA
3) Department of Physics, Universidade Federal de São Carlos, 13565-670 São Carlos-SP, Brazil
4) São Carlos Institute of Physics, Universidade de São Paulo, 13560-970 São Carlos-SP, Brazil

Dielectric and piezoelectric responses of slightly textured, lead barium niobate ceramics are studied. The designed morphotropic phase boundary composition (Pb0.63Ba0.37Nb2O6) shows considerable nonlinear dielectric and piezoelectric responses. While these nonlinear behaviors lead to significant instabilities of the functional properties, interesting features are revealed as a consequence of the texturing effect in the composition studied. An improved dielectric performance and a lower nonlinear piezoelectric response are observed when the electric field is applied to the sample in the forging direction. The results are quantitatively discussed in the framework of the Preisach and Rayleigh models. In this context, a decrease in the nonlinear response can be associated with a lower grain size related to the texture. The results of this work show that texturing is an effective route for controlling the undesirable nonlinear behavior of piezoceramics with tetragonal tungsten bronze structure.

a) jose.eduardo.garcia@upc.edu
I. INTRODUCTION

Ferroelectric ceramics with tetragonal tungsten–bronze (TTB) structure are currently being widely investigated from both the fundamental and applied points of view. Research in TTB ferroelectrics is motivated by the potential use of these ferroelectric materials in a wide variety of technological applications, such as electro-optic, pyroelectric, piezoelectric, and photorefractive devices.\(^1\) Similar to perovskite systems, research on TTB systems is focused on compositions showing morphotropic phase boundary (MPB). The coexistence of two ferroelectric phases in the MPB enhances the functional properties as well as enabling these properties to be controlled through compositional engineering.\(^2,3\) Several TTB-structured solid solutions exist where MPB can be found,\(^4\) one of the most important of which is lead barium niobate, \(\text{Pb}\text{Ba}_{1-x}\text{Nb}_2\text{O}_6\). In this system, the TTB structure spans the interval \(0.20 \leq x \leq 1.00\), exhibiting the MPB in the vicinity of \(x = 0.63\).\(^5\) A compositional phase transition from a ferroelectric tetragonal phase (\(4mm\)) to the ferroelectric orthorhombic phase (\(m2m\)) occurs when \(x\) ranges from low to high values.\(^6\) The \(\text{Pb}_{0.63}\text{Ba}_{0.37}\text{Nb}_2\text{O}_6\) composition (hereafter PBN) exhibits outstanding dielectric and piezoelectric properties at room temperature,\(^7,8\) making these compositions a benchmark in TTB systems. Although PBN exhibits excellent functional properties, very few studies have been focused on the stability of the functional properties, probably as a result of the difficulties encountered when sintering these materials.\(^9\) The vanishing of the anisotropy in polycrystalline PBN as a consequence of the random arrangement of the grains leads to a decrease in the functional properties, which may also account for the lack of research in this system. Nevertheless, promoting the preferential crystallographic arrangement in the ceramic through texturing enables the intrinsic anisotropy to be recovered, thereby enhancing the functional properties in a preferential direction of the material.\(^10\) Indeed, this enhancement of the functional properties through texturing has been verified in perovskite-structured KNN,\(^11\) reinforcing the importance of the role that texture may play in ferroelectric materials.

Stability of the functional properties is an essential feature of piezoelectric materials when they are used in real-world applications. Many piezoelectric materials exhibit variations in their functional properties when moderate external stimuli are applied. These variations are referred to as nonlinear behavior.\(^12\) Conventionally, this nonlinear behavior is related to the piezoelectric microstructure, to the configuration of ferroelectric domains, and to the
Therefore, considering the fundamental role that the nonlinear behavior plays on the performance of piezoelectric materials, the aim of this work is to study the nonlinear behavior of a slightly textured PBN. Two types of nonlinear characterizations are performed: On the one hand, the nonlinear dielectric (NLD) characterization, understood as the study of the variation in the permittivity with the applied electric field, enables the stability of dielectric properties to be revealed. On the other hand, the nonlinear piezoelectric (NLP) characterization, understood as the study of the variation in the piezoelectric coefficient with the applied dynamical stress, which accounts for the stability of the piezoelectric properties. Both nonlinear responses have been successfully described in ferroelectric perovskite systems by the Preisach model\(^\text{14,15}\) and the Rayleigh model,\(^\text{16}\) providing helpful insights into the correlation between microstructure, the non-180° domain walls motion and the functional properties stability of the piezoelectric materials. The results show that texturing is an effective option for controlling the undesirable nonlinear behavior in TTB-structured piezoceramics.

