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Mechanically clamped PZT ceramics investigated by First-order reversal curves diagram

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Abstract

The First Order Reversal Curves (FORC) diagrams method was developed for characterizing the switching properties of ferroelectrics. In the present paper, the FORC method was applied for hard Pb(Zr,Ti)O_3 ceramics with symmetric and asymmetric clamping. An ideal high-oriented single-crystalline ferroelectric with rectangular P(E) loop would be characterised by a delta-function FORC distribution, while real ferroelectrics and mostly the polycrystalline ceramics show dispersed FORC distributions. All the investigated ceramics show FORC distributions with non-Gaussian shape, slightly elongated along the coercitive axis, meaning a high dispersion of the energy barriers separating the two bi-stable polarizations ±P. The degree of dispersion is enhanced by clamping. The maximum FORC coercivity is located at ~ (1.9-2) MV/m for all the hard ceramics. The FORC cycling experiment causes the reversal of the initial poling and result in a positive/negative bias on the FORC diagrams. According to the observed features, it results that FORC coercivity is more related to the nature of the material, while the bias field is more sensitive to the electrical and mechanical boundary conditions in which the ferroelectric ceramics evolves while switching.

***Keywords**: hard PZT, clamping, First-order reversal curves (FORC)*

I. Introduction

The polarization switching is the most important characteristics of ferroelectrics, macroscopically related to the hysteresis loops $P(E)$. The polarization reversal is a very complex and inhomogeneous phenomenon, involving complicated reversible/irreversible domain wall motions and being strongly influenced by local material properties and/or to local electric fields. The macroscopic polarization under a given field sequence is an average property of the overall local responses. A classical method for describing hysteretic responses is the Preisach model, a mathematical approach initially formulated for magnetic systems, which considers the resulting loops as being a statistically averaged sum of independent rectangular hysteresis local loops attributed to some dipolar entities [1–3]. In the pioneering works of Turik [3], the Preisach model was proposed for describing hysteresis loops also in ferroelectrics; most recently the Preisach approach has been largely applied for characterization of the switching properties of ferroelectric films and ceramics [4–7]. While applying the classical Preisach model for switching in ferroelectrics, the sample is considered to consist of a collection of independent elementary bi-stable units (described by ide-

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al rectangular hysteresis operator called "hysteron"), each one being characterized by its positive/negative coercive fields E_c^+, E_c^- (or alternatively, coercive and bias fields E_c, E_{bias}). The polarization response of a given ferroelectric under a field-sequence is fully described by a double-integral of the Preisach distribution function over all the possible switching thresholds of the elementary hysteresis operator, i.e. over all the coercive and bias fields [1,2].

Inspired by the Preisach approach, the first-order reversible curves (FORC) distribution was proposed to identify the Preisach distribution within the Classical Preisach Model (CPM) for magnetic systems [1] and then extended to any hysteretic system [8], having a higher degree of generality because is not limited to any model restriction. It was extensively applied in past years for describing switching phenomena in ferroics, including ferroelectrics [9–14]. The application of the FORC method involves simple experiments, in which the system's polarization $p_{FORC}^{\pm}(E_r, E)$ is recorded when the system is cycled between a maximum saturation field ($\pm E_{sat}$) and a set of variable reversal fields $E_r \in (\pm E_{sat}, \mp E_{sat})$. The FORC diagram is a contour plot of the FORC distribution $\rho^{\pm}(E_r, E)$, defined as the mixed second derivative of polarization with respect to E and E_r [9]:

$$\rho^{\pm}(E_r, E) = \frac{1}{2}\frac{\partial^2 p_{FORC}^{\pm}(E_r, E)}{\partial E_r \partial E} = \frac{1}{2}\frac{\partial \chi_{FORC}^{\pm}}{\partial E_r} = \rho(E_c, E_{bias}) \quad (1)$$

