First order reversal curves diagrams for describing ferroelectric switching characteristics

Liliana Mitoseriu[1,*], Laurentiu Stoleriu[1], Alexandru Stancu[1], Carmen Galassi[2], Vincenzo Buscaglia[3]

[1]*Department of Physics, Al. I. Cuza University, Bv. Carol I 11, Iasi 700506, Romania*
[2]*Institute of Science &Technology of Ceramics ISTEC-CNR, Via Granarolo 64, Faenza I-48018, Italy*
[3]*Institute of Energetics & Interphases IENI-CNR, Via de Marini 6, Genoa I-16149, Italy*

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Abstract

First Order Reversal Curves (FORC) are polarization-field dependences described between saturation field E_{sat} and a variable reversal field $E_r \in (-E_{sat}, E_{sat})$. The FORC diagrams were proposed to describe some characteristics of the switching process in ferroelectrics. The approach is related to the Preisach model which considers the distribution of the elementary switchable units over their coercive and bias fields. The influence of the anisotropic porosity in $Pb(Zr,Ti)O_3$ bulk ceramics on the FORC distributions demonstrated the existence of a positive/negative bias as a result of the confinement induced by anisotropy. The reducing of grain size in $Ba(Zr,Ti)O_3$ ceramics causes an increase of the ratio of the reversible/irreversible components of the polarization on the FORC distribution indicating the tendency of system towards the superparaelectric state. The FORC method demonstrates to provide a kind of 'fingerprinting' of various types of switching characteristics in ferroic systems.

Keywords: *switching, Preisach model, First order reversal curve, PZT*

I. Introduction

The hysteretic phenomena are related to the lag between the system's input and output [1,2]. The most common lag-effects are observed under applying a magnetic or electric variable field (e.g. sinusoidal) and, the magnetic moment or, respectively the polarization, follow the same time dependence of the field, but with a certain phase-lag. One classical method of describing hysteresis is the Preisach model [3]. It was developed for describing interacting system of single domain ferromagnetic particles. In this approach, each isolated particle of the system has its individual hysteresis loop depending on the particle's shape, anisotropy, volume, etc. Smaller particles do not have a hysteresis loop and the dependence of the magnetic moment on the applied field is fully reversible. This behaviour is called superparamagnetic and is described by the fact that the energy barrier existing between the two stable equilibrium orientations (characteristic to a single domain ferromagnetic particle with hysteresis) is smaller or at least comparative with thermal energy [4,5]. A particulate recording medium with stable single-domain particles, well aligned with their easy axes along the applied field is usually taken as reference for the Classical Preisach Model [6]. The elementary hysteresis loop used in the initial version of the Preisach model (known as the Classical Preisach Model - CPM) is called *hysteron* or *rectangular hysteron* [7–9]. In an aligned magnetic particulate system each particle is associated to a hysteron. However, the hysteresis loop of one isolated particle is not identical with the loop of the same particle when is measured inside the system during various magnetization/polarization processes. In CPM is assumed that the *interaction field* created by all the neighbours is aligned with the easy axes and the applied field and does not depend on the total magnetic moment of the sample. The effect of this field is a shift of the hysteron along the field axis with an amount equal to the interaction field. If the interaction field is positive, the positive switch will be facilitated by this field, while the negative switch is more difficult. So, the loop will be shifted in the negative direction of the field axis by a positive interaction

* Corresponding author: tel: +40 232 201 176
fax: +40 232 201 205, e-mail: *lmtsr@uaic.ro*

field and in the positive direction of the field axis by a negative interaction field. As a consequence of interactions the switching fields are different in absolute value (Fig. 1) and in the Preisach model these fields are used as coordinates in the Preisach plane (Fig. 2).