II. PREISACH AND RAYLEIGH MODELS

The Preisach model describes the nonlinear behavior in hysteretic systems containing a collection of simple bistable units, with both states contributing independently to the total response by the same amount ±\(P_0\). These units are characterized by an internal field \(F_i\), and a coercive field \(F_C\) (Fig. 1(a)). Thus, the set of bistable units exhibits a statistical distribution \(f(F_i, F_C)\) that depends on the parameters \(-\infty < F_i < \infty\) and \(0 < F_C < \infty\).

The nonlinear response to a general driving field \(F = F_b + F_0e^{i\omega t}\) depends on the number of bistable units switched inside the triangular region of the Preisach plane (Fig. 1(b)), and can be obtained from:\(^\text{17}\)

\[
R_{NL}(F_0, F_b) = 2P_0 \int_0^{F_0} \int_{F_b - F_0}^{F_b + F_0 + F_C} f(F_i, F_C) dF_i dF_C. \tag{1}
\]

Considering the response \(R_{NL}(F_0, F_b)\) as the nonlinear electric displacement \(D_{NL}^i(F_0, F_b) = (\Delta y' - \Delta y'')(F_b + F_0e^{i\omega t})\), the variations in the real and imaginary parts of the coefficients in-phase \((\Delta y')\) and quadrature-phase \((\Delta y'')\) with the corresponding driving field follow the relations:

\[
\Delta y' = \frac{1}{F_0} \left[ \frac{1}{\pi} \int_0^{2\pi} D_{NL}^i(\omega t) \cos(\omega t) d(\omega t) \right], \tag{2}
\]
\[ \Delta y'' = \frac{1}{F_0} \left[ \frac{1}{\pi} \int_0^{2\pi} D_{NL}(\omega t) \sin(\omega t) d(\omega t) \right]. \] (3)

Hence, the variations in the real \( (\Delta \epsilon') \) and imaginary \( (\Delta \epsilon'') \) parts of the permittivity can be calculated by selecting the electric field \( E = E_0 e^{i\omega t} \) as the driving field. Meanwhile, the variations in the real \( (\Delta d') \) and imaginary \( (\Delta d'') \) parts of the piezoelectric coefficient can be obtained by selecting the dynamical stress \( T = T_{DC} + T_0 e^{i\omega t} \) as the driving field.

Figure 1. Schematic representation of the Preisach model. Panel (a) shows the bistable unit and its characteristic parameters. Panel (b) shows a representation of a flat distribution function in the Preisach plane and the triangular region contributing to the nonlinear response. Panel (c) displays a representation of a symmetric distribution function (two Gaussian-like functions) in the Preisach plane, while (d) illustrates a zoom of the red square corresponding to the sub-switching regime.

The description of the Preisach formalism from the microscopic point of view has been previously discussed.\textsuperscript{14} Several equivalent descriptions of the concept of the switchable bistable unit have been used. For instance, domain walls that move in a well-defined potential profile,\textsuperscript{14} or ferroelectric domains with a distribution of coercive and internal fields have been considered as bistable switchable units.\textsuperscript{18,19}
On the other hand, the phenomenological Rayleigh model postulates a linear dependence of the variation of the coefficients with the amplitude of the alternating driving field, \( F = F_b + F_0 e^{i\omega t} \). According to this model, the variation in the real and imaginary parts of the coefficients contributing to the nonlinear response at the main frequency of \( F \) can be obtained as:

