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Compositionally induced ferroelectric-relaxor crossover in $Ba(Zr,Ti)O_3$ ceramics

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$Ba(Zr_xTi_{1-x})O_3$ ceramics with various compositions x =0, 0.10, 0.15 and 0.18 have been prepared by solid state reaction using nanometric precursors of $BaCO_3$, TiO_2, and ZrO_2. The processing parameters were optimized to obtain pure perovskite phase and homogeneous microstructures and densities higher than 90% for all the samples. The dielectric data showed a ferroelectric-relaxor crossover and a shift of the Curie temperature towards lower values with increasing x. Using the modified Landau model for relaxors, the local order parameter as a function of temperature has been calculated. It was demonstrated that the relaxor character is more evident with increasing the Zr addition. The values obtained by fits with empirical equations of the dielectric data indicated a mixed ferroelectric-relaxor character for all the compositions and an increasing relaxor character with Zr addition.

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1. Introduction

$BaTiO_3$ – based perovskites are known as high permittivity ceramics for MLCCs (Z5U and Y5V types), high electrostrictive coefficients materials for electronic, electrostriction and pulse generating devices, transducers, infrared detectors, tunable devices for microwave electronics etc. [1-4]. In addition, $BaTiO_3$ is an environment-friendly dielectric system with similar performances as showed by *Pb*-based electroceramics.

The solid solution $BaTiO_3$–$BaZrO_3$ presents a great interest due to the different character of the dielectric response which can be tuned by composition. The $BaZr_xTi_{1-x}O_3$ ceramics have perovskite ABO_3 structure and *Zr* ion occupy *B* site positions, replacing the *Ti* ions. The Zr^{4+} ion is chemically more stable than Ti^{4+} and has a larger ionic size (atomic radius of 206 pm by comparison with 176 pm of *Ti*) to expand the perovskite lattice, resulting in interesting features of the dielectric behavior. The dielectric data from literature reported for $BaZr_xTi_{1-x}O_3$ ceramics suggested a normal ferroelectric behavior for $0<x<0.1$, a diffuse phase transition in the range $0.1<x<0.2$ and a relaxor character for $0.2<x<0.5$ [5-13]. The degree of diffuseness of the ferro-para phase transition is increasing with the *Zr* addition [5-7]. For $x>0.5$, the system does not present ferroelectric distortion. These limits are very sensitive to the preparation method, the presence of possible secondary phases and to the microstructural characteristics.

In the last years, $BaZr_xTi_{1-x}O_3$ system became again attractive from the point of view of its characteristics related to its local polar properties [8], the phase formation mechanism [9, 10] and for the dielectric/tunability properties in the view of microwave applications [11, 12]. Simon *et al.* [13] investigated the possibility of inducing relaxor character by both homo- (*Zr* on the *Ti* sites) and heterovalent (*Bi* on the *Ba* sites) substitutions in order to obtain lead-free relaxor materials based on the $BaTiO_3$ ceramics. They concluded that high substitution rate $x>0.35$ is necessary to induce relaxor state if using homovalent substitution only. Therefore, by analogy with magnetic systems, it was postulated the possibility to induce superparaelectric state characteristic of relaxor or spin-glass systems by reducing grain size in ferroelectrics [14-16]. It results that by choosing appropriate compositions, it seems possible to disrupt the long-range order typical for the ferroelectric state and to induce the relaxor one by diminishing the grain size in ceramic.

In the present work, $BaZr_xTi_{1-x}O_3$ (BZT) ceramics with $x \in [0, 0.18]$ were prepared by solid-state reaction using nanometric precursors of $BaCO_3$, TiO_2, and ZrO_2 [17-19]. The nanopowders were used for reducing the calcination temperature in order to be able to obtain also ceramics with submicron grain size. The processing parameters were optimized in order to obtain pure perovskite phase after sintering and to have homogeneous microstructures and densities higher than 90% for all the samples.

2. Sample preparation and experiment

$BaZr_xTi_{1-x}O_3$ (BZT) ceramics with various compositions $x=0,\ 0.10,\ 0.15$ and 0.18 were prepared by solid-state reaction (mixed-oxides) [17] technique using the following chemical reaction:

$$BaCO_3+(1-x)TiO_2+xZrO_2 \rightarrow Ba(Zr_xTi_{1-x})O_3+CO_2\uparrow \cdot \quad (1)$$

High-purity starting nanopowders of: $BaCO_3$ (Solvay), TiO_2 (Toho) and ZrO_2 (Tosoh) were weighted in stoichiometric proportions in order to obtain 25g of $BaZr_xTi_{1-x}O_3$ solid-solution after the chemical reaction [19]. The oxides were then wet-mixed with distilled water for 48 h. After freeze-drying, the powders were calcined at 1000^0C for 6 hours to promote the solid-state reaction (1). The calcined powders were passing through a screen and manually re-milled. The re-milled powders were compacted in cylinders (length ~2-3 cm, diameters of ~1cm) by cold isostatic pressing at 1500 bar. The pellets were sintered at different temperatures (1350-1500^0C) for 2 hours.

