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The nonlinearity and subswitching hysteresis in hard and soft PZT

Maxim Morozov*, Dragan Damjanovic, Nava Setter

Ceramics Laboratory, Swiss Federal Institute of Technology, EPFL, 1015 Lausanne, Switzerland

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Abstract

Nonlinear dielectric response of soft and hard PZT is experimentally studied at subswitching conditions. The correlations between defect disordering and parameters of nonlinear dielectric response and hysteresis are demonstrated and discussed.

Keywords: PZT; Ferroelectric properties

1. Introduction

The dielectric nonlinearity (field dependence of permittivity) and hysteresis in ferroelectric ceramics have been of interest since these materials found application in various electronic devices. Both hysteresis and nonlinearity are undesired in high precision actuators and sensors. In most widely used ferroelectric materials, such Pb(Zr,Ti)O_3 or PZT family, the nonlinearity and hysteresis are primarily due to displacement of domain walls.[1] PZT ceramics are usually prepared with various dopants and additives that improve the electrical properties of the ceramics. Acceptor dopants render materials hard whereas donor dopants lead to soft materials.[2] The defects associated with dopants influence domain walls displacement and thus have an effect on the nonlinearity and hysteresis. This is evident through presence of well known pinched hysteresis in hard ferroelectrics and square hysteresis in soft materials. Most of the studies in the literature on this subject have been focused on large signal response (switching hysteresis). Such studies led to model of hardening in which polar defect dipoles orient along polarization vector in individual domains effectively clamping domain walls.[3] It is interesting that there are still no models that would convincingly explain mechanisms of softening in donor doped materials.

In this paper we show that dielectric nonlinearity and hysteresis at subswitching (subcoercive) fields are sensitive to presence of softening and hardening defects and that their study can give valuable information on defect processes in hard and soft materials. In particular we show that hardening effects can be relaxed by thermally disordering defects and that under those conditions nonlinear behavior of hard ceramics is qualitatively similar to that of soft materials.

2. Experimental

The ceramic samples of $Pb(Zr_{0.58}Ti_{0.42})O_3$ were prepared by conventional solid state process from oxide precursors. The samples were doped with 0.1, 0.5 and 1.0 at.% Fe^{3+} (hard materials) and 0.2, 0.5, and 1.0 at.% Nb^{5+} (soft materials). Dopants were added by mixing Fe_2O_3 and Nb_2O_5 oxides with PbO, TiO_2 and ZrO_2 precursors, assuming dopants substitution on (Zr, Ti) site. The nonlinear dielectric response of the samples was investigated under subswitching ac-fields using lock-in technique. The amplitude of the sinusoidal field applied to the samples varied from 0 to 5 kV/cm and its frequency was 1 kHz. The hysteresis measurements were done using a charge amplifier and an oscilloscope.

3. Results and discussions

In general the nonlinear polarization response to periodic input signal can be described by developing $P(E, t)$ in a

* Corresponding author. Tel.: +1 21 693 5869.
E-mail address: maxim.morozov@epfl.ch (M. Morozov).