\[
\Delta y' = \alpha F_0, \quad (4)
\]

\[
\Delta y'' = \frac{4}{3\pi} \alpha F_0, \quad (5)
\]

where \( \alpha \), known as the Rayleigh coefficient, quantifies the nonlinear effect and is therefore a measure of the coefficient instability. A value of \( \alpha = 0 \) implies that there is no variation in the coefficient, thereby indicating null nonlinear response (i.e., the related functional property is stable). The ratio between the imaginary and the real parts is a constant value:

\[
m = \frac{\Delta y''}{\Delta y'} = \frac{4}{3\pi}. \quad (6)
\]

This value (\( m \approx 0.42 \)) is independent of the crystallographic phase of the material and states that an increase in the real part entails an increase in the imaginary part. It is well established that the real part of the coefficients (in-phase with the driving field) is related to functional properties, while the imaginary part (in quadrature-phase with the driving field) is the dispersive term related to physical losses in the material.

The Rayleigh model assumes that the irreversible motion of any interface within a randomly distributed pinning energy profile produces a nonlinear response. Different types of interfaces such as ferroelastic domain walls (non-180° domain walls), ferroelectric domain walls (180° domain walls) or crystallographic phase boundaries motion, could contribute to the nonlinear response of piezoelectric materials.\(^{20,21}\) Regardless of the nature of the interface, the ratio between the increments of the imaginary and the real part of the coefficients will remain constant (i.e., \( m = 0.42 \)). Therefore, experimentally obtained values higher than the expected value (i.e., \( m > 0.42 \)) suggest the existence of at least one physical phenomenon (different from the interface motion described in the Rayleigh model) that makes a greater contribution to the dispersive term than that predicted by the model. On the other hand, values lower than the expected value (i.e., \( m < 0.42 \)) suggest the existence of at least one physical phenomenon that makes a lower contribution to the dispersive term than that expected by the model.
The Rayleigh model can be derived from the simplest development of the Preisach model, which corresponds to a flat uniform distribution function \( f(F_i, F_C) = g_0 \) (Fig. 1(b)). By substituting this distribution function into the Eqs. (2) and (3), the variation in the coefficients related to a property can be obtained as:

\[
\Delta y' = P_0 g_0 F_0, \tag{7}
\]

\[
\Delta y'' = \frac{4}{3\pi} P_0 g_0 F_0, \tag{8}
\]

which show a linear dependence with the amplitude of the driving field, as anticipated by the Rayleigh model. Comparison of Eqs. (4) and (7) lead to a simple relation \( \alpha = P_0 g_0 \) between the coefficients of both models. Furthermore, the ratio \( \frac{\Delta y''}{\Delta y'} = \frac{4}{3\pi} \) from Eqs. (7) and (8) is the same value as that provided by the Rayleigh model.

### III. EXPERIMENTAL PROCEDURE

A ceramic powder with nominal formula \( \text{Pb}_{0.63}\text{Ba}_{0.37}\text{Nb}_2\text{O}_6 \) (PBN) was prepared by the solid-state reaction method. Analytical grade precursors (PbO, BaCO\(_3\), and Nb\(_2\)O\(_5\)) were mixed in a ball mill in polyethylene pots containing isopropyl alcohol and stabilized ZrO\(_2\) cylinders. The powder was calcined at 1200 °C for 3 h in air without any special precaution for avoiding PbO losses since PbO volatilization occurs at temperatures above 850 °C.\(^{22,23}\) In the case of PBN synthesis, intermediate phases are formed between 850 °C and 1050 °C and, therefore, the presence of PbO is not expected in these materials.\(^{24}\) After that, the powders were uniaxially cold-pressed in a rectangular die and, then, an isostatic cold pressing was applied in order to minimize density gradients. The sintering was performed in oxygen atmosphere (35 kPa) at 1270 °C for 2 h by the hot forging technique. A rectangular refractory die was used to obtain the texturing of the ceramics conditioning the grain growth in a preferential direction perpendicular to the pressure axis (Fig. 2(a)). The sintering method and texturing technique enabled uniform microstructured and textured ceramics to be obtained. A more detailed information about the sample processing and texture evidences can be found in a previous work.\(^{25}\)