After sintering, the density was measured, the phase purity was determined by X-ray diffraction and the microstructures were examined by Scanning Electron Microscopy, as described in the following. The phase purity of the calcined powders and sintered ceramics was checked by X-ray diffraction (XRD, Philips, Model PW 1710) using CoK_α radiation of 0.179 nm with a secondary graphite monochromator, a step size of $2\alpha=0.03^0$ and sampling time of 10s.

The degree of mixing for various additions of polyacrylic acid (PAA) and after various mixing times was examined by Scanning Electronic Microscopy (SEM, Philips, Model 515) analysis. For the electric measurements, Ag–Pb electrodes were deposited on the plane-parallel polished surfaces of the ceramics followed by annealing in air at 500^0C for 12 h. The impedance spectroscopy system was composed of an impedance analyzer (Solartron, SI 1260, 0.5V excitation voltage) and an oven with a digital temperature controller (temperature sensor Pt100) assisted by PC-based custom applications within the LabView program. The complex impedance in the frequency domain (1–10^6)Hz and temperatures ranging from 20^0C to around 200^0C was determined.

3. Results and discussions

3.1 Phase purity and microstructural characterization

Fig. 1 shows the XRD pattern of the calcined powders, for different compositions of *Zr*, *x=0.10, 0.15, 0.18*. The XRD analysis proved that after calcination at 1000^0C for 6 h all the compositions show the presence of the major titanate phase with cubic or pseudo-cubic symmetry and some wt% of orthorhombic $BaCO_3$ (features at $2\theta\sim51^0$). Slow step scanning XRD analysis performed at a few calcination steps revealed that $BaTiO_3$ phase starts forming from ~700^0C while $BaZrO_3$ from ~800^0C. The XRD patterns suggest that the rate of $BaZrO_3$ formation is lower than that of $BaTiO_3$.

After sintering the pellets at different temperatures (1350^0C, 1400^0C, 1450^0C and 1500^0C) for 2 h, the pure perovskite phase was fully formed (Fig. 2). Thus, above 1350^0C, the BZT phase formation increases rapidly due to the interdiffusion between *BT* and *BZ* components. The secondary phases, if present, are below the XRD detection limit in all the sintered samples.

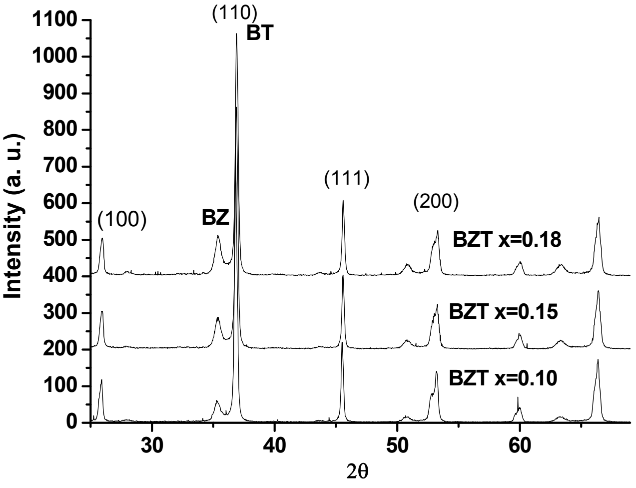


Fig. 1 XRD patterns of the powders calcined for 6 h at 1000^0C for different compositions.