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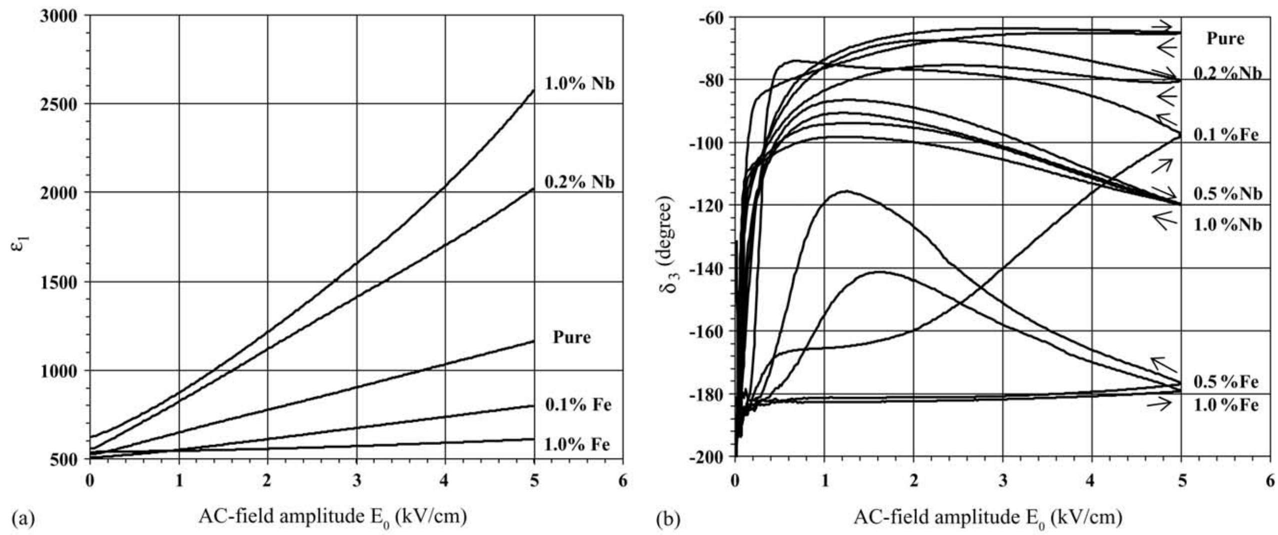

Fig. 1. Dielectric permittivity ε_1 derived from the first harmonic (a) and phase angle of the third harmonic δ_3 (b) of the polarization response as a function of driving ac-field amplitude (1 kHz) for Hard (Fe-doped), pure (undoped) and soft (Nb-doped) $Pb(Zr_{0.58}Ti_{0.42})O_3$ ceramics.

Fourier series. The resulting general function is:

$$P(E_0, t) = \sum_n P'_n(E_0)\sin(n\omega t) + P''_n(E_0)\cos(n\omega t) \qquad (1)$$

where E_0 is the amplitude of the driving field, P_n are Fourier coefficients and components of the complex permittivity are defined by $\varepsilon'_n(E_0) = P'_n(E_0)/E_0$, $\varepsilon''_n(E_0) = P''_n(E_0)/E_0$. Fig. 1a, which shows $\varepsilon_1 = \sqrt{(\varepsilon'_1)^2 + (\varepsilon''_2)^2} = \sqrt{(P'_1)^2 + (P''_2)^2}/E_0$ demonstrates clearly that the nonlinearity of the dielectric response continuously increases as the dopants type and concentration are changed from 1% Fe via undoped samples to 1% Nb. This result is expected and has been discussed by many authors.[4–6] While Fig. 1a shows the permittivity of the response measured at the first harmonic it is interesting to look at information that can be obtained by analyzing other nonlinear parameters.

It has been shown[7,8] that the subswitching polarization hysteresis and nonlinearity in materials whose response is dominated by domain walls displacement in a medium with randomly distributed pinning centers can be described by Rayleigh relations:

$$P(E) = (\varepsilon_{\text{init}} + \alpha_\varepsilon E_0)E \pm \frac{\alpha_\varepsilon}{2}(E_0^2 - E^2) \qquad (2)$$

$$\varepsilon(E_0) = \varepsilon_{\text{init}} + \alpha_\varepsilon E_0 \qquad (3)$$

where $\varepsilon_{\text{init}}$ designates the value of dielectric permittivity ε at zero field and α_ε is called the nonlinear dielectric coefficient. These relations are valid only in the case of perfectly random distribution of the properties of pinning centers for domain walls. When this distribution is not random (as usually is the case) the linear relationship (3) must be replaced by additional terms $\varepsilon(E) = \varepsilon_{\text{init}} + \alpha_\varepsilon E_0 + \beta E_0^2 + \gamma E_0^3 + \ldots = \varepsilon_{\text{init}} + \alpha^*_\varepsilon(E_0)E_0$. The physical justification of these additional terms is easily seen in the framework of Preisach formalism.[9] In those cases, the hysteresis can still be described by Eq. (2) if parameter α is replaced by α^*_ε. The link between hysteresis and nonlinearity indicated by relations (2) and (3) (or their modifications) is one of the most important implications of the Rayleigh law.

