Composition and grain size-driven ferroelectric-relaxor crossover in $Ba(Zr,Ti)O_3$ ceramics

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Abstract

First $Ba(Zr_xTi_{1-x})O_3$ (BZT) ceramics with various compositions prepared by solid state, with high density, homogeneous microstructures and grain sizes in the range (0.7–4) μm were studied. Besides the dielectric and ferroelectric investigations, First Order Reversal Curves method was employed to describe the changes of the switching properties induced by composition and grain size, related to the ferroelectric-relaxor crossover. The dielectric and ferroelectric data for ceramics with similar grain sizes demonstrated the expected ferroelectric-relaxor crossover induced by increasing x. For a given composition (x = 0.10), the relaxor character increases whit reduction of the grain size. The FORC distribution shows almost zero reversible contribution and well-separated sharp irreversible component for larger grains, while more diffuse distribution with a continuous extension from E_c=0 (reversible) to $E_c \neq 0$ (irreversible, switching) is typical for finer grains.

Keywords: *BZT ceramics, grain size, relaxor, First Order Reversal Curve*

I. Introduction

In recent years, a large number of Pb-free perovskite ceramics, mainly based on $BaTiO_3$ solid solutions, have been studied because of their potentials as environment-friendly materials. Barium titanate ($BaTiO_3$) is one of the most used ferroelectrics in the electronic industry, finding extensive application as dielectric material in multilayer ceramic capacitors (MLCCs), piezoelectric actuators, electro-luminescent panels, pyroelectric detectors, embedded capacitance in printed circuit boards, positive temperature coefficient of resistivity (PTCR) sensors, controllers and pulse generating devices [1–6].

One of the $BaTiO_3$ solid solutions, $BaZr_xTi_{1-x}O_3$ (BZT), is one of the most important compositions used as dielectric in MLCCs. The presence of Zr in the $BaTiO_3$ unit cell results in a strong increase in the permittivity. At the same time, the temperature characteristic is smoothed due to the broadening of the permittivity-temperature dependence and the material can be adapted to meet the Z5U specifications for being used in MLCCs [1]. The system $Ba(Zr_xTi_{1-x})O_3$ started to be recently investigated also for more fundamental studies related to the solubility limits, phase diagrams and effects on the functional properties derived from the $BaTiO_3$ ones, induced by very low substitutions, various types of defects (like O-vacancy or others), different grain size or grain boundary phenomena.

The dielectric data of $BaZr_xTi_{1-x}O_3$ (BZT) ceramics suggests a normal ferroelectric behaviour for $0 < x < 0.1$, a diffuse phase transition in the range $0.1 < x < 0.2$ and a relaxor character for $0.2 < x < 0.5$. The degree of diffuseness of the ferro-para phase transition increases with the Zr addition [7–9]. For $x > 0.5$, the system does not present anymore a ferroelectric distortion. These limits are very sensitive to the preparation method, presence of possible secondary phases and microstructural characteristics. Recently, a detailed study concerning the dielectric and switching characteristics in BZT ceramics as a function of composition and grain size was performed, in

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the way to demonstrate a ferroelectric-relaxor crossover [10–14]. The present work reports on the main dielectric and ferroelectric results related to the ferroelectric-relaxor crossover induced by composition in $BaZr_xTi_{1-x}O_3$ and by the grain size in $BaZr_{0.10}Ti_{0.90}O_3$ ceramics.

II. Experimental

$BaZr_xTi_{1-x}O_3$ (BZT) ceramics with various compositions (x = 0, 0.10, 0.15 and 0.18) were prepared by solid-state reaction, as described in detail elsewhere [13,14]. The microstructures were checked by scanning electron microscopy (SEM, Philips, Model 515). The grain size was estimated by line intercept method. The phase formation after calcination and in bulk ceramics was analysed by X-ray diffraction (XRD, Philips, Model PW 1710). High density ceramics (relative density > 90%) were obtained by sintering the calcined powder at different temperatures (1350–1500°C) for 2 hours. By changing the sintering temperature, ceramics with composition $BaZr_{0.10}Ti_{0.90}O_3$ with grain sizes in the range of 0.75 – 3.3 μm were obtained, allowing the investigation of some features related to grain size effects. An impedance spectroscopy system (Solartron, SI 1260, 0.5V excitation voltage) was used to study the dielectric properties as a function of temperature and frequency in the range of (1–10^6) Hz. The *P(E)* loops and First Order Reversal Curves (FORC) were recorded under sinusoidal waveform by using a modified Sawyer–Tower circuit.