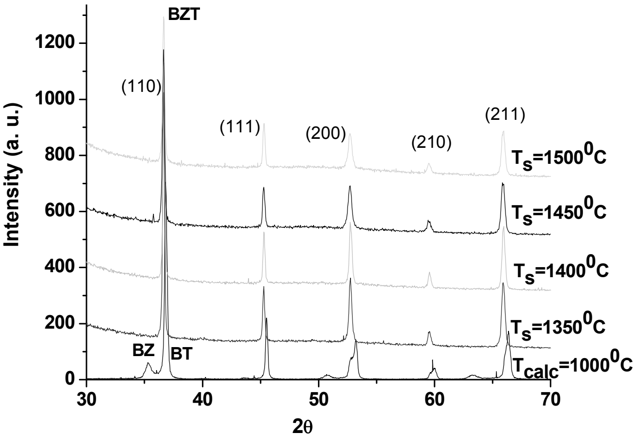
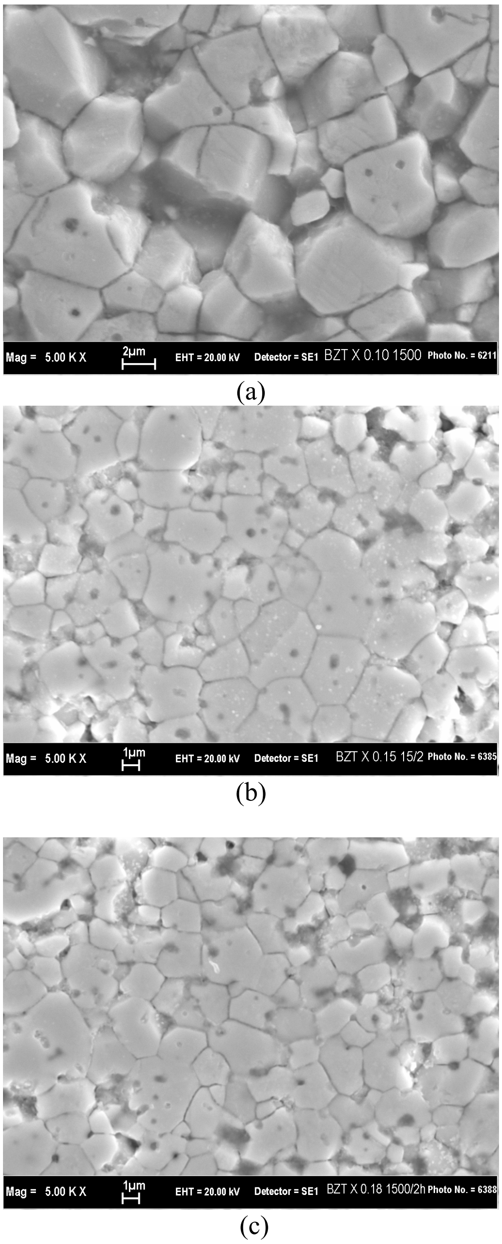


Fig. 2. XRD patterns of the $BaZr_{0.10}Ti_{0.90}O_3$ calcined powder and ceramics sintered at 1350^0C, 1400^0C, 1450^0C and 1500^0C.

For the SEM analysis the surfaces of the samples were polished on the emery paper with different granulation (from 4000nm to 800nm), then the sample surfaces were cleaned with acetone. Both fractured and polished surfaces of the ceramics were observed by SEM. For a better observation of the grain boundaries and a more precise determination of the grain size, the polished surface of some samples were chemically attacked with acid and then observed by SEM. The back-scattering SEM was also used to check the local phase purity. The average grain size was determined by line-intercept method on the SEM micrographs.

The SEM analyses showed that the grain size of the BZT samples with x=0.10, 0.15, 0.18 Zr content, for the same temperature of sintering of 1500°C, decreases with increasing the Zr addition (being of 3.27µm, 1.8µm and 1.54µm, respectively) (Fig. 3). The decrease in grain size with increase in Zr content seems to be associated with the lower grain-growth rate cased by slow diffusion of the Zr^{4+} ion, which has a longer radius than Ti^{4+}. This consideration is supported by a different, but related study in which the addition of Sr to the $BaTiO_3$ lattice increased the grain size in crystallized films [20], because Sr^{2+} has a smaller ionic radius than Ba^{2+}.



(a)

(b)

(c)

Fig. 3. SEM micrographs of the $BaZr_xTi_{1-x}O_3$ *ceramics with different content of Zr. The average grain size is: (a) ~3.27µm, (b) ~1.8µm, and (c) ~1.54µm.*

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

For the study of the dielectric properties as a function of temperature and frequency, it was used the Impedance Spectroscopy system, allowing to determine not only the rough dielectric properties, but to find characteristics derived by the presence of different dielectric and conductive properties in some regions of the sample, like for example grain boundary-grain bulk, electrode-ceramic interfaces, regions with accidental compositional inhomogeneity, if present, etc. [21-23]. The method was applied to determine the dielectric constant and losses of the present $BaZr_xTi_{1-x}O_3$ ceramics and to check the presence of the relaxor behavior.

