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FIRST ORDER REVERSAL CURVES DIAGRAMS APPLIED FOR THE FERROELECTRIC SYSTEMS

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First Order Reversal Curve (FORC) diagrams are proposed for the description of switching properties in ferroelectrics. Non-symmetric P(E) hysteresis loops of $Pb(Zr,Ti)O_3$ ferroelectric films, recorded between various reversal fields and the saturation field were used in order to calculate the FORC distributions. A clear separation of the reversible and irreversible contributions to the ferroelectric polarization was obtained on these diagrams. The FORC diagrams are sensitive to various parameters, such as frequency, fatigue state and crystallite orientation in the sample. The FORC susceptibilities show the critical regimes for the linear/nonlinear behaviour of the ferroelectric material and their characteristics.

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1. Introduction

The First Order Reversal Curves (FORC) diagrams represent a method of investigation [1] which was proposed to describe the switching properties of various materials, such as geological ferromagnetic systems, recording media, spin glasses and ferrofluids [1-2]. This method involves the measurement of minor hysteresis loops obtained by cycling the sample between saturation and a variable reversal field. For the magnetic materials, the experimental FORC diagrams give a more accurate description of the hysteretic system than other macroscopic measurements and rich information on the microscopic mechanisms involved in the magnetic switching [1-4]. Together with the acquisition of experimental FORCs for various hysteretic systems, many efforts have been dedicated in modeling, aimed to disclose the information contained in these diagrams [3-5]. Since the method can be applied for any hysteretic system with non-local memory [6], it was recently proposed for the first time in describing the switching characteristics of the ferroelectric materials [7]. In the present work, experimental FORC diagrams of $Pb(Zr,Ti)O_3$ (PZT) thin films were obtained and an interpretation of the mechanisms involved in the observed patterns is proposed.

2. Experiment and definition of the FORC diagrams

RF – sputtered $Pb(Zr,Ti)O_3$ (PZT) films with Pt electrodes were used for experiments [8]. The P(E) hysteresis loops have been measured with a FCE ferroelectric tester (Toyotechnica). Single pulse hysteresis measurements in 500Hz triangular signal with a maximum amplitude of 10V have been performed according to the sequence: (i) saturation under a positive field $E \geq E_{sat}$ =400kV/cm; (ii) ramping the field down to a 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

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family starting on the descending MHL branch is denoted as $p^{-}_{FORC}(E_r, E)$, as presented in Fig. 1. A few experimental FORCs determined at reversal fields in the range $E_r \in (0, -400) kV/cm$ for the PZT films are showed in the inset of Fig. 1. Similarly, the FORCs $p^{+}_{FORC}(E_r, E)$ can be obtained using the ascending branch of the MHL. The FORC diagram represents a contour plot of the FORC distribution, defined as the mixed second derivative of polarization with respect to E_r and E [1, 4]:

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

in which $\chi^{-}_{FORC}(E_r, E)$ are the differential susceptibilities measured along the FORCs. The distribution $\rho(E_r, E)$ was determined using the numerical method presented in [1] and it describes the variation of polarization with respect to modifications in both the reversal field E_r and actual electric field E. By changing the coordinates of the FORC distribution from (E_r,E) to {E_c=(E-E_r)/2, E_i=(E+E_r)/2}, where E_c and E_i play the role of local coercive field and interaction field respectively, $\rho(E_c, E_i)$ becomes a distribution of the switchable units over their coercive and bias fields. The FORC and Preisach distributions are identical for systems correctly described by the classical Preisach model [4], in which the hysteretic system is described by an ensemble of microscopic bistable polarizing units ("hysterons") characterized by rectangular elementary hysteresis loops with distributed internal bias (E_i) and coercive (E_c) fields [9]. The Preisach theories were recently used for simulating the ferroelectric and piezoelectric properties of other materials [10-13].