where $\chi_{FORC}^{\pm}(E_r, E)$ are the differential susceptibilities measured along the FORCs. The low-field (reversible) contribution of the FORC distribution to the polarization is:

$$\rho_{rev}^{\pm}(E_r) = \lim_{E \to E_r, E > E_r} \rho_{FORC}^{\pm}(E_r, E) \quad (2)$$

and $E_c = (E - E_r)/2$, $E_{bias} = (E + E_r)/2$ play the role of local coercive and bias fields, respectively, and consequently, $\rho(E_c, E_{bias})$ becomes a distribution of the switchable units over coercive and interaction (bias) fields. The application of FORC investigation for a few specific ferroelectric systems demonstrated the high sensitivity of this method in describing the ratio of reversible/irreversible contributions to the ferroelectric polarization [9,10], fatigue effect in films and ceramics [9,10,13], composition and grain size-induced ferroelectric-relaxor crossover [12,14], the role of anisotropic porosity in $PbZr,TiO_3$ (PZT) ceramics [13], tunability [12,14] etc. Being related to the reversible/irreversible domain walls movements, they should be also sensitive to the electrical and mechanical boundary conditions.

Piezoelectric materials and mainly PZT ceramics are widely used for applications in microelectronics or power transducers. In order to suit some specific requirements for certain applications, different properties are induced by doping with various ions as Nb, Li, Er, Fe, etc., giving rise to *hard* or *soft* PZT [15,16]. In PZT compositions (near the morphotropic phase boundary MPB), several acceptor ions can be incorporated into the A site (e.g. K^+, Na^+) or B site (e.g. Fe^{3+}, Al^{3+}, Mn^{3+}) in *hard* PZT and several donor ions at the A site (e.g. La^{3+}) or B site (e.g. Nb^{5+}, Sb^{5+}) in *soft* PZT. In general, hard PZTs are difficult to pole and usually have less pronounced piezoelectric characteristics [16]. The acceptor dopants create oxygen (anion) vacancies, while donor dopants create metal (cation) vacancies and facilitate domain wall motion in the material. In general, acceptor doping creates *hard* PZT, while donor doping creates *soft* PZT. *Hard* and *soft* PZT's generally differ in their piezoelectric constants: piezoelectric constants are proportional to the polarization or to the electrical field generated per unit of mechanical stress, or alternatively is the mechanical strain produced by per unit of electric field applied. In general, *soft* PZT has higher piezoelectric constant, but larger losses in the material due to internal friction. In *hard* PZT, domain wall motion is pinned by the impurities, thereby lowering the losses in the material, but at the expense of a reduced piezoelectric constant.

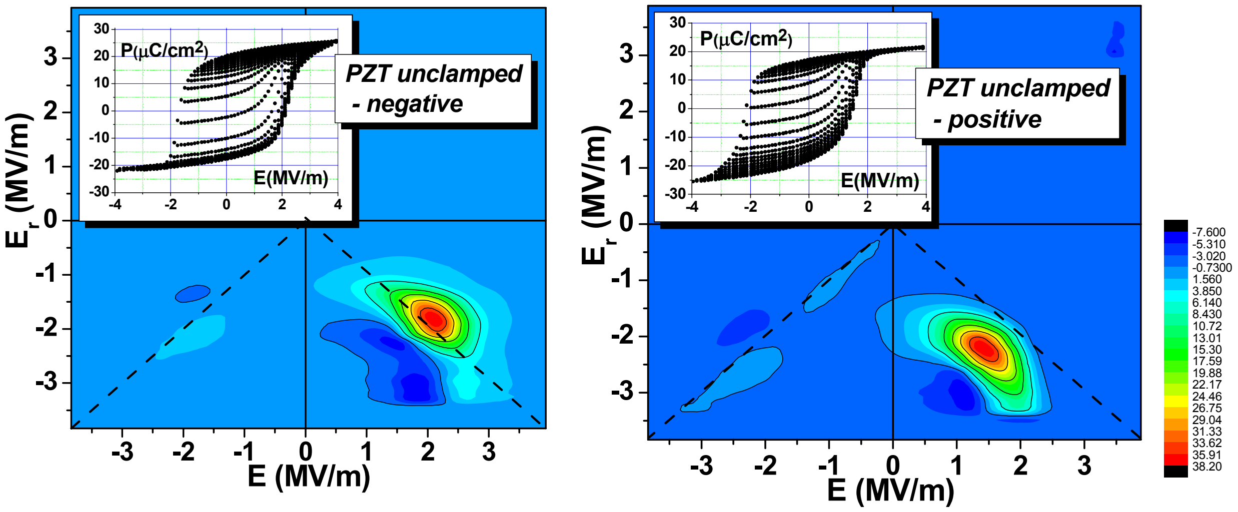
The switching responses of piezo/ferroelectrics are strongly affected by electrical and mechanical boundary conditions, in addition to other material and input excitation parameters (field type, history, etc.) and temperature [15]. In the present paper, the FORC method is used in an attempt to observe some specific features of the switching characteristics in hard PZT ceramics with different types of clamping [17–19].