The FORC diagrams method is a new tool for characterizing the switching process in ferroelectrics, considering the distribution of the elementary switchable units over their coercive and bias fields in relationship with classical Preisach model [15,16]. The FORC measurements involve the recording of minor loops between saturation E_{sat} and a variable reversal field $E_r \in (-E_{sat}, E_{sat})$, the polarization along FORCs $p^-_{FORC}(E_r, E)$ being a function of the actual, E, and reversal fields, E_r, respectively. The FORC distribution is defined as the mixed second derivative of polarization with respect to E_r and E [17]:

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

where $\chi^-_{FORC}(E_r, E)$ are the differential susceptibilities measured along the FORCs. The 3D-FORC distribution $\rho^{\pm}(E_r, E)$ describes the sensitivity of polarization in a given sample with respect to changes of the reversal field E_r and actual electric field E. By changing the coordinates of the FORC distribution from *(E, E_r)* to $\{E = (E - E_r)/2,\ E_{bias} = (E - E_r)/2\}$, where E_c and E_{bias} play the role of local coercive and bias fields respectively, $\rho^{\pm}(E_r, E)$ becomes a distribution of the switchable units over their coercive and interaction (bias) fields. The FORC method was used in this study to demonstrate the effect of composition and grain size in detecting changes of the switching parameters.

III. Results and discussion

3.1. Dielectric properties of $BaZr_xTi_{1-x}O_3$ ceramics

The role of composition on the dielectric properties of $BaZr_xTi_{1-x}O_3$ ceramics sintered at the same temperature can be seen by comparing the dielectric data from the Fig. 1. As expected, the relaxor character is more evident when the *Zr* addition increases (Figs. 1 and 2). This was described with empirical equations, e.g. one proposed in the ref. [18]:

$$\varepsilon = \frac{\varepsilon_m}{1 + \left(\frac{T - T_m}{\delta}\right)^{\eta}} \quad (2)$$

where ε is dielectric constant at a given temperature and ε_m is its maximum value at the corresponding temperature T_m. Equation (2) describes dielectric properties in relaxors, even in the dielectric dispersion region, with unique values of parameters δ and η for all frequencies [18]. The coefficient η gives information on the character of the phase transition: for η = 1, normal Curie–Weiss law is obtained, η = 2 describes a full relaxor state with completely diffuse phase transition and $\eta \in (1,2)$ a combined ferroelectric/relaxor state with a certain degree of diffuseness in the phase transition. The parameter δ indicates the temperature extension for the diffuse phase transition, which is correlated with the dielectric permittivity broadening. The values of these parameters obtained by fitting the dielectric data with the equation (2): η = 1.5 and δ = 20°C for x = 0.10, η = 1.65 and δ = 32°C for x = 0.15 and η = 1.7 and δ = 36°C for x = 0.18 [19]. These values indicate a mixed ferroelectric-relaxor character for all compositions and an increased relaxor character with Zr addition. The parameter δ, correlated with the dielectric permittivity broadening, shows a gradual increase of the diffuse character of the phase transition with increased Zr concentration. It is worth to mention that when we increase the Zr content, a reduction of the average grain size takes place in ceramics sintered under the same conditions [11]. Moreover, the grain size distribution in ceramics might also induce an increased character of the ferro-para phase transition. Therefore, the increased relaxor character observed with Zr addition is a combined effect of the increasing chemical heterogeneity, reducing grain size and broadening of the grain size distribution in the ceramics.

The composition-induced shift of the ferro-para phase transition at a fixed frequency (f = 80 kHz) is visible in the Fig. 2, where the temperature-dependence of the dielectric constant of the BZT solid solutions in comparasion with a $BaTiO_3$ ceramics is reported. The difference between the sharp ferroelectric-paraelectric phase transition in $BaTiO_3$ (fully ferroelectric) and the diffuse phase transitions in the solid solutions is clearly shown in this figure.

