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Characterisation of porous PZT ceramics by first-order reversal curves (FORC) diagrams

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Abstract

The method of investigation based on the first-order reversal curves (FORC) is proposed for describing the role of porosity on the switching properties of Nb–PZT ceramics with anisotropic porosity prepared using lamellar graphite as pore-forming agent. The experimental FORC diagrams have two distinct parts attributed to the reversible and irreversible components of the ferroelectric polarization. A more localized distribution was found in the dense material, while in the porous one (40% porosity) the distribution is broad and spread towards higher fields, due to the local depolarising field created at the boundaries. The FORC susceptibilities indicate the degree of tunability of the permittivity under the applied field. In this analysis it was found that porosity has a detrimental effect on the tunability of the system in the same range of the electrical fields.

Keywords: Porosity; Ferroelectric properties; PZT

1. Introduction

The main characteristic of ferroelectrics, i.e. polarization reversal (switching) is a complex phenomena involving reversible and irreversible ferroelectric domain dynamics. Finding the relationship between the switching characteristics and composition/processing parameters determining the microstructure of a given ferroelectric system is a very important task, needing appropriate characterization methods and modelling tools. Recently, a method of investigation was proposed for describing the switching properties of ferroelectrics, based on the first-order reversal curves (FORC) analysis.[1–4] This approach is related to the Preisach models,[5–8] 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); and (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 $p^-_{FORC}(E_r, E)$. 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:[1,9]

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

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 both the reversal 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 (which is identical with the Preisach distribution for Classical Preisach systems[6]).

Porous piezoelectric materials are interesting for applications as low frequency hydrophones and sensors, due to their high piezoelectric figure of merit. Nb–PZT ceramics with anisotropic porosity and particular dielectric and piezoelectric properties,

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were prepared using lamellar graphite as pore-forming agent.[10] The switching characteristics in such ceramics having the same composition and different porosity are investigated by means of the FORC method.

2. Ceramic preparation and experiments

Powders with composition $Pb(Zr_{0.52}Ti_{0.48})_{0.976}Nb_{0.024}O_3$ were prepared via solid state reaction (calcined at 850 °C/4 h). To obtain porous ceramics, fine-grained graphite powder was mixed with the calcined powders at different graphite contents. Lamellar porosity preferentially oriented perpendicular to the direction of the applied pressure was formed during the cold pressing step. The green bodies were sintered at 1150 °C for 2 h. The ceramics have open porosity tri-dimensionally interconnected; the dense part of the porous ceramics has the same microstructural characteristics and density as the 95% dense sample. X-ray diffraction studies did not reveal any relevant differences between the dense and porous ceramics in terms of composition and tetragonal distortion, meaning that the difference in the final microstructures is mainly the degree of porosity. The experimental $P(E)$ loops and FORCs were recorded under a sinusoidal waveform of amplitude $E_0 = 2.5$ kV/mm and frequency $f = 1$ Hz, using a modified Sawyer–Tower circuit. The results found for a dense (95% relative density) and a porous sample with 40% porosity are reported for comparison in the present study.

3. Results and discussions

A few FORCs obtained for the dense and porous Nb–PZT ceramics are shown in Figs. 1 and 2 and in Figs. 3 and 4 their corresponding 3D FORC distributions $\rho(E_r, E)$, calculating using the numerical procedure described in ref.[9] Less rectangular $P(E)$ loops, lower values of polarizations and more distributed coercivities are the main characteristics of the porous material in comparison to the dense one. The distributions of the data for both the dense and porous ceramics show two well-defined components, corresponding to the reversible (caused

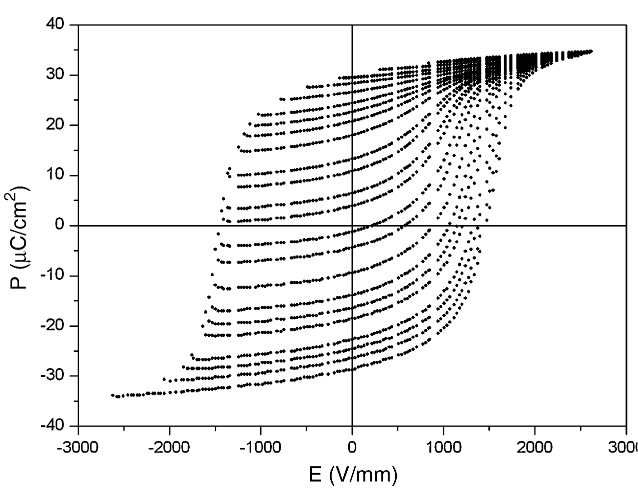

Fig. 1. The first-order reversal curves (FORC) $p^{-}_{FORC}(E_r, E)$ obtained for the dense Nb–PZT ceramic.