II. Experimental

A few PZT piezoelectric ceramics with hard (PZT8D) characteristics for transducers [17–19] (unclamped, symmetric/asymmetric clamping with metal plate or cymbal) [20,21] were used in order to evidence, if present, some effects related to the role of mechanically clamping on the FORC diagram characteristics. Prior to the experiment, the ceramics have been poled at room temperature at a field of $E = 3$ MV/cm. The experimental FORC loops were recorded at room temperature under a sinusoidal waveform of various amplitudes and at the frequency of 1 Hz, by using a modified Sawyer-Tower circuit, under the following field sequence [22]: (i) Saturation under a positive field $E \geq E_{sat}$; (ii) ramping the field down to a negative reversal value E_r, following the descending branch of the major hysteresis loop; (iii) increasing the field back to the positive saturation, describing the positive FORC $p_{FORC}^{+}(E_r, E)$. Positive (from positive saturation towards the negative one with respect to the poling direction) and negative (from negative saturation towards positive one) experiments were performed. The FORC diagram was calculated as described in details in the refs. [9] and [13]. An ideal high-oriented single-crystalline ferroelectric with rectangular $P(E)$ loop should be characterised by a delta-function FORC distribution (zero everywhere, except for the values of its coercive and bias field), while real ferroelectrics and mostly the polycrystalline ceramics show dispersed FORC distributions, due to the fact that their dipolar unit switch at various field values around the coercive and bias fields. An ideal relaxor system practically switches at zero coercivity, since its $P(E)$ dependence has almost zero coercivity. In addition, the ideal relaxor has almost zero switching polarisation and this means that in the FORC representation it should be described by a distribution centred on zero coercivity (on the first bisector of the Preisach plane), having only reversible polarisation component. A real relaxor characterised by an almost continuous distribution of the energy barrier values corresponding to the equilibrium polarisation should present a continuous FORC distribution (with non-separated reversible $E_c = 0$ and irreversible $E_c \neq 0$ components) along the coercivity axis (i.e. the second bisector of the Preisach plane) from zero to higher field values [22].

