Hysteresis and tunability characteristics of Ba(Zr,Ti)O$_3$ ceramics described by First Order Reversal Curves diagrams

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Available online 19 March 2007

Abstract

The First Order Reversal Curves (FORC) diagrams method is proposed for the characterization of the switching process and ac-tunability in BaZr$_{0.10}$Ti$_{0.90}$O$_3$ ceramics prepared via solid state reaction. The properties induced by different microstructures, having two extreme grain sizes of 0.75 and 3.3 μm are investigated by monitoring the changes of the FORC diagrams. The maximum of FORC distribution is located at low fields independently on the grain size and no clear separation between the reversible/irreversible contributions to the polarization are found. A higher degree of the local inhomogeneity is characteristic to the fine ceramic. The FORC susceptibility related to the ac-tunability determined on the major hysteresis loop is very sensitive to the grain size: it is much smaller in the fine material, due to the pinning of the domain walls by different types of defective areas.

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Keywords: Ferroelectric properties; Tunability; BaTiO$_3$; Titanates

1. Introduction

Environmental concerns are a contributing factor driving the exploration for lead-free piezoelectric and dielectric materials, taking into account the high toxicity of lead oxide and its high vapour pressure during processing.[1,2] BaTiO$_3$-based solid solutions represent an alternative for the replacement of Pb-based piezoceramics. Substitution of other ions for host cations at the A or B site in BaTiO$_3$ perovksite cell leads to remarkable changes of its characteristics.[3,4] Due to excellent dielectric and promising piezoelectric/electrostrictive properties,[5] BaTi$_{1-x}$Zr$_x$O$_3$ (BZT) ceramics[6,7] and thin films[5,8,9] became attractive for multilayer ceramics capacitors and piezoelectric sensors/actuators applications.[5–9] As other BaTiO$_3$-based systems, BZT solid solutions are also electric field-tunable dielectrics with potential use in devices for wireless communications as variable capacitors, phase shifters and voltage-controlled oscillators.[10] The ferroelectric properties of BZT are largely dependent on the amount of Zr substitution.[6,7,11] The system exhibits a pinched phase transition with increasing Zr concentration (at $x \approx 0.15$, the three phase transitions are merged into one broad peak). Normal ferroelectric behavior was observed for $0 < x < 0.1$, relaxor when $x > 0.25$ and antiferroelectric properties for high Zr addition. These limits are sensitive to the preparation method, to the presence of secondary phases and to the microstructural characteristics as porosity degree, grain size, etc. For a given composition it is interesting to see how these parameters affect the ferroelectric and tunability properties.

The tunability of a ferroelectric describes the ability to change its permittivity by the electric field. This property is directly related to the non-linear variation of polarization (and implicitly of the permittivity) with the applied field. The field-induced polarization $P(E)$ is accompanied by hysteresis and involves reversible/irreversible domain dynamics. Apart the classical

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methods of investigating, the more recent one based on the First Order Reversal Curves (FORC),[12,13] related to the Preisach model in ferroics,[14,15] proved its sensitivity to the crystallite orientation, imprint effects in films[12,13] and anisotropic porosity in ceramics,[16] giving also information on the field-dependence of the differential susceptibility.[16] This approach is used here to describe the switching and ac-tunability characteristics in $BaTi_{1-x}Zr_xTiO_3$ ceramics with two grain sizes: 0.75 and 3.3 μm.

2. Experiment

$BaZr_{0.10}Ti_{0.90}O_3$ (BZT) ceramics were prepared by solid-state reaction starting from high-purity $BaCO_3$ (Solvay), TiO_2 (Toho) and ZrO_2 (Tosoh) that were wet-mixed, dried, calcined at 1000 °C/6 h, re-milled, pressed and then sintered at 1350–1500 °C/2 h.[17] The microstructures were examined by Scanning Electronic Microscopy (SEM, Philips, Model 515). The $P(E)$ loops and FORCs were recorded under sinusoidal waveform by using a modified Sawyer–Tower circuit. The FORC measurements involve the recording of minor loops between saturation E_{sat} and a variable reversal field $E_r \in (-E_{sat}, E_{sat})$,[12,13] the polarization along FORCs $p^-_{FORC}(E_r, E)$ being a function of the actual and reversal fields E, E_r. The FORC distribution is defined as the mixed second derivative of polarization with respect to E_r and E[12]:

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

in which $\chi^-_{FORC}(E_r, E)$ are the differential susceptibilities along the FORCs. The 3D-distribution $\rho(E_r, E)$ describes the sensitivity of polarization with respect to the reversal E_r and actual field E or, by changing variables, to the coercive and bias fields: $\rho(E_c, E_i)$.