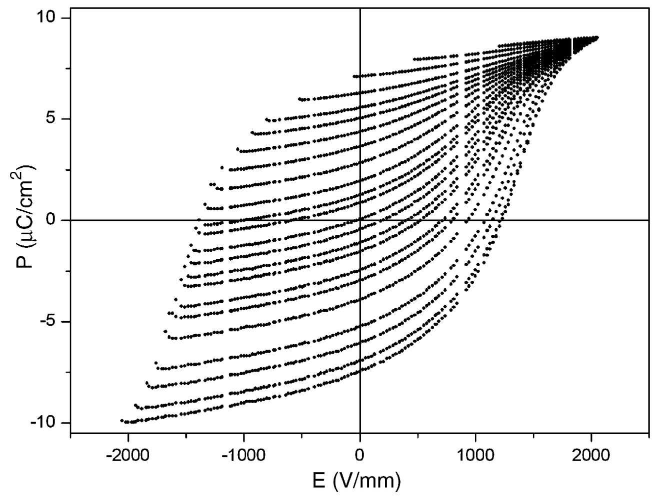

Fig. 2. The first-order reversal curves (FORC) $p^{-}_{FORC}(E_r, E)$ obtained for the porous (40% porosity) Nb–PZT ceramic.

by domain walls oscillations and lattice intrinsic contributions) and irreversible (caused by domain walls switching) contributions to the ferroelectric polarization. The irreversible part of the FORC distribution has a well-defined sharp maximum in the dense material (Fig. 3) located at $E_{rM} = -1540$ V/mm, $E_M = 1540$ V/mm (corresponding to the coercivity and bias fields of $E_{cM} = 1540$ V/mm and $E_{iM} = 0$). These fields correspond to the highest number of the switchable units of the system causing the highest contribution to the ferroelectric polarization under a given field sequence. In contrast, the irreversible component of the FORC distribution in the porous ceramic has a low intensity and a greater dispersion (Fig. 4). The distribution has an elongated broad maximum on the direction $E = E_r$ at $E_{rM} = -1400$ V/mm, $E_M = 1500$ V/mm (corresponding to $E_{cM} = 1450$ V/mm and having a small positive bias

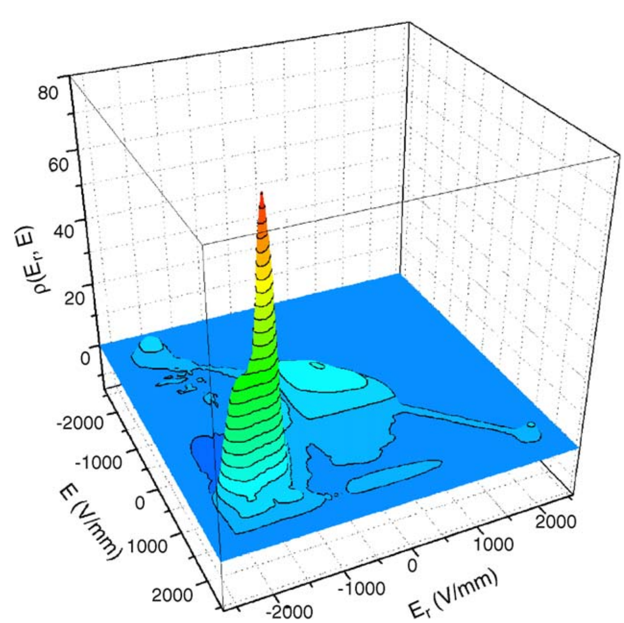

Fig. 3. Experimental FORC distributions $\rho(E_r, E)$ corresponding to the dense ceramic.

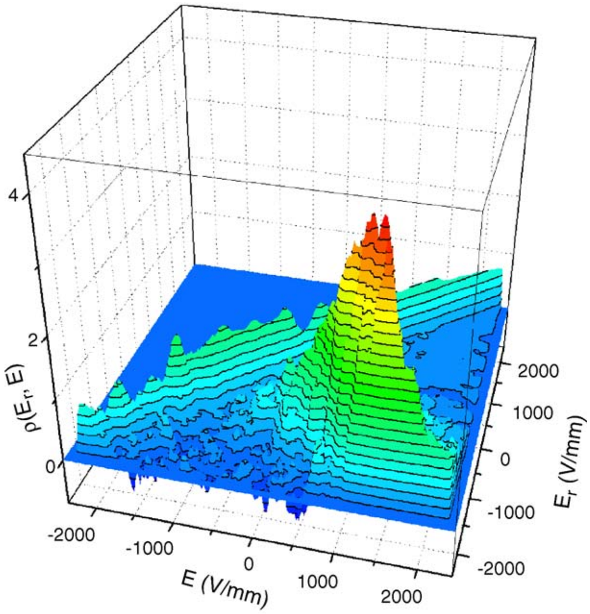

Fig. 4. Experimental FORC distributions $\rho(E_r, E)$ corresponding to the Nb–PZT ceramic with 40% porosity.

$E_{iM} = 50$ V/mm). A large number of dipolar units are spread towards higher/lower values of the reversal and actual fields, due to different mechanical and electrical boundary conditions in the porous material, giving rise to very scattered local fields acting on individual dipolar units. This FORC diagram is describing a more inhomogeneous ferroelectric system from the point of view of its switching properties.