The effect of composition on the dielectric data of $BaZr_xTi_{1-x}O_3$ ceramics with the compositions x=0.10, *0.15*, *0.18* are shown in the Fig. 4. As expected, the relaxor character is more evident as increasing the Zr addition. This was demonstrated by the results of fits with the empirical eq.:

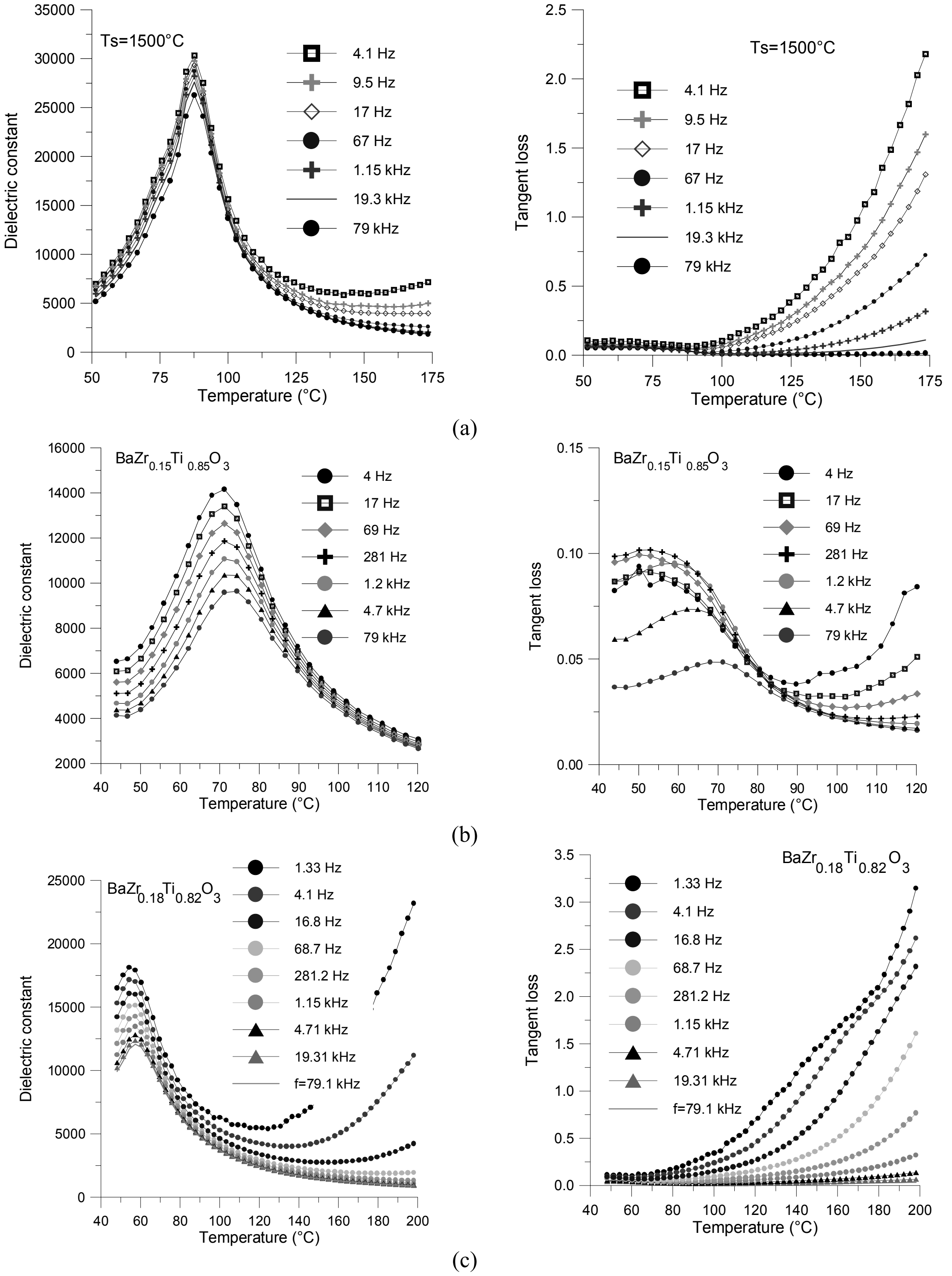
$$\varepsilon = \frac{\varepsilon_m}{1 + \left(\frac{T - T_m}{\delta_4} \right)^{\eta}}, \qquad (2)$$

of the dielectric data of the BZT with various compositions, at the frequency of 79 kHz. The computed values of these parameters are:

- $\eta=1.5$ and $\delta=20^0C$ for $x=0.10$,
- $\eta=1.65$ and $\delta=32^0C$ for $x=0.15$ and
- $\eta=1.7$ and $\delta=36^0C$ for $x=0.18$.