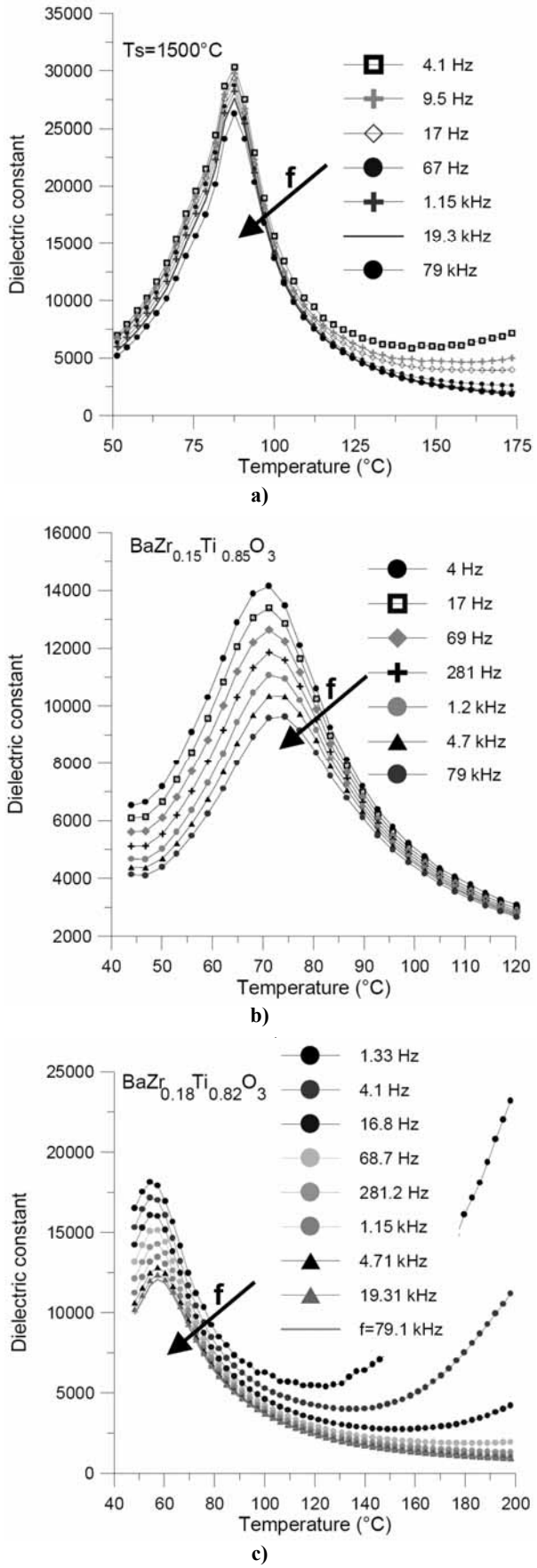

Figure 1. Real part of the dielectric constant vs. temperature for: a) $BaZr_{0.1}Ti_{0.9}O_3$, b) $BaZr_{0.15}Ti_{0.85}O_3$ and c) $BaZr_{0.18}Ti_{0.82}O_3$ ceramics, sintered at 1500°C at a few frequencies (ε decreases with the increase of f)

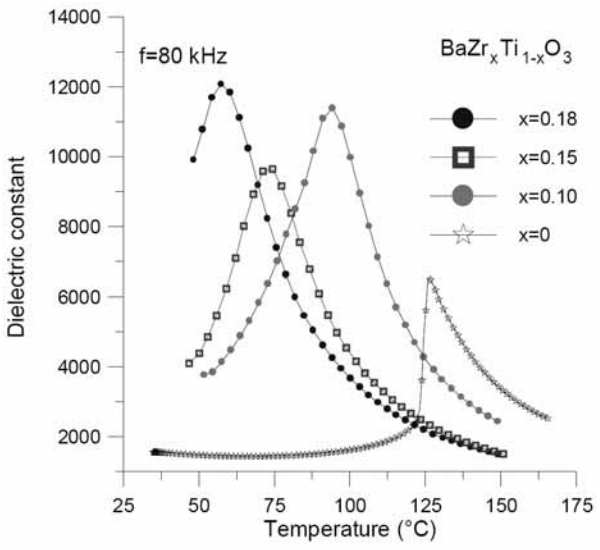

Figure 2. Real part of the dielectric constant vs. temperature for the $BaZr_xTi_{1-x}O_3$ ceramics with x = 0, 0.10, 0.15 and 0.18 at a fixed frequency, illustrating the compositionally-induced shift of the Curie temperature.