Interesting properties of Rayleigh relations can be obtained from the expansion of Eq. (2) into Fourier series considering polarization response to periodic signal $E = E_0 \sin(\omega t)$:

$$P(t) = (\varepsilon_{\text{init}} + \alpha_\varepsilon E_0)E_0\sin(\omega t) - \frac{4\alpha_\varepsilon E_0^2}{3\pi}\cos(\omega t) - \frac{4\alpha_\varepsilon E_0^2}{15\pi}\cos(3\omega t) + \frac{4\alpha_\varepsilon E_0^2}{5\pi}\cos(5\omega t) + \cdots \qquad (4)$$

Note that only odd harmonics are present and that all nonlinear components are quadratic with field and are out-of-phase with the driving sinusoidal signal. This means that, for ideal Rayleigh response (perfectly random distribution of pinning centers), every nonlinear displacement of domain walls is hysteretic. An experimental consequence of this is that all higher harmonics in (4) have phase angle $\pm 90°$. The behavior of real ferroelectric materials often deviates from the ideal Rayleigh behavior, but relationship between hysteresis and nonlinearity still holds. When this is the case (α in Eqs. (2) and (3) must be replaced by α^*) the in-phase nonlinear components will appear in Eq. (4) and the phase angle of higher harmonics will no longer be 90°. But in many other cases, including hard ferroelectric ceramics, the material response is clearly non-Rayleigh. It is most likely that pinning centers in hard ceramics are not randomly distributed but are arranged in such a way to lead to an apparent internal bias field.[3] In this case domain walls do not move in a random potential, but, ideally, in a deep potential well with only one minimum.[10] In such ideal case and at subswitching

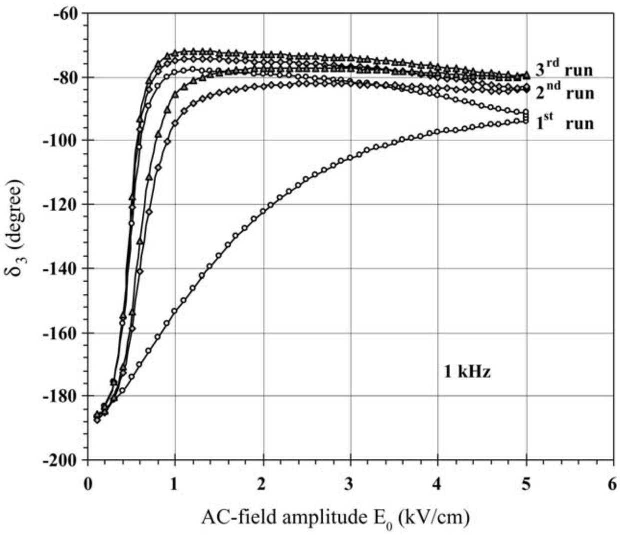

Fig. 2. Effect of field amplitude cycling on the phase angle of the third harmonic (δ_3) of the polarization response for hard $Pb(Zr_{0.58}Ti_{0.42})O_3$ ceramics doped with 0.1 at.% Fe.

weak fields, the displacement of domain walls in hard ceramics is nonlinear but essentially anhysteretic. Thus, clear relationship between nonlinearity and hysteresis that exists in Rayleigh-like systems is lost in hard ceramics. In the case of ideal hard ceramics the phase angle of all higher harmonics is 180° i.e., nonlinearity does not lead to hysteresis. It is clear that the properties of all real materials lay somewhere between these two extreme cases.

The experimental values of phase angles of the third harmonic, δ_3, of hard and soft PZT ceramics are shown on Fig. 1b for increasing and decreasing field amplitude. For simplicity we neglect behavior below threshold field that is evident for most of the samples below approximately 0.5 kV/cm. In the very hard material (1% Fe), and for increasing field, the third harmonic response is predominantly in-phase with the field in quite wide range of ac-field amplitudes. This behavior corresponds to an ideal hard sample. Undoped and soft samples show δ_3 varying around −90°. One slightly hard sample, doped only with 0.1% Fe, demonstrates the transition from predominantly in-phase to predominantly out-phase third

