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Dielectric properties of the (1-x)$BiFeO_3$ – x$BaTiO_3$ multiferroic ceramics

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The solid solutions of (1-x)$BiFeO_3$ – x$BaTiO_3$ with x=0.20 and x=0.30 have been prepared via solid state, by sintering in air or in oxygen atmosphere. Optimum calcination and sintering strategy for obtaining pure perovskite phase, dense ceramics (>97% relative density) and homogeneous microstructures have been determined. Rhombohedral structure for x=0.20 and a pseudo-cubic one (low distortion) for the x=0.30 ceramics were obtained. In spite of the excellent microstructures and phase purity, the ferroelectric-paraelectric transitions at ~145°C and ~230°C for x=0.30 and x=0.20, respectively, found by differential calorimetry study were not confirmed by the dielectric spectroscopy investigations. The dielectric response shows multiple relaxations, high losses mainly at low frequency and high temperatures, which are signs of space charge or Maxwell Wagner phenomena. The complex impedance response for the ceramics sintered in oxygen shows in addition grain boundary effects. It results that in such ceramics, the dielectric response is strongly affected by the extrinsic phenomena rather than by the intrinsic ferroelectric response. The extrinsic properties are impossible to be fully controlled by normal ceramic processing. However, at room temperature and frequencies above 500 kHz, even these ceramics accomplish the dielectric properties requirements for further magnetoelectric applications.

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1. Introduction

$BiFeO_3$ system is one of the single-phase ME multiferroics. It is ferroelectric with the Curie temperature $T_C \approx 830°C$ and antiferromagnetic having the Néel temperature $T_N = 310°C$, also showing a weak ferro/ferri magnetic characteristic in some temperature ranges [1]. In its bulk state, $BiFeO_3$ has a rhombohedral-distorted perovskite structure *R3c* (with the cell parameters a=b=c=5.63Å, $\alpha=\beta=\gamma=59.4°$) at room temperature. Having such a high Curie temperature, it was expected to present a high spontaneous polarization in its ferroelectric state (for example, $PbTiO_3$ with $T_C=1036°C$, has a spontaneous polarization of ~80-100 $\mu C/cm^2$). Practically, only low values of the polarization and of the dielectric constant were determined at room temperature, mainly due to the semiconducting properties of $BiFeO_3$, which does not allow proper electrical poling and leads to high dielectric losses. In ferroelectric ceramics the resolution of dielectric anomaly becomes difficult in such cases. Low resistivity of the sample at room temperature makes the observation of the ferroelectric loop very difficult. Although promising for its multiferroic character, only poor dielectric and ferroelectric properties (low values of the polarization and of the dielectric constant) were found at room temperature in the bulk ceramics, mainly due to the semiconducting character which does not allow a proper electrical poling and lead to high dielectric losses. Some better P(E) characteristics (with $P_s=8.9$ $\mu C/cm^2$, $P_r=4.0$ $\mu C/cm^2$, $E_c=39$ kV/cm under an applied field of 100kV/cm) were observed at room temperature in $BiFeO_3$ ceramics obtained by rapid liquid phase sintering [2]. Only in epitaxial or polycrystalline films of $BiFeO_3$ obtained by Pulsed Laser Deposition (PLD), good dielectric properties were reported [3, 4]. However, even these results and their interpretation is presently under debate between a few groups of researchers [4-6]. In order to reduce the mentioned problems in the bulk form, it was adopted the method of forming binary solid solutions with other perovskites with good dielectric properties as $BaTiO_3$ [7, 8], $PbTiO_3$ [9] or others [10]. However, even in solid solutions, the problems of losses were only partially solved. Even in such solid solutions, the problems of losses were only partially solved and the reported data are often "author dependent". Recently, (1-x)$BiFeO_3$-x$BaTiO_3$ solid solutions with the composition x=0.20 and x=0.30, having excellent phase purity were prepared by classical solid state reaction method and their magnetic and dielectric properties were reported in the ref. [8]. In the present work, the functional properties, mainly the dielectric and ferroelectric ones in (1-x)$BiFeO_3$-x$BaTiO_3$ ceramics prepared by mixed oxides are carefully investigated.

2. Preparation and experimental details

The (1-x)$BiFeO_3$-x$BaTiO_3$ solid solutions were prepared from Bi_2O_3, Fe_2O_3, TiO_2 (99.9% Aldrich) and $BaCO_3$ (99.9%, Solvay Bario Derivati) [8]. The precursors were mixed, milled and calcined at (600–750°C) for 4–8 h with intermediate milling steps. The calcined powders were milled, isostatically pressed at $2x10^8$ Pa and then sintered at 900°C/2h. Both sintering in air and in oxygen atmosphere were performed. The phase composition and crystal structures at different calcinations steps and after sintering were checked by X-ray diffraction (XRD, Co Kα radiation, Philips PW1710, Philips, Eindhoven, The Netherlands). The microstructures were characterized by scanning electron microscopy (SEM, LEO 1450VP, LEO Electron Microscopy Ltd., Cambridge, UK). The Raman spectra in the range of (100, 1000) cm^{-1} wavelength at room temperature were recorded in back-scattering geometry by using a RENISHAW RM2000 micro-Raman spectrometer with 785 nm radiation, 2 μm spot diameter and 10 μm field depth. The dielectric measurements, in the frequency range 10^{-1} to 10^7 Hz, were performed at temperatures of 30–400°C with a heating/cooling rate of 0.5°C/min using an impedance analyzer Solartron SI1260. Differential scanning calorimetry (DSC) measurements were performed on ceramic samples of ≈100 mg in the range 20–250°C at a heating/cooling rate of 10°C/mi and the transition enthalpy was estimated from the area of the DSC peaks.