Gold electrodes were sputtered on the 5 mm x 5 mm rectangular faces of samples of 1 mm thickness to perform the dielectric and piezoelectric characterizations. The samples
Figure 2. Schematic representation of the procedure for the preparation of samples and their microstructure. Panel (a) shows a schematic representation of the rectangular refractory die applied for the hot forging of the PBN ceramics and the expected grain arrangement after forging. Panel (b) describes the labeling of the PBN samples according to the pressure direction (PBN-P) and the forging direction (PBN-F). Panels (c) and (d) show a SEM micrograph of the polished and thermal etched samples for PBN-F and PBN-P, respectively.

with the electrodes in the direction parallel to the axis of the applied pressure are labeled as PBN-P, while the samples with the electrodes in the direction parallel to the axis of the forging pressure are labeled as PBN-F. Fig. 2(b) shows an illustrative scheme.

The PBN-F and PBN-P samples are obtained from the same larger block (Fig. 2(b)) and therefore have an identical composition and microstructure. Hence, the differences
observed between the textured PBN-F and PNB-P samples originate from the intrinsic and extrinsic anisotropic properties. The PBN-F grains show a strong \langle 001 \rangle_{pc} preferred orientation parallel to the polarization direction, while the PBN-P grains show a low \langle 001 \rangle_{pc} orientation. Fig. 2(b) illustrates the difference in the spontaneous polarization distribution of both samples. The spontaneous polarization distribution may be categorized as “disc” or “cone” type. As may be observed, both samples show two “cones” and one “disc”. Due to the preferred \langle 001 \rangle_{pc} orientation of the PBN-F grains, 66% of the PBN-F grains (the two cones) have their polar vectors parallel to the polarization direction. On the other hand, the PBN-P have only 33% of the grains (the disc) with their polar vectors parallel to the polarization direction. The microstructure of the samples was studied by scanning electron microscopy (SEM) of the planes parallel to the gold electrode planes. SEM images similar to those in Fig. 2(c) and (d) would usually represent the microstructure of crystallographically isotropic samples from which the grain size could be obtained. However, the SEM images of the PBN-F and PBN-P samples (Fig. 2(c) and (d)) represent the microstructure projection over the planes parallel to the gold electrode planes from which the planar density of grain boundaries in the \langle 001 \rangle_{pc} direction could be obtained. As may be observed in the SEM images (Fig. 2c) and 2(d)), the PBN-F show a higher planar density of grain boundaries than the PBN-P in the \langle 001 \rangle_{pc} direction.

The NLD characterization was performed by applying a subswitching alternating electric field at different frequencies, from 100 Hz to 1 kHz, using a capacitance comparator bridge especially designed for this type of measurement, as described in detail elsewhere.\textsuperscript{26} The NLP characterization was performed using a Berlincourt-type method. A sinusoidal stress with a frequency of 1 Hz, superimposed onto a uniaxial compression stress, was applied to the samples. The system was set on standby for 30 min after the application of every uniaxial compression stress, providing enough time for the slow processes triggered inside the material to relax. The applied uniaxial compression stress ranged from 22 MPa to 55 MPa. The highest instantaneous compression stress remained below 90 MPa, thereby avoiding the irreversible depolarization of the samples. A more detailed description of the experimental setup for piezoelectric characterization can be found elsewhere [24]. Linear characterizations of the samples were conducted both before and after NLD and NLP characterizations in order to verify that no changes in the macroscopic state of the samples occurred as a consequence of the nonlinear characterizations.
IV. RESULTS AND DISCUSSION