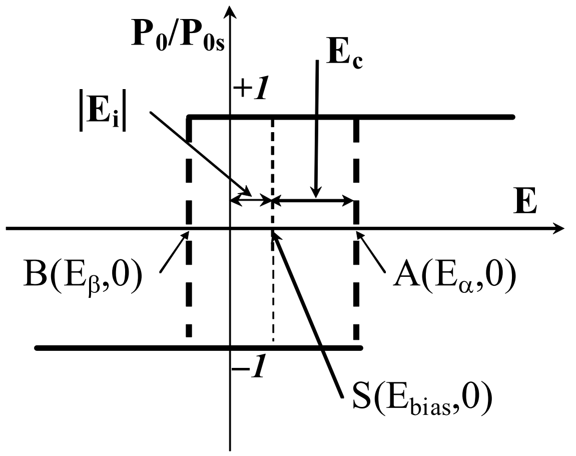

Figure 1. A hysteron associated to the point of co-ordinates (E_α,E_β) in the Preisach plane. The coercive field of particle is $E_c = E_\alpha - E_\beta/2$ and the interaction field is $E_i = -E_{bias} = (E_\alpha + E_\beta)/2$ (E_{bias} is the shift of the rectangular hysteresis loop in the E direction). The polarization is P_0 and the saturation polarization is P_{0s}

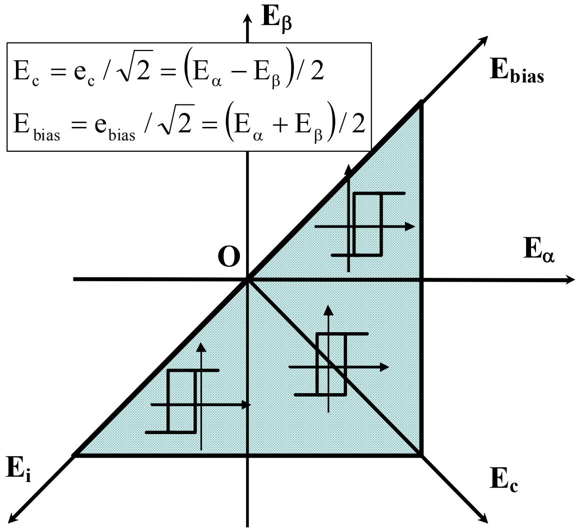

Figure 2. The Preisach plane: E_c is the coercive field of the particle, E_{bias} is the shift of the rectangular hysteresis loop associated to any point in the Preisach plane and $E_i = -E_{bias}$ is the interaction field

The magnetic moment or polarization of a hysteron is associated to a generic point with the switching fields as co-ordinates (in the Preisach plane E_α is the positive and E_β is the negative switching field). The Preisach distribution is obtained by associating all the magnetic moments (or dipolar units) to the Preisach plane (Fig. 2). The Preisach formalism was largely applied for describing the switching properties of ferroics, particularly ferromagnetic [6,7] superconductors [8] spin glasses [9] and, more recently, the polarization and piezoelectric responses in ferroelectric systems [10–14].

II. The First Order Reversal Curve diagram formalism

Derived from the Preisach formalism, a new method of investigation was proposed for describing the switching properties of ferroelectrics, based on the First Order Reversal Curves (FORC) analysis [13,15–17]. This approach is related to the Preisach models, but it has a higher degree of generality and is not limited to any model restriction. It involves measurements of minor hysteresis loops between saturation E_{sat} and a variable reversal field $E_r \in (-E_{sat}, E_{sat})$ according to the sequence: (i) saturation under a positive field $E \geq E_{sat}$; (ii) ramping down to the reversal value E_r, when the polarization follows the descending branch of the Major Hysteresis Loop (MHL); (iii) increasing the field back to the positive saturation, when the polarization is a function of both the actual field E and of the reversal field E_r. The FORC family starting on the descending MHL branch is denoted as $p^-_{FORC}(E_r, E)$ (Fig. 3). The FORC diagram is a contour plot of the FORC distribution, defined as the mixed second derivative of polarization with respect to E_r and E:

$$\rho^-(E_r, E) = \frac{1}{2}\frac{\partial^2 p^-_{FORC}(E_r, E)}{\partial E\, \partial E} = \frac{1}{2}\frac{\partial}{\partial E}\left[\chi^-_{FORC}(E_r, E)\right] \quad (1)$$