The grain size induced changes of the dielectric properties were detected by comparatively analyzing BZT ceramics with x = 0.10 sintered at different temperatures and thus, having different grain sizes in the range of 0.7–4 μm. The permittivity of all these ceramics at room temperature (Fig. 3a) assumes very high values, of around 3000–4000 for the finest ceramics sintered at 1350°C and of 5000–7500 for the coarser ones sintered at 1500°C. At the transition point, T_m, the permittivity reaches 30000 for the coarse ceramics. This is a result of the combined large and homogeneous grain size and the highest densification of this ceramics. Fig. 3a,b shows how the real and imaginary components of the complex permittivity are dependent on the grain size in a heating/cooling cycle. The transition is accompanied by a thermal hysteresis that raises with increasing of the grain size. For the coarse sample, the temperature dependence of the imaginary part of permittivity allows us to identify both the tetragonal-cubic (ferro-para) phase transition at ~90°C, and also the structural orthorhombic-tetragonal (ferro-ferro) transition at ~ 75°C by a small anomaly (Fig. 3b). For the finest ceramics these transitions are overlapped. The fact that the dielectric constant is so high in the temperature range of ~70–100°C is a result of proximity of the both structural phase transitions.

The results of the dielectric study showed that both by increasing the Zr content and reducing grain size, the relaxor character is increased.

3.2 Ferroelectric properties of $BaZr_xTi_{1-x}O_3$ ceramics

Fig. 4 represents the major hysteresis loops (MHLs) for the $BaZr_{0.1}Ti_{0.9}O_3$ samples sintered at 3 different temperatures (T_s = 1350°C, 1400°C and 1500°C). The sample sintered at lower temperature T_s = 1350°C (grain size of ~ 0.75 μm), presents a very tilted *P(E)*