The NDL of the PBN-F and PBN-P are shown in Fig. 3(a) and 3(b). Fig. 3(a) shows the dependence of the real part of the permittivity ($\epsilon'$) with the amplitude of the applied electric field ($E_0$). The first feature that may be observed is the 20% difference in the value of $\epsilon'$ at low $E_0$ (the linear dielectric constant), depending on the texture orientation. The linear dielectric coefficient of the PBN-F exceeds the value of the PBN-P by 200 units, thereby indicating a better dielectric performance in textured samples where the grains are oriented parallel to the applied electric field. This is consistent with the low temperature characterization shown in the inset of Fig. 3(a). The low-temperature $\epsilon'$, which is related to the intrinsic dielectric response, is higher for PBN-F than for PBN-P. Fig. 3(b) shows the dependence of the imaginary part of the permittivity ($\epsilon''$) with $E_0$. As may be observed, $\epsilon''$ values tend to zero at low $E_0$. This is the expected tendency, since $\epsilon''$ is related to the dielectric losses (the dielectric losses vanish at $E_0 = 0$). Both $\epsilon'$ and $\epsilon''$ increase with the increase in $E_0$ for all the frequencies, showing a notable NLD behavior. This nonlinear behavior is stronger for the PBN-P at the lowest frequency, at which $\epsilon'$ reaches 150% of the initial value and $\epsilon''$ increases up to 450 at the highest $E_0$ applied. The high NLD response observed in PBN is in agreement with previous studies on different MPB perovskite-structured ferroelectric materials.\[12,27\]

The NLP response is shown in Fig. 3(c) and 3(d). The increment in the real part of the piezoelectric coefficient ($d_{33}^{Re}$) with the increasing amplitude of the applied dynamical stress ($T_0$) at different uniaxial stresses ($T_{DC}$) is shown in Fig. 3(c). Additionally, Fig. 3(d) displays the increment in the imaginary part of the piezoelectric coefficient ($d_{33}^{Im}$) with the applied $T_0$ at different $T_{DC}$. Both PBN-F and PBN-P show high NLP behavior, which reinforces the observed results of the dielectric characterization. Similar to the NLD response, the strongest NLP behavior is observed in the PBN-P, for which the $d_{33}^{Re}$ value increases up to 150% of the initial value.

Qualitatively, the main difference between the NLD and NLP responses is the difference dependence of the coefficients with the amplitude of the applied stimuli. The NLD characterization shows a nonlinear dependence of $\epsilon'$ and $\epsilon''$ with $E_0$, indicating a non-Rayleigh behavior, and therefore ruling out the use of a flat distribution function in the Preisach model.\[14,15\] On the other hand, the NLP characterization shows a linear dependence of $d_{33}^{Re}$
Figure 3. Nonlinear dielectric and piezoelectric responses for both PBN-F and PBN-P samples.

Variation of the real (a) and imaginary (b) parts of the dielectric permittivity with the amplitude of the applied electric field at different frequencies from 100 Hz to 1 kHz. Variation of the real (c) and imaginary (d) parts of the piezoelectric coefficient with the amplitude of the applied mechanical stress at different pre-stress conditions from 22 MPa to 55 MPa. The inset in panel (a) shows the linear dielectric response at low temperatures. The inset in panel (b) shows the coefficients obtained by the quadratic fit of $\varepsilon'$ and $\varepsilon''$ versus $E_0$ plots following Eqs. (13) and (14). The inset in panel (d) shows the evolution of the coefficient $A(T_{DC})$ obtained from Eq. (15).

and $d_3^{Im}$ with $T_0$, thereby fulfilling the Rayleigh model and enabling the use of a flat distribution function in the Preisach model. Nevertheless, the decrease in the piezoelectric response with the increase in $T_{DC}$ cannot be explained by the Preisach model when using a flat distribution function [15]. For $f(T_i, T_C) = g_0$ and $T_{DC} = 0$, the nonlinear contribution calculated from Eq. (1) is proportional to the area of the triangle ($T_0^2$) in Fig. 1(b). The application of a bias, $T_{DC} > 0$, relocates this triangle to a new position along the $T_i$ axis,
although the area of the triangle does not change, and thus, contrary to the observed experimental behavior, the nonlinear response remains the same. In consequence, a distribution function different from the flat distribution must be chosen to fit the experimental results according to the Preisach model.