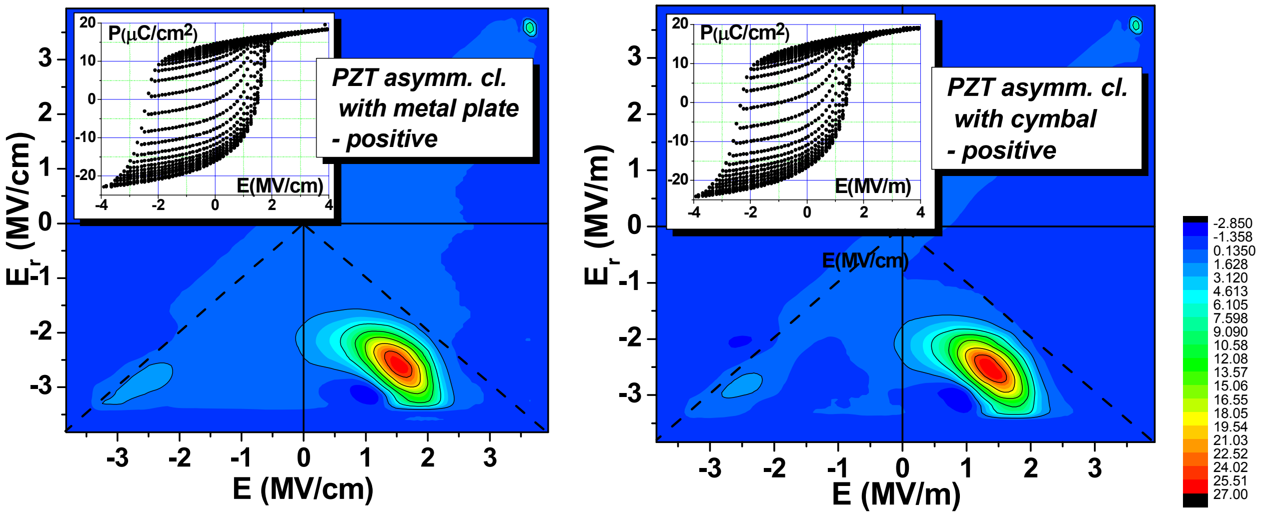
III. Results and discussion

The computed FORC diagrams obtained for the hard PZT ceramics are shown in the Figs. 1-3, together with the corresponding experimental FORC loops. First of all, it was studied the effect of the positive/negative FORC experiment with respect to the poling direction on the unclamped PZT samples; the results are comparatively shown in Fig. 1. The diagrams characteristic to the unclamped ceramics present excellent switching characteristics, with zero reversible component (no distribution along the first bisector of the Preisach plane) and sharp irreversible switching contribution to the polarization (described by a well-localized maximum around the field values of E = 2 MV/cm, E_r = –2 MV/m), as shown in the Fig. 1. The distributions are clearly biased (shifted along the second bisector in the Preisach plane) and well localized. As expected, the bias sign is dependent on the direction of the applied field (the shifts are positive or negative with respect with the second bisector of the Preisach plane). The value of this shift (i.e. the distance measured perpendicular from the maximum to the second bisector) is slightly higher for positive field (Fig. 1b) than for the negative one (Fig. 1a), indicating a kind of as-grown bias of the PZT unclamped sample. In addition, the positive FORC (Fig. 1b) is slightly incomplete by comparison with the negative one (Fig. 1a), meaning that there are in this case still some dipolar units needing higher fields for switching that for the negative one. The explanation for the observed differences is due to a kind of non-symmetry of the ferroelectric/electrodes structure (even unclamped) with respect with the sign of the applied field, possible induced by processing. In spite of an expected local inhomogeneity related to the doping of hard PZT ceramics, the samples do not show any relaxor character [14], since the reversible/irreversible components are very well separated (i.e. the threshold field or energy barriers for switching have always non-zero values [15], since no dipolar units are found in the diagram for fields below 1 MV/m). All the dipolar units are already switched at fields below 3 MV/m, giving rise to a complete FORC diagram. The positive FORC distribution (Fig. 1b) is slightly non-symmetric with respect to the negative one (Fig. 1a), both being non-Gaussian. It is worth to mention that a Gaussian distribution would be represented in the Preisach plane by circular level curves as representing the FORC diagram. Contrary to the original hypothesis of the classical Preisach model for which double-Gaussian dis-



a) b)

Figure 1. FORC diagrams in unclamped PZT obtained for: (a) negative, (b) positive cycle (i.e. from negative/positive saturation towards the positive/negative one, with respect to the poling direction). Inset: *P*(*E*) FORC loops and colour code