in which $\chi^-_{FORC}(E_r, E)$ are the differential susceptibilities measured along the FORCs. The 3D-distribution $\rho(E_r,E)$ describes the sensitivity of polarization with respect to the reversal E_r and actual electric field E or, alternatively, $\rho(E_c,E_i)$ is a distribution of the switchable units over their coercive and bias fields, being identical with the Preisach distribution for Classical Preisach systems [6]. The FORC method is a simple experimental and model independent technique, applicable for describing any ferroic system. Another important advantage of the method represents the possibility it offers to evaluate separately the reversible and irreversible contributions to the total polarization by using the same set of experimental data, together with a proper numerical procedure [15]. The reversible part of the FORC distribution, as due to the low-field contributions to the polarization is calculated as

$$\rho^{\pm}_{rev}(E_r) = \lim_{E \to E_r, E > E_r} \rho^{\pm}_{FORC}\left(E_r, E\right) \quad (2)$$

The reversible contribution revealed by FORCs can be compared with the results obtained by other investigations such as the Rayleigh loops or the low-signal capacitance measurements and gives important information on the sub-switching regime of the polarization-field dependence in a given ferroelectric system.

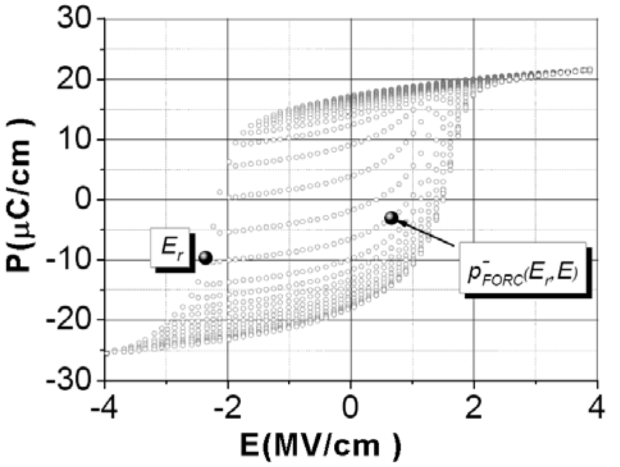

Figure 3. The definition of the First Order Reversal Curves (FORC) $p^-_{FORC}(E_r, E)$ [16]

By analysing the FORC distributions, a few effects related to the role of field frequency (kinetic effects), to the porosity and clamping (mechanical and electrical boundary conditions), crystallinity, anisotropy, grain size, etc. were observed. The main relevant results are reviewed in the following.

III. Results and discussion

3.1. The role of the bias field

A few PZT piezoelectric ceramics with hard characteristics were investigated [19]. Prior to the FORC experiment, the ceramics have been poled at E = 3 MV/cm. The experimental FORC loops were recorded at room temperature under a sinusoidal waveform of various amplitudes and frequencies by using a modified Sawyer-Tower circuit, under the field sequence described before. The FORC diagram was calculated as described in details in the refs. [15,16]. Fig. 4 shows the FORC distribution obtained for a PZT unclamped ceramic [19]. The distribution is non-Gaussian, well localized and clearly biased. In spite of an expected local inhomogeneity related to the doping of hard PZT ceramics, the samples do not show any relaxor character, since the reversible/irreversible components are very well separated (i.e. the threshold field or energy barriers for switching have always non-zero values [20], 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 3MV/m, giving rise to a complete FORC diagram. As result of the positive poling, the sample shows a bias, which is clearly shown as a shift of the FORC distribution maximum along the bias axis (Fig. 4).