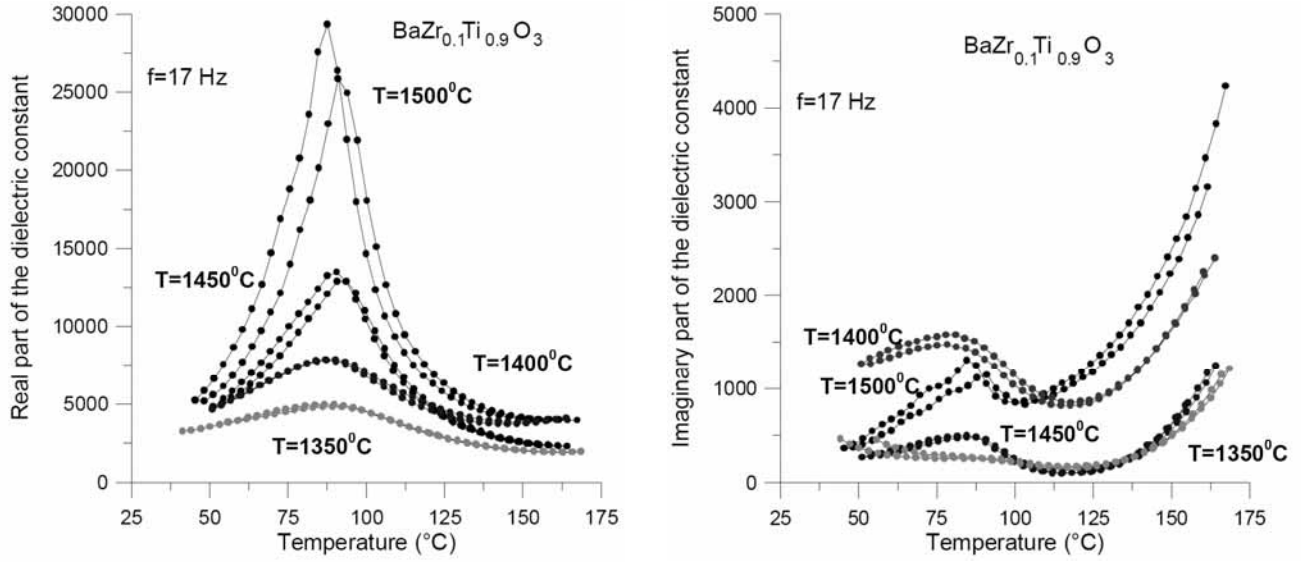

Figure 3. Grain size dependence of the real (a) and imaginary (b) part of the dielectric constant vs. temperature for the $BaZr_{0.1}Ti_{0.9}O_3$ ceramics, sintered at: 1350°C, 1400°C, 1450°C and 1500°C

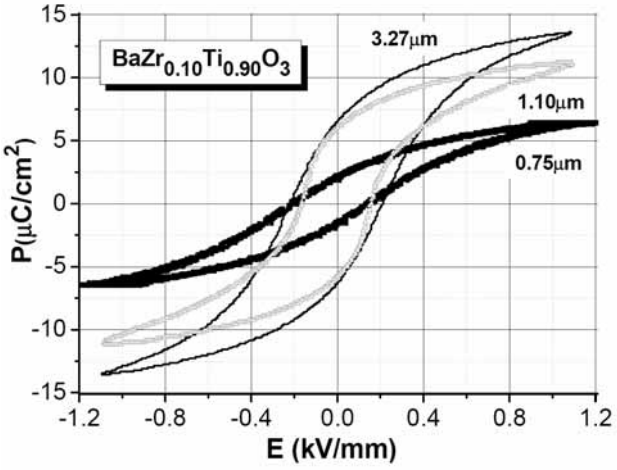

Figure 4 The major hysteresis loops for $BaZr_{0.1}Ti_{0.9}O_3$ ceramics at a few values of the field amplitudes and *f*=10Hz, with three different grain sizes (0.75 μm, 1.1 μm and 3.3 μm)

loop, with a large reversible component, low rectangularity factor, small value of the remanent polarization ($P_r \cong 2.4$ μC/cm²) and coercive field of 0.17 kV/mm. A higher remanent polarization is obtained for the ceramics sintered at 1400°C and 1500°C, due to their larger grain size. The ceramics with the highest density and the largest grain size of ~ 3.27 μm, sintered at 1500°C, has the most rectangular *P(E)* loop and the lowest coercivity (E_c = 0.15 kV/mm), but its saturation polarization is slightly smaller than for the sample sintered at 1400°C having grain size of ~1.1 μm (P_s = 11.12 μC/cm²), while the remanent polarization is almost the same ($P_r \cong 6.5$ μC/cm²). In any case the MHLs obtained in the present ceramics reflect the tendency found by other authors in systems like BT, BZT, BST and PZT thin films [20–24]. When comparing the loops of these samples sintered at different temperatures, one should keep in mind the possible differences caused by extrinsic phenomena. These extrinsic contribution might be different for the samples sintered at 1400°C and 1500°C, and this might explain why a higher saturation polarization was found in the sample with grain size ~ 1.1 μm and not in the one with higher grain size (~ 3.27 μm), in spite its excellent dielectric properties and almost full densification (99% relative density). A possible explanation is related to the anomaly of the dielectric and ferroelectric properties reported in the landmark paper of Arlt et al. [23] in the $BaTiO_3$ ceramics with grain size around ~1μm that might take place also in the BZT ceramics. At a given temperature in the ferroelectric phase, the grain size dependence of the permittivity of $BaTiO_3$ ceramics has a maximum value around this critical grain size of ~ 1 μm. For this grain size, it was supposed that an optimum twinning of the domain walls within the ceramic grains takes place.