These values indicate a mixed ferroelectric-relaxor for all the compositions and an increasing relaxor character with Zr addition. The parameter δ indicates the temperature extension for the diffuse phase transition, being correlated with the dielectric permittivity broadening and shows the gradual increasing of the diffuse character of the phase transition with increasing the Zr concentration.

All the ceramics show at room temperature very high dielectric constant and remarkable low losses. Due to the proximity of the ferro-para phase transition, the sample with composition $x=0.18$ has the highest permittivity at room temperature, above 10000. For the BZT sample with $x=0.10$, the permittivity *vs.* temperature presents a maximum located at low frequency at the temperature $T_m \approx 90^0$C and the losses are below 20% (Fig. 4(a)); while the sample with composition $x=0.15$ has $\varepsilon \approx 10000$ at $T_m \approx 72^0$C ($tan\ \delta < 5\%$ at 80 kHz and <10% for all the frequencies in the temperature range (40-120)^{0}C). It also presents a negligible space charge effect (Fig. 4(b)).



(a)

(b)

(c)

Fig. 4. Real part of the dielectric constant and tangent loss vs. temperature for the $BaZr_xTi_{1-x}O_3$ ceramics, sintered at 1500^0C at a few frequencies, with: (a) x=0.10,(b) x=0.15 and x=0.18.

This sample is the unique one to follow a modified Curie-Weiss dependence in the paraelectric state. For some reasons, a higher degree of electrical homogeneity was obtained for this composition. The ceramic with the composition *x=0.18* has higher losses (in any case smaller than 10% at the room temperature even at *f*=1.33Hz) and a strong space charge contribution, giving rise to losses above unity for $T > 130^0$C (Fig. 4(c)).

The composition-induced shift of the ferro-para phase transition at a fixed frequency f=80kHz is shown in the Fig. 5 where the temperature-dependence of the dielectric constant of the BZT solid solutions by comparasion with a BT ceramic are presented. The difference between the sharp ferro-para phase transition in BT (fully ferroelectric) and the diffuse phase transitions in the solid solutions all of them presenting a mixed ferroelectric-relaxor behavior is visible in this picture.

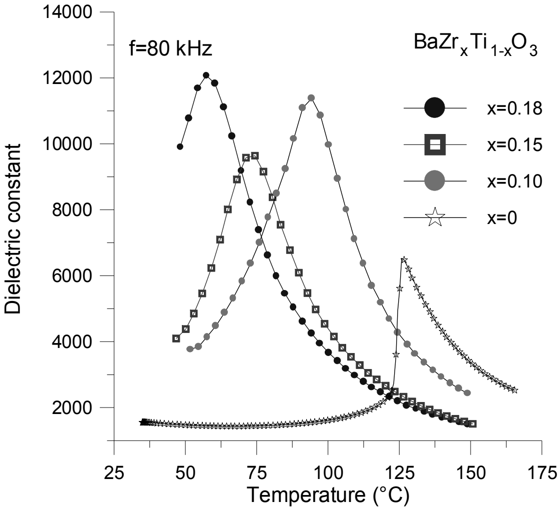


Fig. 5. Real part of the dielectric constant vs. temperature for the $BaZr_xTi_{1-x}O_3$ ceramics with x=0, 0.10, 0.15 and 0.18 at a fixed frequency, illustrating the compositionally-induced shift of the Curie temperature.

The present dielectric data are confirmed by the results of some recent local AFM-piezoresponse comparative study performed on the BZT ceramics with the compositions $x=0.10$ and $x=0.18$ [27]. The main obtained results are summarized below: (i) none of the two compositions could be totally poled or switched, like the normal ferroelectrics; (ii) the samples locally present 4 different types of responses (ferroelectric with a strong piezoresponse, field-induced ferroelectric, polar but non-switchable and non-polar regions); (iii) the regions with a natural strong piezoresponse and ones obtained after poling are larger in size and more stable in time for the sample with $x=0.10$ than for $x=0.18$; (iv) the sample with $x=0.18$ exhibits a diminished piezoresponse compared to the $x=0.10$ one. The observed local features are confirming the ferroelectric-relaxor crossover with increasing x, as observed by the analysis of the dielectric data.

4. Conclusions

The dielectric properties of $BaZr_xTi_{1-x}O_3$ ceramics prepared by solid state reaction are reported. All the ceramic samples have excellent dielectric properties (high dielectric constant above 4000 at room temperature and low dielectric losses, $\tan \delta < 5\%$). The ferroelectric-relaxor crossover induced by the *Zr* addition was demonstrated by the results of fits of the dielectric data for which an increasing extension of the Curie region was obtained when increasing the Zr concentration.

Acknowledgements

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