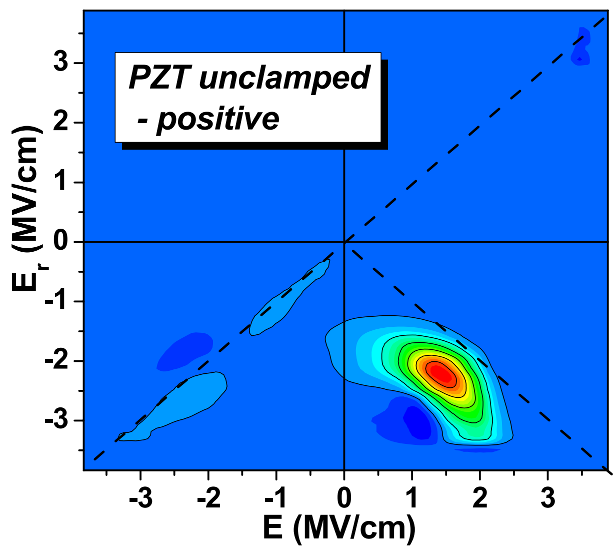

Figure 4. FORC distribution obtained for a PZT unclamped ceramic showing a bias due to a positive poling (shift of the maximum distribution along the bias axis)

3.2 The role of porous anisotropy

The role of porous anisotropy of PZT ceramics on the FORC characteristics were investigated in detail in the ref. [16]. By using PZT porous ceramics with elongated pores for which the electric field for the FORC experiments was applied either parallel or perpendicular to the pore long axis, two different boundary conditions for the polarization evolution under field were realised. Due to the lateral or forward dipolar coupling caused by the confining of the ferroelectric system created by the elongated pores, a positive or negative bias was obtained on the *P(E)* loops of the same PZT ceramic. The positive/negative bias is well described on the FORC distributions (Fig. 5). The experimental findings were explained on the basis of a dipolar model, for which a positive/negative bias on the computed FORC distributions was computed [16].

3.3. The role of the grain size

Recently, a systematic study on the composition and grain size induced ferroelectric-relaxor crossover in $Ba(Zr_{0.1}Ti_{0.9})O_3$ (BZT) ceramics was performed [17]. One of the most interesting results of this study is related to the deformation of the FORC distribution when reducing the ceramic grain size. The results are shown in the Fig. 6, in which the FORC distributions of two ceramics with the same composition and two grain sizes of 0.75 μm and 3.3 μm are shown. The maximum is located at low coercivities, of ~5 kV/m for both BZT ceramics, indicating low energy barriers for the large part of irreversible domain walls movements. Only a small number of dipolar units are switchable under higher fields. There is not a net separation between the reversible (along the bias axis E_c = 0) and the irreversible (for E_c = 0) components of the polarization on the FORC distribution as in other ferroelectrics, it is likely that a continuous distribution of energy barriers from zero to non-zero values is characteristic to these BZT ceramics. By considering also the compression of the FORC diagram towards E_c = 0 with diminishing grain size, it seems that a tendency of the BZT system towards the