Additional information on the switching properties is given by the FORC analysis. The FORC distributions for the BZT samples with x = 0.10 and extreme grain sizes are shown in Fig. 5a,b. Remanent polarization of ~ 3.4 μC/cm² for $BaZr_{0.1}Ti_{0.9}O_3$ with small grains and ~ 7 μC/cm² in $BaZr_{0.1}Ti_{0.9}O_3$ with large grain size and apparently similar coercivities of around 0.25 MV/m were obtained. The computed 3D-FORC distributions (Fig. 5a,b) show a small bias, i.e. the maximum of the FORC distribution is shifted towards negative bias fields: E_{bias} = -2.19kV/mm for the sample sintered at 1350°C and E_{bias} = -2.16kV/mm for the sample sintered at 1500°C. Dealing with bulk structures with symmetric electrodes, the possible origin of this bias as coming from the interfaces ceramics-electrodes is excluded. Since the negative bias is typical to all samples investigated, it results that this is an intrinsic effect caused either from the processing (one-directional pressing) or by dipolar defects contributions intrinsic to this type of material.

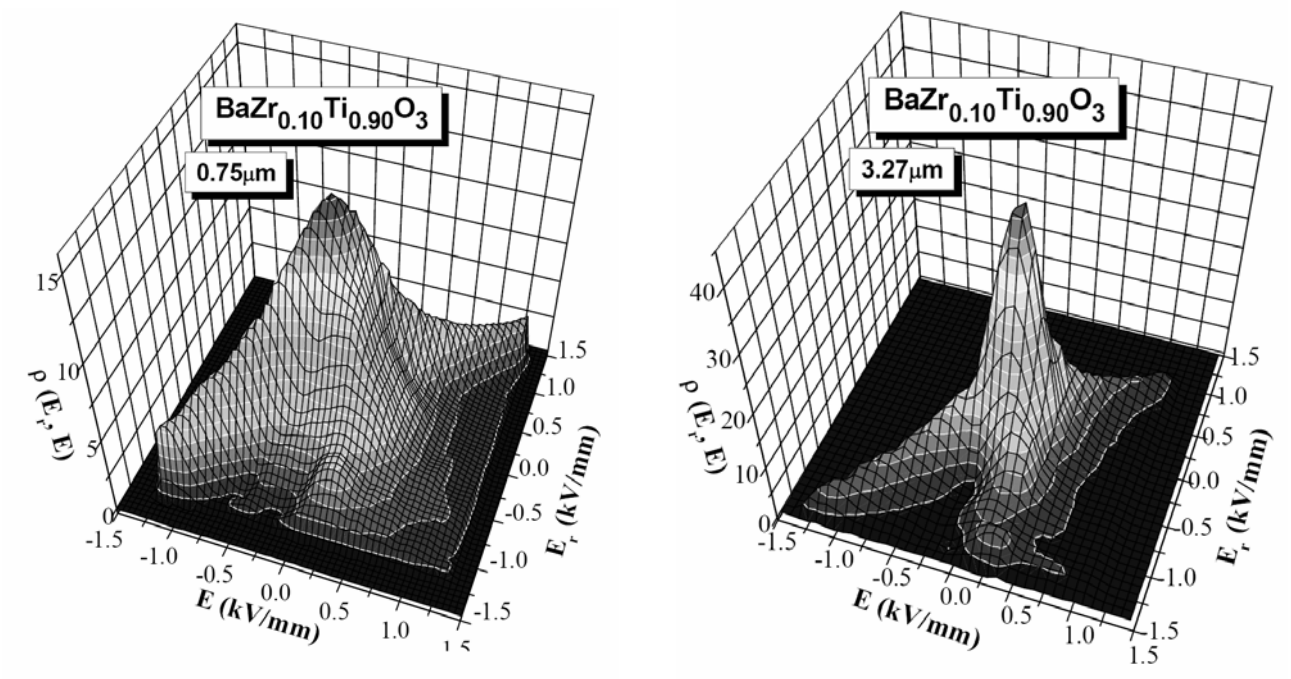

Figure 5 Three-dimensional FORC distributions $\rho(E_r, E)$ of $BaZr_{0.1}Ti_{0.9}O_3$ ceramics sintered at: a) 1350°C (grain size 0.75 μm) and b) 1500°C (grain size of 3.27 μm)