3. Results and discussions

The structural data demonstrate the formation of pure perovskite phase in all the samples. The samples used in the present study were sintered at 1350 and 1500 °C/2 h. Homogeneous microstructures with average grain size of 0.75 μm (BZT1) and 3.3 μm (BZT2) and relative densities of 90 and 99% were obtained (Fig. 1). The expected differences in the switching and tunability properties result from the combination of grain size and porosity effects. The decreasing grain size causes a reduction of the tetragonality and spontaneous polarization, together with frozen-polarization and "dilution" effects due to the large number of non-ferroelectric grain boundaries.[18] In addition, due to the porosity, the dipolar units located inside a grain or in contact with pores act under different mechanical and electrical boundary conditions.

The FORC data for the two samples are shown in Fig. 2a and b. Remanent polarization of $\sim$3.4 μC/cm^2 for BZT1 and $\sim$7 μC/cm^2 in BZT2 and apparently similar coercivities of around 0.25 MV/m were obtained. The computed 3D-FORC distributions (Fig. 3) show a small bias, i.e. the maximum of the FORC distribution is shifted towards negative bias fields:
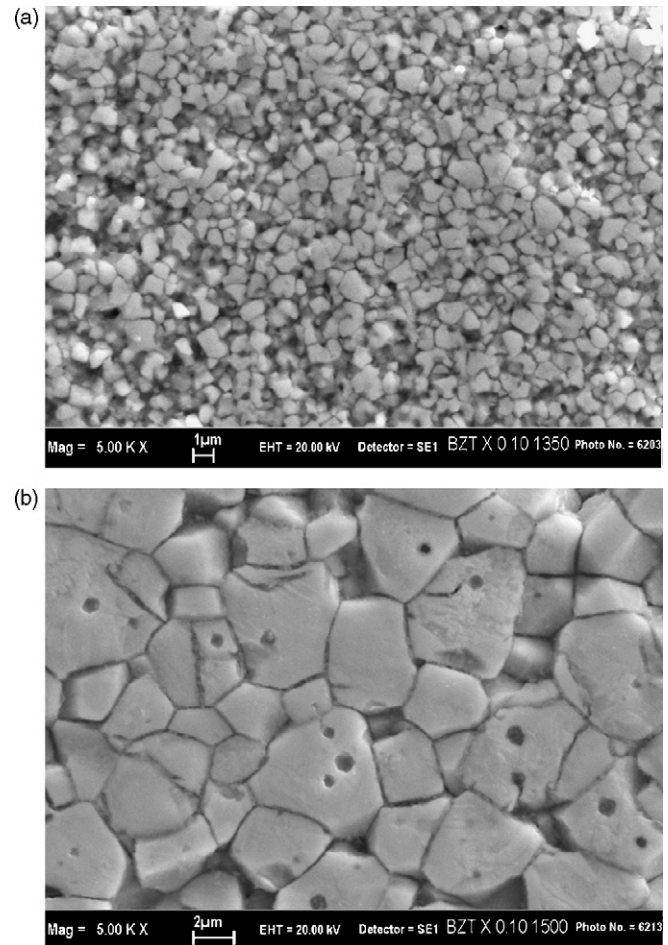

Fig. 1. SEM micrographs of $BaZr_{0.1}Ti_{0.9}O_3$ ceramics sintered at: (a) 1350 °C (BZT1: 0.75 μm); (b) 1500 °C (BZT2: 3.3 μm).

E_i = 17 kV/m in BZT1 and E_i = 8 kV/m in BZT2. The maximum is located at low coercivities, of $\sim$5 kV/m for both samples, indicating low energy barriers for the large majority of irreversible domain walls movements. Only a small number of dipolar units are switchable under higher fields. Since there is not a net separation between the reversible (along the bias axis E_c = 0) and the irreversible (for $E_c \neq 0$) components of the polarization on the FORC distribution as in other ferroelectrics,[12,16] it results that a continuous distribution of energy barriers from zero to non-zero values is characteristic to these BZT ceramics. A similar behavior was found for some BST compositions[13] and is related to the high degree of local compositional inhomogeneity of the solid solutions, giving rise to broad distributed Curie temperatures and coercivities. Therefore, the sample BZT2 is much homogeneous from the switching point of view, i.e. the large majority of the dipolar units are switchable at similar fields, giving rise to a very sharp FORC distribution (Fig. 3b). This is a result of two effects: larger grains and small non-ferroelectric grain boundary volume resulting in switching characteristics closer to the single-crystal behavior; (ii) high density, putting the overall dipolar units into similar boundary conditions. The enlarging FORC distribution by porosity effects was also observed in PZT ceramics with high degree of porosity.[16]