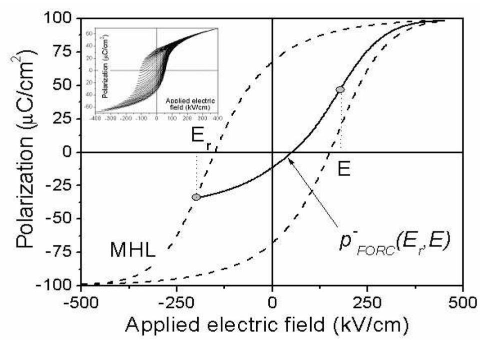

Fig. 1. The definition of FORC curves $p^{-}_{FORC}(E_r, E)$. Inset: family of experimental FORCs of PZT films under 500Hz triangular signal of 10V amplitude.

3. Results and discussion

Figs. 2 and 3 show the representation of the FORC distribution $\rho(E_r, E)$ and its contour plot (*i.e.* the FORC diagram), respectively, obtained for the PZT film in its fresh state. The FORCs were also recorded in a well-fatigued state [14], after the film was subjected to 10^9 switching cycles (±400kV/cm), when the MHL shows a strong reduction of the switched polarization. The FORC diagram characteristic to the fatigued state is represented in Fig. 4. In the fresh state of the ferroelectric film the FORC diagrams show two well-defined components corresponding to the reversible and irreversible contribution to the polarization (Figs. 2-3). It turns out that the present method allows the separation of the reversible and irreversible contributions to switching. The reversible component of the FORC distribution can be calculated as:

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

The characteristics of the reversible component can be further compared with the results obtained from other investigations such as the measurements of Rayleigh loops or low signal capacitance [15]. At low reversal fields E_r, ρ^-_{rev} is higher and tends to saturate to a lower value for $E_r \to -E_{sat}$. This can be explained by considering that at low E_r, domain wall (DW) oscillations and lattice intrinsic contributions are present into ρ^-_{rev}, while at high fields only the intrinsic part is expected, since the DWs are driven-out of the ferroelectric. The irreversible component of the FORC distribution has a well-defined sharp maximum (Figs. 2-3) located at $E_{rM} = -0.3E_{sat}$, $E_M = 0.1E_{sat}$ (or the corresponding local coercive field $E_{cM} = 0.2E_{sat}$ and bias field $E_{iM} = -0.1E_{sat}$). These are the most probable fields for the highest number of the switchable units of the system, causing the highest contribution to the ferroelectric polarization under the specific field sequence. An asymmetry of the irreversible FORC distribution along $E_M = 0.2E_{sat}$ is also observed in the fresh state (Figs. 2-3), which may be due to the preferential polarization of the switching units located at the bottom electrode/ferroelectric film interface [7]. Similar asymmetric FORC diagrams were reported in laminated antiferromagnetically coupled media [16].

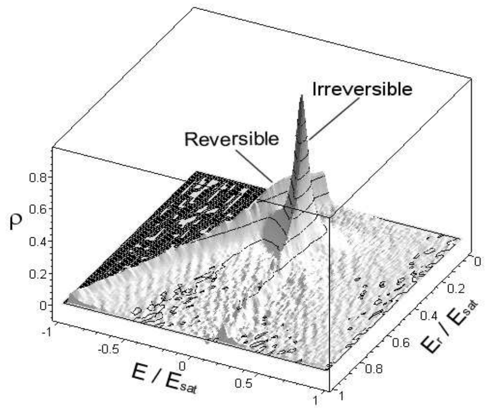

Fig. 2. Plot of the 3-D FORC distribution $\rho^-_{FORC}(E_r, E)$ of PZT in the fresh state.

The FORC diagram dramatically changes for the system set in a fatigued state after the application of 10^9 switching cycles, using square pulses of 5kHz frequency and 10V amplitude (Fig. 4). The irreversible component of the FORC distribution becomes broad and has a lower intensity maximum shifted towards higher fields $E_{rM} = -0.6E_{sat}$, $E_M = 0.3E_{sat}$. A large number of polarization units become widely distributed in the range of higher coercivities and bias fields. This result is in agreement with the mechanisms proposed in literature for fatigue [17]. A remarkable effect is the increase of the reversible contribution to the total polarization in the fatigue state, by comparison with the fresh one (Figs. 3 and 4), reflecting that a large number of the polarization units lose their ability to switch during fatigue.

