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Study of the frequency-dependence of the complex permittivity in Ba(Zr,Ti)O_3 ceramics: evidences of the grain boundary phenomena

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The frequency-dependence of the complex permittivity of some Ba(Zr,Ti)O_3 ferroelectric ceramics was investigated, with the aim to evidence different behaviors related to microstructural characteristics. Ferroelectric $BaZr_{0.10}Ti_{0.90}O_3$ sintered at two temperatures gave different types of impedance spectra due to their differences in the microstructures. The multiple components in the complex impedance diagram result from the grain boundary phenomena, i.e. from local differences in the conductivity and dielectric properties of the ceramic grain bulk and ceramic grain boundary.

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1. Introduction

One of the most used method of characterisation the dielectric properties of materials is the impedance spectroscopy. It has been widely used to study the dielectric behavior of the crystalline and polycrystalline ceramic materials [1-5]. Generally, the dielectric properties of the ferroelectric and magnetic ceramics are due to intra-grain, inter-grain and electrode effects. The motion of charges could take place by charge displacement, dipole reorientation, space charge formation, hoping and other mechanisms. In order to understand the electrical properties of a given sample, the ceramic grain, the grain boundary and the electrode contributions must be separated. The inter-grain boundaries in ceramics are defective regions (Oxygen vacancies are typical defect in perovskites) as well as the place of segregated impurities or dopants. Accordingly, it is expected that from the electrical point of view, the grain bulk and the grain boundary regions have different dielectric and conductive properties. In addition, the ceramic region in contact with electrodes might be “modified” with respect to the inner part of the bulk: different Fermi levels of the two materials in contact give rise to Schottky barriers, imperfect conductivity of the electrodes create a screening region changing the potential distribution in their neighborhood and metallic ions might diffuse into the ceramic creating a doped interface regions [6]. In any of these situations, the dielectric and conductive properties at the contact electrode-ceramics might be different with respect to the rest of material. The complex impedance analysis has proved as a very powerful tool for separating these contributions. In order to illustrate the complex relaxation behavior in electroceramics and to check if such kind of inhomogeneities give different dielectric responses, this method was used in the present paper for ferroelectric relaxor $BaZr_{0.10}Ti_{0.90}O_3$ ceramics.

A homogeneous dielectric is described by the Debye eq. [7]:

$$\varepsilon^* - \varepsilon_\infty = \frac{\varepsilon_s - \varepsilon_\infty}{1 + i\omega\tau}, \tag{1}$$

Cole-Cole [8]:

$$\varepsilon^* - \varepsilon_\infty = \frac{\varepsilon_s - \varepsilon_\infty}{(1 + i\omega\tau)^{1-\alpha}}, \tag{2}$$

or more generally, by the *universal relaxation power-law* as proposed by Jonsker [9]:

$$\varepsilon^* = \frac{\varepsilon_s + \varepsilon_\infty (i\omega\tau)^q}{1 + (i\omega\tau)^q}, \tag{3}$$

where:

$$\varepsilon^* = \varepsilon' - i\varepsilon'' \tag{4}$$

is the complex permittivity, ε_s is the static component (at zero frequency), ε_∞ is the permittivity at very high frequency and α and q some non-dimensional parameters. In terms of the complex dielectric constant representation (ε'' *vs.* ε') or complex impedance representation (Z'' *vs.* Z'), an ideal simple Debye relaxation will be represented as a semicircle in the complex plane. The data for real homogeneous dielectrics actually fit an arc of a circle with the center below the real axis [9] and are described by an RC-equivalent circuit. In this case, a correct estimation of the complex permittivity and losses are obtained, by determining the RC components and then by using geometrical data on the ceramic capacitor.

For a polycrystalline ceramic material with electrodes, a more complex model is appropriate, in which different groups of RC-circuits describing: (a) the ceramic grain, (b) the ceramic grain boundaries, (c) the electrode-ceramic interfaces (Fig. 1).

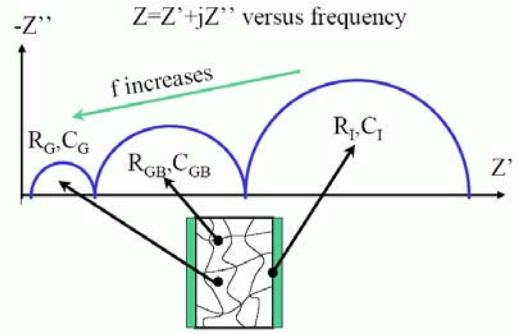


Fig. 1 Model adopted for a real electroded polycrystalline ceramic containing three distinct contributions: ceramic grain (R_G, C_G), ceramic grain boundaries (R_{GB}, C_{GB}) and electrode-ceramic interfaces (R_I, C_I).