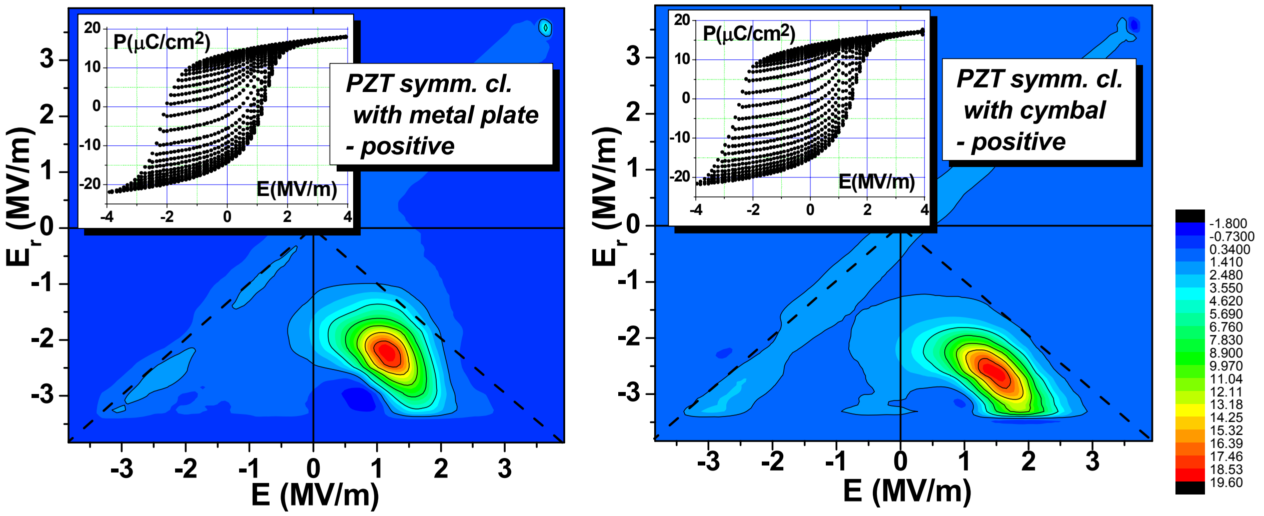
a) b)

Figure 2. FORC diagrams obtained for a positive cycle in asymmetrically clamped PZT: (a) with metal plate, (b) with cymbal. Inset: *P*(*E*) FORC loops and colour code.

tribution over (E_c, E_{bias}) were proposed [1–5], the large majority of ferroelectric systems, including the present ones, show non-symmetric distributions as due to many reasons, like the interactions between the hysterons, local fields, charged defects, "dead-layer" effects, etc. [6,7,9–11,13,14]. The values for the coercivity E_c and bias E_{bias} corresponding to the maximum of the irreversible FORC and representing the characteristic fields activating the largest majority of hysterons are: E_c = 1.95 MV/m for both cases, while a small change in the sign of the bias is induced by the poling direction: E_{bias} = 0.45 MV/m (positive FORC) and E_{bias} = –0.05 MV/m (negative FORC). It results that the initial bias induced by poling can easily be modified in these systems by the FORC experiment itself and is very sensitive to the field history of the ceramics, while the coercivity is practically unchanged. The bias field changes the sign after the FORC experiments with very similar values in all the investigated samples from values in the range E_{bias} = (0.45, 0.6) MV/m (for positive FORC) to E_{bias}= (–0.05, –0.2) MV/m (for negative FORC), the shift of the bias field as induced by the FORC experiment of ~ 0.75 MV/m being observed for the non-symmetric clamping. As expected, the non-symmetric mechanical clamping seems to favour a larger bias in the hard PZT ceramics than the symmetrical clamping.