The switching characteristics revealed by the experimental FORC diagrams can be explained in terms of the mechanism of switching in the polycrystalline ferroelectrics and the microstructural features of the samples, which are strongly related to the defect structure. The homogeneous and defect-free ferroelectric ceramic shows homogeneous switching properties because the group of individual switching units is subjected to very similar local fields and they evolve under the same boundary conditions. Due to this, they are characterised by a well-defined FORC distribution (Fig. 3) with a sharp maximum of the irreversible component and an almost zero reversible part. In comparison, the porous ceramic has very inhomogeneous switching properties derived from its particular microstructure. The ceramic grains are subjected to different boundary conditions if they belong to a dense region or if they are in contact with porosity. The uncompensated charges located at these interfaces create depolarising fields, strongly dependent on the pore shape and morphology. With respect to these features, the description of the porous ceramic by a dispersed and broad FORC distribution with a higher contribution to the reversible part of the polarization at the expense of the irreversible one (Fig. 4) is in agreement with the expected switching behaviour derived from the microstructure. In order to calculate the theoretical FORCs and to compare them with experiment, Preisach models with using microstructure-related hypothesis will be employed. Additional important information obtained from the FORC analysis is the field dependence of susceptibility, i.e. the tunability of the

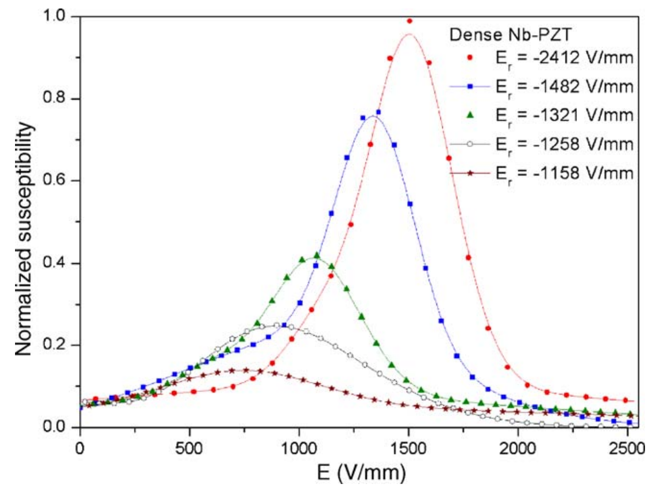

Fig. 5. Normalized FORC susceptibilities for the dense Nb–PZT ceramic indicating the tunability of the dielectric constant. Notice that dielectric constant can be increased of maximum 10 times with fields in the range (0, 1500) V/mm.

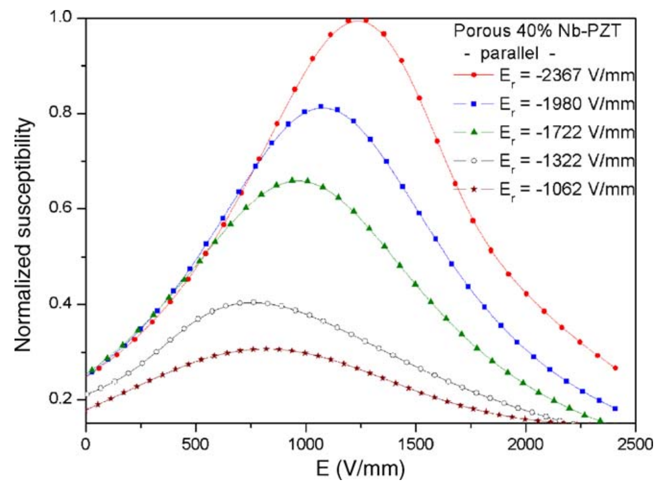

Fig. 6. Normalized FORC susceptibilities for the porous Nb–PZT ceramic. The dielectric constant can be increased of maximum four times ranging the fields in the domain (0, 1500) V/mm.

system.[11] For a fixed value of the reversal field E_r, the differential susceptibilities measured along the FORCs $\chi^{-}_{FORC}(E_r, E)$ are shown in Figs. 5 and 6. They are also strongly dependent on the degree of porosity: higher tunability is obtained for the dense ceramic along the MHL (E_r corresponding to the saturation field). An increasing variation of the dielectric constant of 10 times can be obtained in the dense material by increasing the actual field E from zero to around 1500 V/mm, while for the porous one, a tunability of only four times is found for the same field range. This is further proof of the strong dependence of the tunability of the dielectric constant on the microstructure of the ceramic, particularly on its porosity.

4. Conclusions

Nb-doped PZT piezoelectric materials with anisotropic porosity, high piezoelectric figure of merit and with particular dielectric and piezoelectric properties, were investigated.

The switching characteristics in such ceramics having the same composition and different porosity were studied by means of the FORC method. Particular features attributed to the effect of porosity have been found both in the FORC distributions and in the FORC susceptibilities describing the tunability of the dielectric constant under applied fields. The FORC method proved to be very sensitive to porosity effects in ferroelectric ceramics and can be further accurately described in the frame of Preisach–Néel models.

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