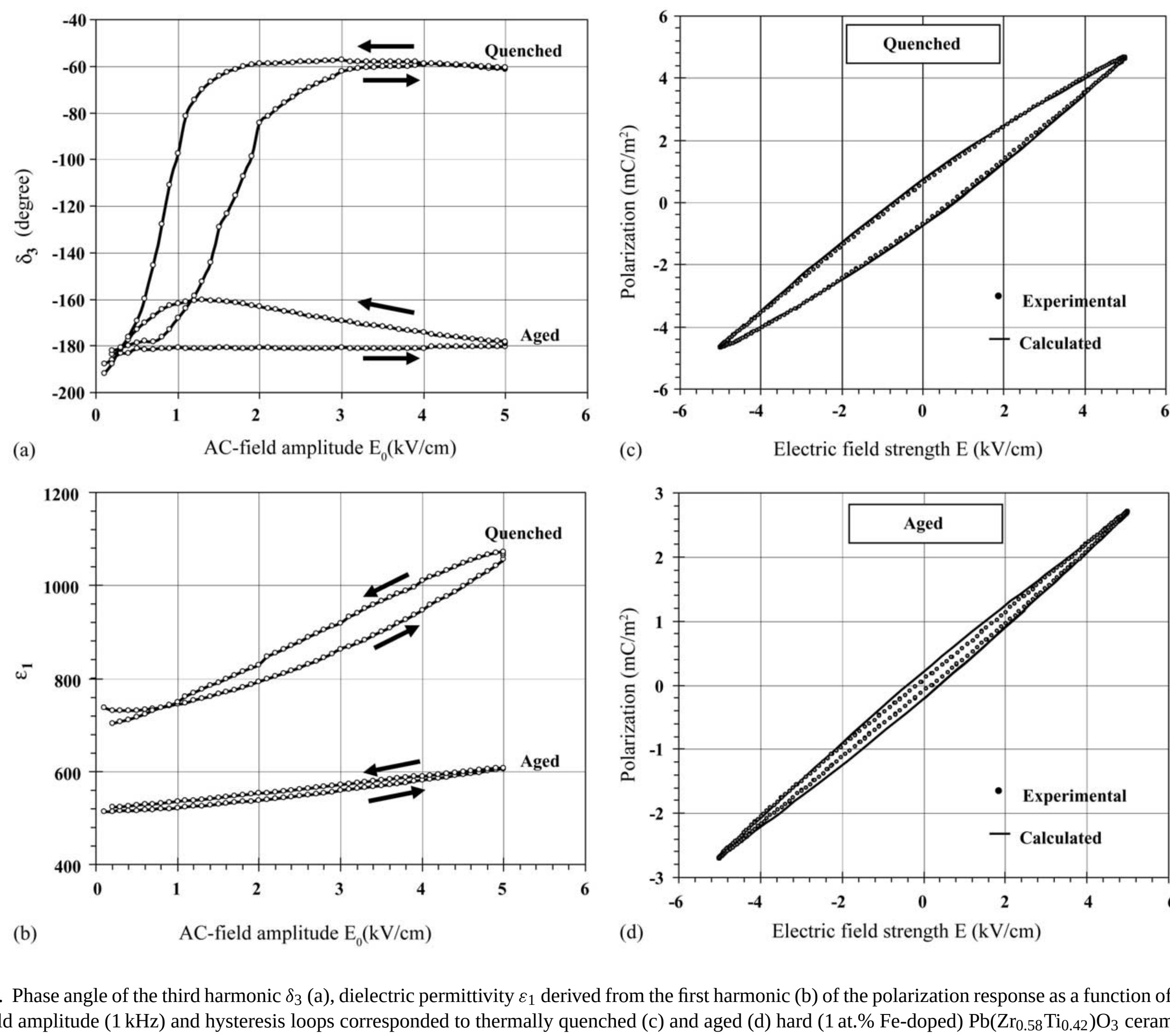

Fig. 3. Phase angle of the third harmonic δ_3 (a), dielectric permittivity ε_1 derived from the first harmonic (b) of the polarization response as a function of driving ac-field amplitude (1 kHz) and hysteresis loops corresponded to thermally quenched (c) and aged (d) hard (1 at.% Fe-doped) $Pb(Zr_{0.58}Ti_{0.42})O_3$ ceramics.