The maximum is located at low coercivities of ~ 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 is switchable under higher fields. Since there is no net separation along the bias axis between the reversible ($E_c = 0$) and the irreversible (for $E_c \neq 0$) components of the polarization on the FORC distribution as in other ferroelectrics [25,26], it results that a continuous distribution of energy barriers from zero to non-zero values is characteristic for these BZT ceramics. A similar behaviour was found for some BST compositions [27] 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 $BaZr_{0.1}Ti_{0.9}O_3$ sintered at T_s = 1500°C 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 with a peak maximum of ~ 45% (Fig. 5b) in comparison with a broad peak with maximum of ~ 15.5% for the fine grained ceramic (Fig. 5a). This is result of two effects: (i) larger grains and small non-ferroelectric grain boundary volume, resulting in switching characteristics closer to the single-crystal behavior; (ii) high density, causing similar boundary conditions for the overall dipolar units. The enlarged FORC distribution by porosity effects was also observed in PZT ceramics with high degree of porosity [27].

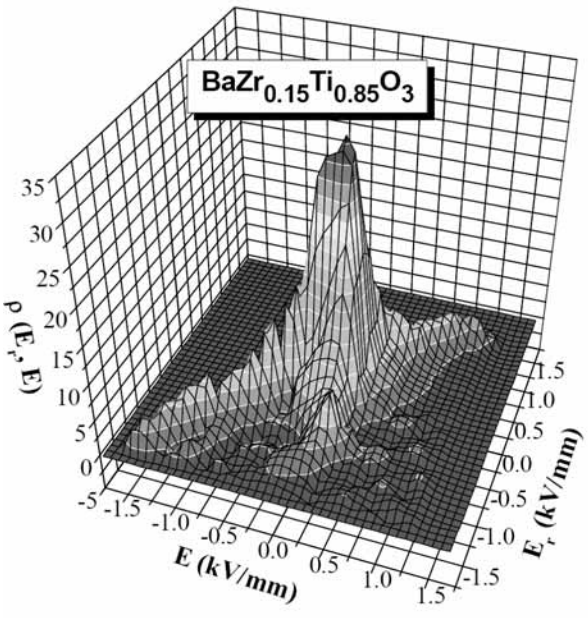

Figure 6. Three-dimensional FORC distribution $\rho(E_r, E)$ obtained for $BaZr_{0.15}Ti_{0.85}O_3$ ceramics sintered at 1500°C

The role of composition on the FORC diagram can be observed by comparing the Figs. 5b and 6, where the FORC distribution of BZT ceramics with x = 0.10 and x = 0.15, sintered at the same temperature, are shown. The maximum of the FORC distribution for the $BaZr_{0.1}Ti_{0.9}O_3$ ceramic is much sharper than in the case of the $BaZr_{0.15}Ti_{0.85}O_3$ sample (maximum of ~35%) and the irreversible component of the $BaZr_{0.1}Ti_{0.9}O_3$ sample is wider in comparison with $BaZr_{0.15}Ti_{0.85}O_3$ composition and it has a maximum located close to the second bisecting line at the coercivity E_{cM} = 0.17 kV/mm and bias E_{bias} = 0.13 kV/mm. Therefore, by analysing these 3D-FORC diagrams, a clear tendency towards the relaxor state with increased Zr content is observed, by

the constriction of the irreversible component towards smaller coercivities. Another tendency observed on the FORC distribution of $BaZr_{0.15}Ti_{0.85}O_3$ composition is the increase of the local inhomogeneity of the sample, causing multiple maxima distribution, related to multiple polar mechanisms for polarization. These results were also confirmed by a dc-tunability analysis [28].

IV. Conclusions

The dielectric and ferroelectric analysis of the BZT ceramics with similar grain size demonstrated the expected ferroelectric-relaxor crossover induced by increased Zr content. For the $BaZr_{0.1}Ti_{0.9}O_3$ ceramics sintered at different temperatures, the relaxor character is increased with the reduction of the grain size. The FORC distribution shows almost zero reversible contribution and well-separated sharp irreversible component for larger grains, while more diffuse distribution with a continuous extension from $E_c = 0$ (reversible) to $E_c \neq 0$ (irreversible, switching) is typical for finer grains.

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