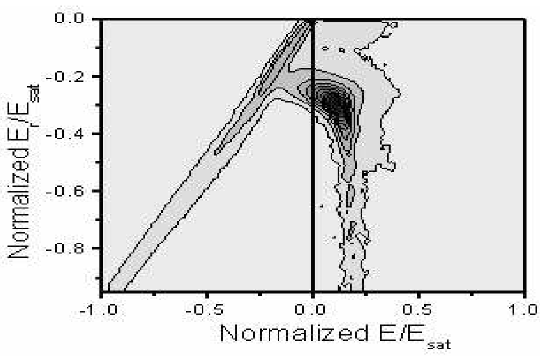

Fig. 3. Experimental FORC diagram characterizing the fresh state of the ferroelectric PZT film.

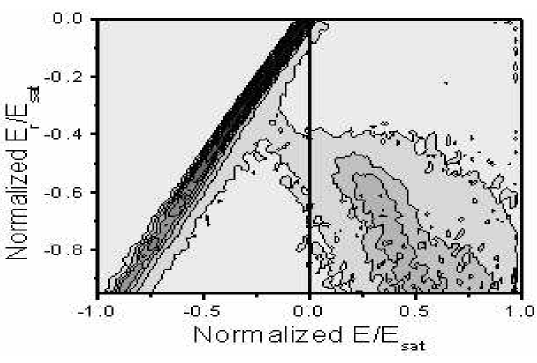

Fig. 4. Experimental FORC diagram of PZT film in the fatigued state (after 10^9 switching cycles).

Another piece of information directly available from the FORC analysis is given by the differential FORC susceptibility. The field dependence of the normalized FORC susceptibilities is represented for a qualitative comparison in Figs. 5 (a-b), for the fresh and fatigued state, respectively. Three distinct regions are observed on these pictures: (I) the low-field region $E_r<E_{th1}$, where the dielectric constant is field-independent; (II) for $E_r \in (E_{th1}, E_{th2})$, the susceptibility is increasing linearly with the applied field and (III) the saturation region for $E_r>E_{th2}$. These regions are not so well defined in the fatigued state (Fig. 5b) although the same type of behaviour with other characteristics can be found. Region (I) can be identified as the sub-switching regime of the reversal process of PZT film [18-19], in which the dielectric constant is determined by the lattice (intrinsic) contribution only. It seems that in the fatigued state this region extends towards higher fields more than in the fresh state.

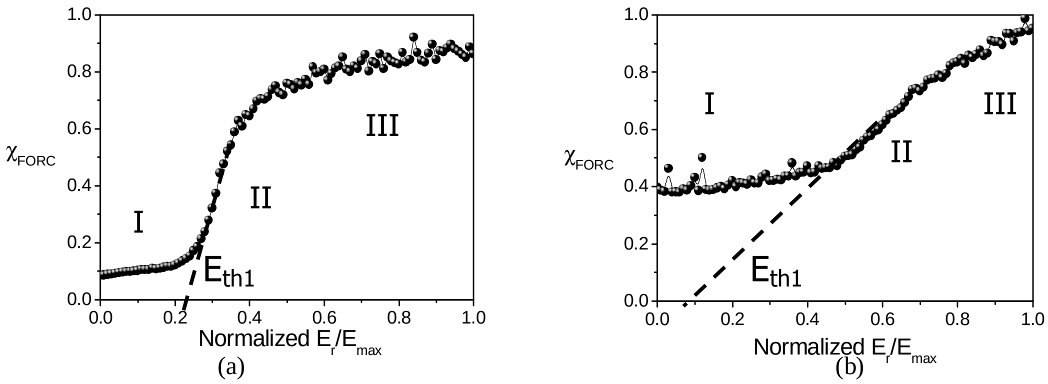

Fig. 5. Experimental normalized FORC susceptibility as a function of the reversal field for the PZT film in the: (a) fresh state; (b) fatigued state (after 10^9 switching cycles).