Taking into account that the nonlinear characterizations were performed at sub-switching conditions (far away from the coercive field and mechanical depolarization), it is possible to use an expanded Maclaurin series of an \( a \ priori \) unknown distribution function to fit the experimental data. The schematic representation of the triangular area corresponding to the Preisach plane is shown in Fig. 1(d). The expanded distribution function can be written as:

\[
f(F_i, F_C) = g_0 + g_1 F_i + g_C^1 F_C + g_2 F_i^2 + g_C^2 F_C^2,
\]

(9)
dismissing the cross term. Taking into consideration the symmetry in the vertical axis of the Preisach plane, it has to be \( g_1 = 0 \). Once the \( F_C \) second-order term is discarded for simplicity, the distribution function can be written as follows:

\[
f(F_i, F_C) = g_0 + g_C^1 F_C + g_2 F_i^2,
\]

(10)
where the term \( g_C^1 F_C \) accounts for the quadratic behavior of \( \epsilon' \) and \( \epsilon'' \) with \( E_0 \), while the term \( g_2 F_i^2 \) accounts for the variation of the NLP response with \( T_{DC} \).

On replacing the distribution function given by Eq. (10) in Eq. (1), and assuming a generic external stimulus \( F = F_b + F_0 e^{i\omega t} \), the calculated real (Eq. (2)) and imaginary (Eq. (3)) parts of the coefficients are:

\[
\Delta y' = P_0 g_0 F_0 \left[ 1 + \frac{g_2}{g_0} F_b^2 + \frac{7}{48} \frac{g_2}{g_0} F_0^2 + \frac{5}{16} \frac{g_C^1}{g_0} F_0 \right],
\]

(11)
and

\[
\Delta y'' = \frac{4}{3\pi} P_0 g_0 F_0 \left[ 1 + \frac{g_2}{g_0} F_b^2 + \frac{1}{10} \frac{g_2}{g_0} F_0^2 + \frac{1}{2} \frac{g_C^1}{g_0} F_0 \right].
\]

(12)

Taking into account that the external stimulus in the NLD characterization has no bias field (\( F = E_0 e^{i\omega t} \)), Eqs. (11) and (12) transform into:

\[
\Delta \epsilon' = P_0 g_0 E_0 \left[ 1 + \frac{7}{48} \frac{g_2}{g_0} E_0^2 + \frac{5}{16} \frac{g_C^1}{g_0} E_0 \right],
\]

(13)
\[
\Delta \epsilon'' = \frac{4}{3\pi} P_0 g_0 E_0 \left[ 1 + \frac{1}{10} \frac{g_2}{g_0} E_0^2 + \frac{1}{2} \frac{g_C^1}{g_0} E_0 \right].
\]

(14)
The calculated $\Delta \epsilon'$ and $\Delta \epsilon''$ match the nonlinear quadratic dependence with $E_0$ observed in Fig. 3(a) and 3(b). The fitting results show higher values of the linear and quadratic terms for PBN-P than for PBN-F; that is, $(P_0 g_0)^{PBN-P} > (P_0 g_0)^{PBN-F}$ and $(P_0 g_1^{C})^{PBN-P} > (P_0 g_1^{C})^{PBN-F}$, as may be observed in the inset of Fig. 3(b). The terms $P_0 g_2$ were discounted from the analysis, because their values were significantly low in both samples. Since the microstructure is the same in both samples, it is possible to assume that $P_0^{PBN-P} = P_0^{PBN-F}$. Thus, the differences displayed in the inset of Fig. 3(b) must be related to different distribution functions. It is inferred from the fitting results that the amount of switchable bistable units for the same Preisach plane area is higher in the PBN-P than in the PBN-F; that is, $f(E_i, E_C)^{PBN-P} > f(E_i, E_C)^{PBN-F}$ for all $E_i, E_C$.