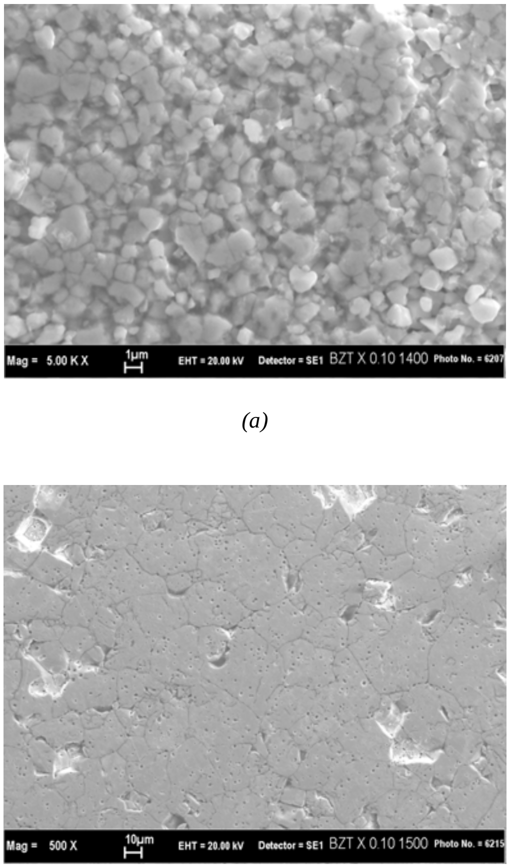
The last one gives a very important contribution mainly in ultrathin film structures, because the “modified” ceramic at the interface with electrode occupies an important volume ratio of the sample. The second component is missing in single-crystals and is enhanced in nanosized ceramics, due to the large number of grain boundaries in such structures. Dependent on their electrical properties (values of the equivalent impedance of the regions), the contributions are often convoluted and in such a case their separation is very difficult. In this case, it is impossible to correctly estimate the complex permittivity associated to these regions since their geometry is not strictly determined. However, an effective complex permittivity might be used to describe the obtained dielectric data, but it should be kept in mind that this is a characteristic of the system (ceramic grains/ceramic grain boundaries/electrodes) and not of the material itself. This is the reason for which the complex representation (*Z'' vs. Z'*) is normally used for such ceramics and not the Cole-Cole plot (ε'' *vs.* ε').

2. Sample description and experimental details

The impedance spectroscopy investigation was employed for the $BaZr_{0.10}Ti_{0.90}O_3$ bulk ceramics to illustrate the two types of relaxation behaviors and to check if local dielectric and conductive different properties will give rise to multiple Debye relaxations.

$BaZr_{0.10}Ti_{0.90}O_3$ ceramics were prepared by solid state reaction [10] starting from high-purity precursors ($BaCO_3$, TiO_2 and ZrO_2) which have been wet-mixed, dried, calcined at 1000°C/2h. After checking the phase purity of the calcined powders by X-ray diffraction analysis (XRD), they were manually milled in an agate mortar, then isostatically pressed at $2x10^8$ Pa and sintered at 1400°C/1h and at 1500°C/1h to obtain two types of microstructure of the same composition. The impedance spectroscopy system composed by an impedance analyzer (Solartron, SI 1260, 0.5V excitation voltage) and an oven with digital temperature controller (temperature sensor Pt100) assisted by PC-based custom applications within the LabView program allowed the measurement of the complex impedance between the frequencies (0.1-$5x10^6$) Hz.

The phase and crystallographic microstructure of the ceramics were examined by Scanning Electronic Microscopy (SEM, Philips, Model 515) analysis. Fig. 2 shows the obtained microstructures of the $BaZr_{0.10}Ti_{0.90}O_3$ ceramics sintered at 1400°C/1h (a) and at 1500°C/1h (b).



(a)

(b)

Fig. 2 SEM micrographs of the $BaZr_{0.10}Ti_{0.90}O_3$ ceramic sintered in air at: 1400°C/2h (bar: 1μm), (b) 1500°C/2h (bar: 10μm).

The phase purity was maintained in both cases after the sintering step, as checked by the XRD analysis. A higher sintering temperature led to smaller porosity and bigger grains, as visible in the Fig. 2 b, by comparison with Fig. 2 a. While the fine ceramic presents an open porosity, the coarse one shows mainly a closed porosity. It is clear that the two samples have completely different microstructures with various types of grain boundaries and boundary conditions and these might result in visible effects on their impedance responses, in spite of the same composition.

3. Results and discussions

Fig. 3 and Fig. 4 show the impedance spectra at T=50°C and at T=150°C, resulted for the ceramics sintered in air at T_s=1400°C and T_s=1500°C, respectively.