The positive FORC diagrams characteristic to asymmetric clamping are shown in the Fig. 2. While the macroscopic polarization is smaller than in the unclamped ceramics, no major changes of the distributions were induced by the asymmetric clamping, except a small increase of the coercive field characteristic to the maximum distribution E_c = (2–2.1) MV/m by comparison with the unclamped ceramics (Fig. 1b) and irrespective to the fixing type (metal plate or cymbal) of clamping. This results in an incomplete switching (some dipolar units need higher fields to switch than the available experimental fields, causing an incomplete FORC distribution). The FORC diagrams look just shifted along the coercivity axis (second bisector of the plane (E, E_r)) with a small quantity of (0.05–0.015) MV/m, meaning that all the dipolar units of the clamped structures need a slightly higher field for switching than the unclamped ceramics. Such an effect is produced by the homogeneous stress induced by the mechanical clamping, which is the same if metal plate or cymbal structure are employed.

The symmetrical clamping (Fig. 3a,b) causes more visible effects on the FORC diagrams, in spite the *P(E)* loops look very similar and this demonstrates the importance of the FORC method used as additional tools to detect small changes of the ferroelectric structures induced by clamping, in this case. A small reversible contribution to the polarization located on the first bisector axis of the plane (E, E_r) appears, although the FORC distribution remains still sharp and well localized, i.e. the overall switching behaviour is not serious altered by clamping. Again the type of fixing has practically no role on the observed properties: similar coercive and bias fields are characterizing the irreversible part of the distribution. However, the FORC diagram (Fig. 3b) shows a higher dispersion both along the bias field axis (first bisector), but mainly along the coercivity axis (second bisector). This means a higher degree of the local inhomogeneity, causing various values of the energy barriers separating the two bi-stable positions ±P of the ferroelectric ceramic. At the fields available in this experiments (< 4 MV/m), still some dipolar units were not switched, as proved by the incomplete FORC distribution at high fields (Fig. 3b).



a) b)

Figure 3. FORC diagrams obtained for a positive cycle in symmetrically clamped PZT: (a) with metal plate, (b) with cymbal. Inset: *P*(*E*) FORC loops and colour code

The observed properties of hard PZT ceramics are in agreement with the domain boundary pinning effects which are believed to be the origin of hard ferroelectric behaviour [5,15]. Interactions between defects and domain boundaries stabilize the microstructure and make the domain wall motion more difficult. Additional contributions (e.g. increase of the density of pinning centres, increase of the local energy barriers for switching) are caused by clamping, which also influences the domain reorientation processes by imposing specific mechanical boundary conditions. The present results are also in agreements with the results of the investigations of switching properties in hard/soft PZT ceramics subjected to compressive stresses [23]. The stress-induced domain wall suppression processes caused by clamping by its forced accommodation to rigid substrates/bonds are responsible for the changes observed in the switching properties, as probed by the FORC analysis.

IV. Conclusions

Hard $Pb(Zr,Ti)O_3$ ceramics with various types of clamping are investigated by means of First-order reversal curves (FORC) diagrams. For unclamped ceramics, the FORC distributions show excellent switching character, with almost zero reversible contribution and well separated reversible/irreversible components. Non-Gaussian and slightly elongated along the coercitivity axis FORC distributions were observed. A small reversible component was induced by symmetrical clamping. The nature of fixing (cymbal or metal plate) has no influence on the switching parameters. Very small increase of coercivity is caused by clamping and overall shift towards higher coercive fields for symmetric clamping, resulting in an incomplete FORC distribution. The sign of bias field is changed by the positive/negative FORC cycling. The higher bias and shift of the bias as induced by positive/negative FORC experiment is favoured in asymmetric clamped structures. Apart the small observed effects, the FORC coercivity is less sensitive to poling fields and mechanical clamping type, being more related to the nature of the material than to the electrical and mechanical boundary conditions, while the bias field is more affected by the electrical and mechanical boundary conditions during polarization reversal.

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