Regarding the NLP response (Fig. 3(c) and 3(d)), the different external stimuli applied must be taken into consideration. In this case, the applied driving field consists of an alternating mechanical stress with a superimposed uniaxial mechanical bias, $T = T_{DC} + T_0 e^{i \omega t}$, such that $T_{DC} > T_0 e^{i \omega t}$ for all $t$. The increments of the real and imaginary parts of the longitudinal piezoelectric coefficient are obtained from Eqs. (11) and (12) as:

$$
\Delta d_{33}^{Re} = P_0 g_0 T_0 \left[1 + \frac{5}{16} g_1^C T_0 + \frac{g_2}{g_0} T_{DC}^2 + \frac{7}{48} \frac{g_2}{g_0} T_0^2\right],
$$

(15)

$$
\Delta d_{33}^{Im} = \frac{4}{3\pi} P_0 g_0 T_0 \left[1 + \frac{1}{2} \frac{g_1^C}{g_0} F_0 + \frac{g_2}{g_0} T_{DC}^2 + \frac{1}{10} \frac{g_2}{g_0} T_0^2\right].
$$

(16)

The last term could be discarded in both equations, since $T_{DC} > T_0$. The resulting second-order polynomial equations follow: $A(T_{DC}) T_0 + BT_0^2$. The evolution of the coefficient $A(T_{DC}) = P_0 g_0 + P_0 g_2 T_{DC}^2$, obtained from Eq. (15) is plotted in the inset of Fig. 3(d). Similar to the NLD data, the NLP fitting results confirm a higher density of switchable bistable units in the PBN-P than in the PBN-F; that is, $A^{PBN-P} > A^{PBN-F}$ for all $T_{DC}$.

The results obtained from the Preisach model may be correlated to the samples texture, taking into account the anisotropy of the measured coefficients. The different texture of the samples leads to a different distribution of the polar vectors, as may be observed in the schematic representation in Fig. 4(a). The PBN-F (PBN-P) show a distribution of polar vectors with two cones parallel (perpendicular) and one disc perpendicular (parallel) to the direction of the applied field. In the unpoled state, the polar vectors are distributed equally between the two cones and the disc. However, the polarization process breaks the balance in favor of the domains with polar vectors aligned with the electric field. The new domain
configuration constrains the switching by at least 33% of the PBN-F polar vectors, leaving the rest of the polar vectors free to switch and contribute to the nonlinear response. On the other hand, only 17% of the polar vectors are fixed in the PBN-P. By taking into account that the amount of free-to-switch polar vectors is directly proportional to the amount of switchable bistable units, it is possible to assume a higher density of switchable bistable units in the PBN-P than in the PBN-F. This assumption is confirmed by the experimental results given above.

Furthermore, the analysis of the ratio between the variation in the real and imaginary parts of the permittivity obtained from Eqs. (13) and (14) is a helpful tool (from the Rayleigh
model) that provides insights into the stability of the dielectric properties. Discarding the terms $P_0g_2$, the ratio is:

$$m_e = \frac{\Delta \epsilon''}{\Delta \epsilon'} = \frac{4}{3\pi} \left[ \frac{1 + \frac{1}{2} \frac{g_C}{g_0} E_0}{1 + \frac{5}{16} \frac{g_C^2}{g_0^2} E_0} \right],$$  \tag{17}$$

where the expected value from the Rayleigh model ($m_e = \frac{4}{3\pi}$) is recovery assuming $g_0 \gg g_C^1$, which is equivalent to presupposing a flat distribution function.

Fig. 4(b) shows the linear fit of $\Delta \epsilon''$ versus $\Delta \epsilon'$ for both samples. The shift to higher than expected values of the Rayleigh slope in both samples ($m_e > 0.42$) reveals the existence of a contribution to the increment in the dispersive term of at least one more phenomenon than expected by the Rayleigh model. This phenomenon could be related to the high conductivity of the PBN, which may contribute more to $\Delta \epsilon''$ than to $\Delta \epsilon'$.