The field E_{th1} represents the threshold field for the onset of the nonlinearity of the ferroelectric polarization, *i.e.* for the linear behaviour of the permittivity in the low-field region (II).To know exactly the value of this field for a given ferroelectric material is highly important in applications in which a linear/nonlinear behavior of the ferroelectric device under a certain field is desired [20]. The FORC analysis allows the precise determination of this threshold field and opens the possibility of further study for finding its dependence on various parameters such as temperature, composition, frequency and field sequence, by comparison with the information obtained by the Rayleigh analysis [18-19]. Region (II) in which the susceptibility linearly increases with the field is a result of both intrinsic and reversible domain wall contributions involving a pinning mechanism of the domain walls [18], while in the saturation zone (III), the irreversible domain walls contribution is present at high fields $E_r>E_{th2}$. For the available fields used in this experiments, the fatigued sample was not saturated. It results that from the proposed FORC analysis, data about the subswitching/switching regions of the polarization reversal process in ferroelectric are available, without additional low-field experiments.

4. Conclusions

In conclusion, the experimental FORC diagrams give a phenomenological description of the switching properties and can be applied at large scale for easy characterisation of various ferroelectric systems. The FORC diagrams have been shown to be sensitive to the changes of hysteresis loops induced by fatigue and possibly by other degradation of the ferroelectric polarization. The FORC susceptibility gives important information concerning the critical fields for its field-dependences which can be used instead of other complicated low-field measurements.

References

[1] C. R. Pike, A. P. Roberts, K. L. Verosub, J. Appl. Phys. **85**, 6640 (1999); Geophys. J. Int. **145**, 721 (2001).

[2] H. G. Katzgraber, F. Pazmandi, C. R. Pike, K. Liu, R. T. Scalettar, K. L. Verosub, G. T. Zimanyi, Phys. Rev. Lett. **89**, 257202 (2002).

[3] C. R. Pike, A. P. Roberts, M. J. Dekkers, K. L. Verosub, Phys. Earth and Planetary Interiors **126**, 11 (2001).

[4] A. Stancu, C. Pike, L. Stoleriu, P. Postolache, D. Cimpoesu, J. Appl. Phys. **93**, 6620 (2003).

[5] C. Enachescu, Ph. D. Thesis, Univ. of Versailles, France, 2003.

[6] I. Mayergoyz, Mathematical Models of Hysteresis, Springer, New York, 1991.

[7] A. Stancu, D. Ricinschi, L. Mitoseriu, P. Postolache, M. Okuyama, Appl. Phys. Lett. **83**, 3767 (2003).

[8] D. Ricinschi, M. Okuyama, Appl. Phys. Lett. **81**, 4040 (2002); Integr. Ferroel. **50**, 149 (2002).

[9] F. Preisach, Z. Phys. **94**, 277 (1935).

[10] A. V. Turik, Sov. Phys-Solid State **5**, 885 (1963); **5**, 1751 (1964).

[11] A. T. Bartic, D. J. Wouters, H. E. Maes, J. T. Rickes, R. M. Waser, J. Appl. Phys. **89**, 3420 (2001).

[12] G. Robert, D. Damjanovic, N. Setter, J. Appl. Phys. **90**, 2459 (2001).

[13] L. Cima, E. Laboure, P. Muralt, Rev. Sci. Instrum. **73**, 3546 (2002).

[14] Thin Film Ferroelectric Materials and Devices, Edited by R. Ramesh, Kluwer Academic, Boston, 1997; O. Auciello, J. F. Scott, R. Ramesh, Phys. Today, **51**, 22 (1998).

[15] D. Bolten, U. Böttger, R. Waser, J. Appl. Phys. **93**, 1735 (2003).

[16] C. Hee, J. Yin, S. Piramanayagam, S. Pang, J. Wang, 4^{th} Annual Conference on Magnetism and Magnetic Materials, Tampa, Nov. 2002, Paper ET-11.

[17] D. Ricinschi, M. Okuyama, M. Shimizu, Ferroelectrics **262**, 81 (2002).

[18] V. Mueller, Q.M. Zhang, Ferroelectrics **206-207**, 113 (1998).

[19] D. V. Taylor, D. Damjanovic, J. Appl. Phys. **82**, 1973 (1997).

[20] L. E. Cross, Ferroelectric Ceramics: Tayloring Properties for Specific Applications, in Ferroelectric Ceramics, Ed. N. Setter, E.L. Colla, Birkhaeuser Verlag, Basel, 1993.