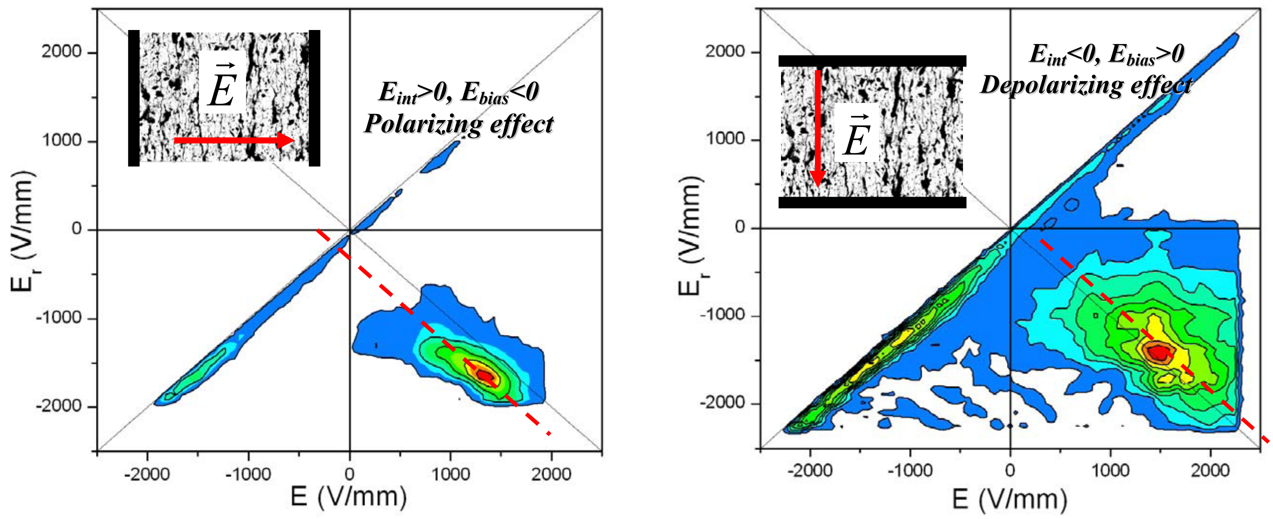

Figure 5. FORC distributions obtained for porous PZT ceramics showing: polarizing, (b) depolarizing effect due to the porous anisotropy

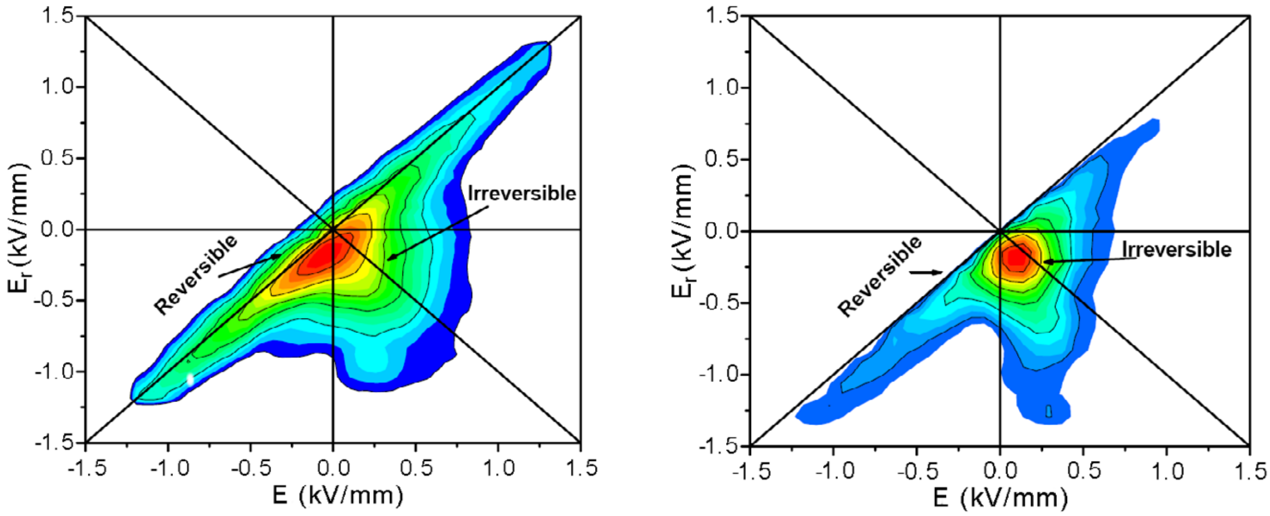

Figure 6. FORC distributions of $Ba(Zr_{0.1}Ti_{0.9})O_3$ ceramics: (a) 0.75 µm, (b) 3.3 µm. By reducing grain size, the FORC distribution is compressed towards the $E_c = 0$ axis

superparaelectric switching when reducing the grain size might cause the observed behaviours.

IV. Conclusions

The experimental-numerical method of investigation of First Order Reversal Curves (FORC) diagrams, related to the Preisach model approach was proposed to describe some specific characteristics of the switching process in ferroelectrics. In the present paper, a few features revealed on the FORC distributions related to: (i) the bias caused by poling, (ii) the influence of the anisotropic porosity on the FORC distributions demonstrated the existence of a positive/negative bias as a result of the confinement in PZT ceramics and (iii) the role of reducing grain size in BZT ceramics related to the tendency of system towards the superparaelectric state are shown. The method proved to be an additional valuable tool in describing the ferroelectric polarization processes in particular systems.

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