harmonic response as the field is increased. It is interesting to notice, that while pure and soft ceramics demonstrate similar dependence of δ_3 on increasing and decreasing field amplitude, for hard material the field dependence of δ_3 is quite different for increasing and decreasing fields. In Fig. 2 the results of the field cycling are shown for a sample doped with 0.1% Fe. This figure demonstrates that applied electric field as well as time during which the field is applied changes the properties of this material. This may be consequence of well known aging-deaging effects in hard ferroelectric ceramics.[3,11]

The defect-controlled domain pattern in hard PZT can be destabilized by thermal quenching. The dependences of the dielectric permittivity (ε_1) and phase angle of the third harmonic δ_3 on field amplitude for thermally quenched (disordered pinning centers) and aged (ordered pinning centers) in hard PZT ceramics are shown in Fig. 3a and b along with related hysteresis loops. The thermal quenching leads to an increase of the nonlinearity of dielectric permittivity and also affects δ_3. After quenching the hysteretic, out-phase component, is dominant in the third harmonic response. As expected, in quenched samples the hysteresis and nonlinearity are found to be relatively well described by corresponding Rayleigh relations (Fig. 3a and c). This is not the case for the aged hard ceramics (Fig. 3b and d) where the hysteresis calculated from nonlinearity using Eqs. (2) and (3) is larger than actual hysteresis indicating that at least part of nonlinearity is not hysteretic.

4. Conclusions

Analysis of the polarization nonlinearity and subswitching hysteresis in soft, udoped and hard PZT ceramics suggests that soft materials can be described by a relative disorder of pinning centers for the domain walls, while nonlinear behavior of very hard materials indicates strong ordering of pinning centers. The nonlinearity is very sensitive to the state of ordering of pinning centers as demonstrated by quenching experiments. Hard ceramics with thermally disordered pinning centers behave qualitatively as soft materials.

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References

1. Berlincourt, D. and Krueger, H. H. A., Domain processes in lead titanate zirconate and barium titanate ceramics. *J. Appl. Phys.*, 1959, **30**(11), 1804–1810.
2. Jaffe, B., Cook, W. R. and Jaffe, H., *Piezoelectric Ceramics*. Academic, New York, 1971.
3. Carl, K. and Haerdtl, K. H., Electrical after-effects in Pb(Ti,Zr)O_3 ceramics. *Ferroelectrics*, 1978, **17**, 473–486.
4. Pérez, R., Garcia, J. E. and Albareda, A., Nonlinear dielectric behavior of piezoelectric ceramics. In *Proceedings of the 2000 12th IEEE International Symposium on applications of ferroelectrics*, ed. S. K. Streiffer, B. J. Gibbons and T. Tsurumi. IEEE Service Center, Piscataway, NJ, Honolulu, 2001, pp. 443–446.
5. Hagemann, H. J., Loss mechanisms and domain wall stabilization in doped BaTiO3. *J. Phys. C: Solid State Phys.*, 1978, **11**, 3333–3344.
6. Hall, D. A., Nonlinearity in piezoelectric ceramics. *J. Mater. Sci.*, 2001, **36**, 4575–4601.
7. Boser, O., Statistical theory of hysteresis in ferroelectric materials. *J. Appl. Phys.*, 1987, **62**(4), 1344–1348.
8. Taylor, D. V. and Damjanovic, D., Domain wall pinning contribution to the nonlinear dielectric permittivity in Pb(Zr,Ti)O_3 thin films. *Appl. Phys. Lett.*, 1998, **73**(14), 2045–2047.
9. Robert, G., Damjanovic, D. and Setter, N., Preisach distribution function approach to piezoelectric nonlinearity and hysteresis. *J. Appl. Phys.*, 2001, **90**(5), 2459–2464.
10. Robels, U. and Arlt, G., Domain wall clamping in ferroelectrics by orientation of defects. *J. Appl. Phys.*, 1993, **73**(7), 3454–3460.
11. Jonker, G. H., Nature of Aging in Ferroelectric ceramics. *J. Am. Ceram. Soc.*, 1972, **55**, 57–58.