The imaginary versus the real part of the piezoelectric coefficient are plotted in Fig. 4(c) in order to analyze the NLP response from the Rayleigh model point of view. Eq. (18) shows the expression of $m_{d33}$ obtained from Eqs. (15) and (16):

$$m_{d33} = \frac{\Delta d_{33}^m}{\Delta d_{33}^{Re}} = \frac{4}{3\pi} \left[ \frac{1 + \frac{1}{2} \frac{g_C}{g_0} T_0 + \frac{g_2}{g_0} T_{DC}^2}{1 + \frac{5}{16} \frac{g_C^2}{g_0^2} T_0 + \frac{g_2^2}{g_0^2} T_{DC}^2} \right].$$  \tag{18}$$

The quadratic term was discarded in virtue of $T_{DC} > T_0$. Similar to the dielectric case, the expected value from the Rayleigh model is recovery assuming $g_0 \gg g_1^C$ and $g_0 \gg g_2$. The evolution to higher values of the $m_{d33}^{PBN-F}$ with $T_{DC}$ (Fig. 4 inset) suggests the existence of a phenomenon favored by the increasing $T_{DC}$ and which contributes more to the mechanical losses than to the piezoelectric effect, whereas the evolution of the $m_{d33}^{PBN-F}$ with $T_{DC}$ shows a saturation value of 0.42 at high $T_{DC}$, thereby fulfilling the Rayleigh model. Values of $m_{d33}$ lower than 0.42 have been reported in previous studies for hard-PZT. The pinning of the domain wall motion by the complex defects presented in the hard-PZT explain the low $m_{d33}$ values. Nonetheless, such complex defects do not exist in PBN, and therefore low $m_{d33}$ values at low $T_{DC}$ may be related to the texture of the PBN samples.
CONCLUSIONS

The stability of the functional properties of slightly textured PBN is studied in a composition near to the MPB. The texture samples were obtained by the hot forging technique. The anisotropy generated by this technique plays a fundamental role in the functional properties of the textured PBN. The sample with a texture favoring the grains alignment in the ⟨001⟩pc direction (PBN-F) showed better dielectric and piezoelectric performance. Analysis of the nonlinear dielectric and piezoelectric responses conducted by means of the Preisach model enables correlation of the nonlinear responses and the texture of the PBN samples, thereby showing that is possible to enhance the stability of the functional properties by controlling the amount of switchable bistable units through texturing. Analysis of the nonlinear dielectric and piezoelectric responses by means of the Rayleigh model showed that the PBN samples exhibit notable nonlinear responses compared to perovskite-structured piezoceramics. Nevertheless, the dependence of the nonlinear behavior with texture indicate the possibility of reducing such nonlinear behavior. The results show that the texture leads to an enhancement of the stability of the functional properties, which constitutes one of the fundamental factors for integrating piezoceramics in functional devices. The stability of the functional properties of PBN still falls far short of practical requirements. However, this work paves the way towards controlling the nonlinearity through texturing in tetragonal tungsten-bronze-structured piezoceramics.

ACKNOWLEDGMENTS

Support from FAPESP and CNPq, two Brazilian research-funding agencies, are gratefully acknowledged. J. E. García wishes to thank the JPI-2012 Santander-Universidades program for their financial support.
REFERENCES


(a) polar axes distribution
unpoled
poled
1/3
1/3
1/3
1/3
1/6

(b) $m_\varepsilon = \frac{\Delta \varepsilon''}{\Delta \varepsilon'}$

(c) $m_{d_{33}} = \frac{\Delta d_{33}^{Im}}{\Delta d_{33}^{Re}}$

$\Delta \varepsilon''$
$\Delta \varepsilon'$
$\Delta d_{33}^{Im}$
$\Delta d_{33}^{Re}$
$f(\text{Hz})$
$T_{DC}(\text{MPa})$