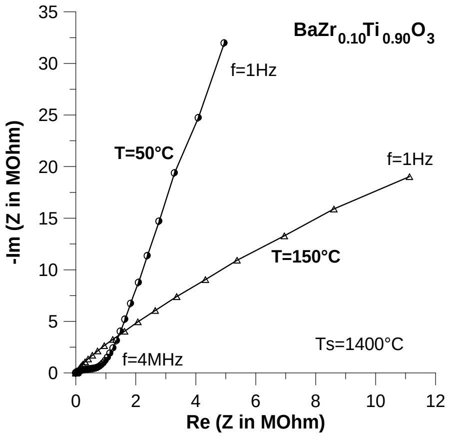


Fig. 3 Impedance spectra of $BaZr_{0.10}Ti_{0.90}O_3$ ceramic sintered in air at T_s=1400°C, showing two components of the impedance at T=50°C which reduce to one component for T=150°C. The equivalent RC components are temperature-dependent.

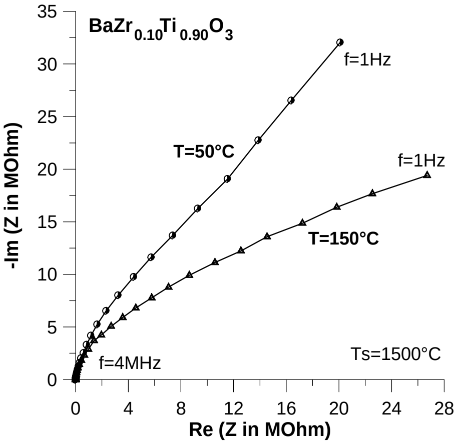


Fig. 4 Impedance spectra for the ceramic $BaZr_{0.10}Ti_{0.90}O_3$ ceramic sintered in air at T_s=1500°C, at two temperatures: T=50°C and T=150°C.

While the sample sintered at lower temperature shows two distinct components at room temperature, clearly illustrating an inhomogeneity attributed to grain boundary phenomena, the ceramics sintered at T_s=1500°C has a better dielectric and conductivity homogeneity as demonstrated by an apparent single component in the complex impedance plot (Figs. 3 and 4). It means that at room temperature the sample sintered at T_s=1400°C acquired during the sintering/cooling stages a certain differences between the grain boundaries and grain bulk from the dielectric and transport properties point of view. This difference is most probably due to the higher number of grain boundaries present in this ceramic (as a consequence of its smaller average grain size) by comparison with one sintered at T_s=1500°C, apparently looking more homogeneous. Since the XRD did not detect any secondary phases in both $BaZr_{0.10}Ti_{0.90}O_3$ ceramic samples, it results that the main difference between the bulk and grain boundaries most probably comes from different oxygen stoichiometry in the two regions. The oxygen vacancies with a higher density at the ceramic grain boundaries are producing a depleted region and thus, the ceramics is characterized by two equivalent different RC for the two regions causing two distinct contributions in the impedance plot. The sample with a lower density of grain boundaries has less depleted areas and consequently, if present, a smaller component due to the boundaries and a large contribution from the grain bulk. Both contributions show temperature-dependent equivalent RC components, due to the fact that the ceramics are ferroelectric with field-dependent permittivity and losses.

Both $BaZr_{0.10}Ti_{0.90}O_3$ ceramics have at high temperature (T=150°C) an apparent single component in the impedance plot, due to the fact that the differences between the properties of the grain boundary and grain bulk are less important when the ferroelectric is in its paraelectric state (the Curie temperature for this composition being ~90°C [6]).

By fitting the data with the Debye model (eq. 1), the characteristic relaxation times for the homogeneous sample sintered at 1500°C are: τ~1.6 s at T=50°C and a bit smaller τ~0.9 s at T=150°C. Both are evidences of slow relaxation dielectric processes [9] which are thermally-activated The ceramic with two components in the impedance plot shows two Debye relaxations: a slow one with similar characteristic times of ~1 s and in addition, a faster process with τ~50 ms. The fast component in the higher frequency region may be due to the orientational intergrain boundary, and the slow component in the lower frequency region is interpreted in the literature as the formation and migration of ions at the grain boundary surface interfacial polarization [11].

4. Conclusions

The dielectric response determined by impedance spectroscopy in ferroelectric polycrystalline $BaZr_{0.10}Ti_{0.90}O_3$ ceramics was investigated: two types of microstructures were obtained for the same composition by sintering the samples at 1400°C/1h and at 1500°C/1h, respectively. The ferroelectric ceramics show an impedance response with two components for the lower sintering temperature, most probably caused by the inhomogeneity associated to the small grain size.

Acknowledgements

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