3. Results and discussions

3.1 Phase purity and microstructures

The X-ray diffraction patterns of Fig. 1 show the phase purity of the solid solution (1-x)$BiFeO_3$ – x$BaTiO_3$ ceramics with the compositions x=0.30 and x=0.20 sintered at 900°C/2h in air. Only the perovskite phase peaks (denoted as BF) and very small traces of $Bi_{25}FeO_{40}$ were obtained (ICSD 75324). The relative density for all the present ceramics samples was above 97%. The gradual change of the rhombohedral (Rh) *R3c* structure toward a cubic one with the increase of the $BaTiO_3$ addition is proved by the cancellation of the XRD splitting specific to pure $BiFeO_3$. While the rhombohedral split is still visible in the Fig. 1 for the ceramic x=0.20 for which the Ritveld analysis gives the cell parameters a=5.6152Å, c=13.9085 Å of the trigonal/Rh structure with Rwp=11%, for the ceramics with composition x=0.30, similar fits were obtained for a cubic structure (a=3.9945 Å, R_{wp}=11% for the cubic phase) by comparison with a Rh one, with a very low distortion (a=5.642 Å, c=13.8852 Å and R_{wp}=14.44% for the trigonal/Rh structure). It results that the composition x=0.30 is close to the cubic state. However, the presence of first order Raman activity, not allowed for a centrosymmetric state, clearly shows that the solid solution with x=0.30 is not really cubic, but slightly distorted. A similar result was obtained for another set of (1-x)$BiFeO_3$ – x$BaTiO_3$ ceramics prepared by solid state route with two-steps sintering method (pre-sintering step followed by the final sintering) [11]. The Raman spectra at room temperature are shown for both compositions of the present study in the Fig. 2. Small changes in the Raman modes, *e.g.* the higher intensity of the mode at 200 cm^{-1} assigned to a component of the longitudinal optical A1(LO) mode [12] for x=0.20 and some shifts in the positions of the Raman peaks and changes of their relative intensity are due to the compositional and symmetry differences between the two ceramics.

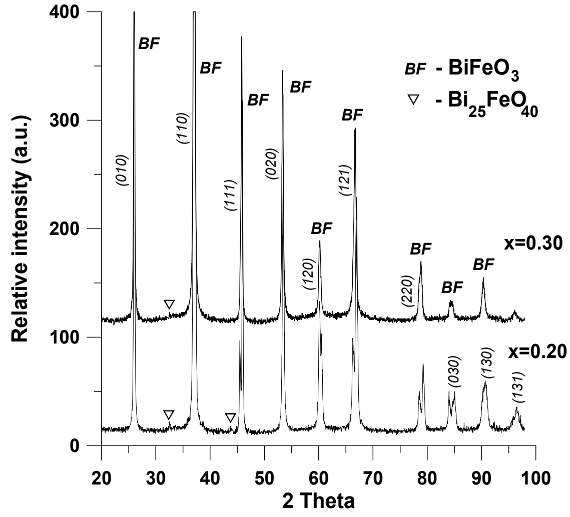


Fig. 1 X-ray diffractograms of the (1-x)$BiFeO_3$ – $BaTiO_3$ ceramics with the compositions x = 0.30 and x = 0.20 sintered at 900°C/2h in air.

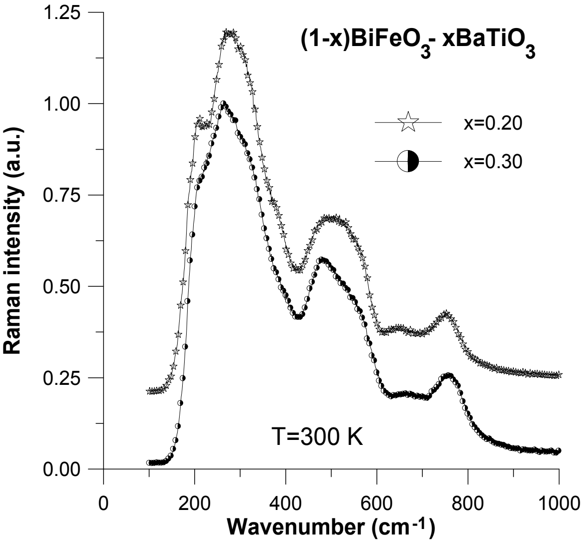
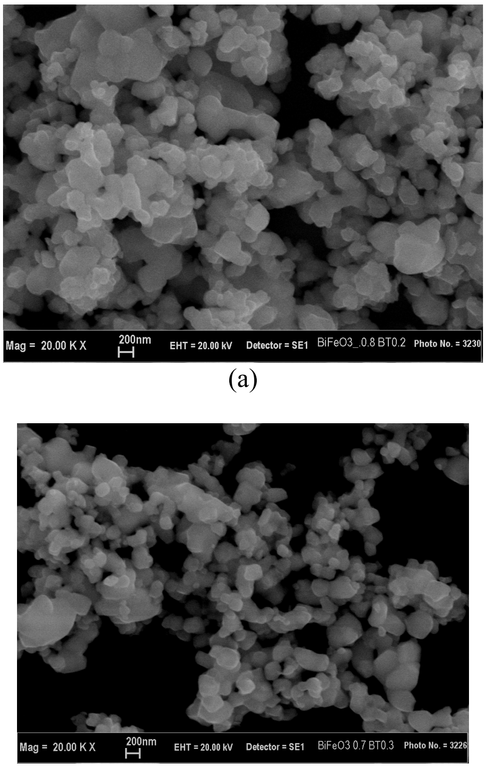


Fig. 2 Raman spectra at room temperature collected for the (1-x)$BiFeO_3$ – x$BaTiO_3$ ceramics with the compositions x=0.30 and x=0.20 sintered at 900°C/2h in air.

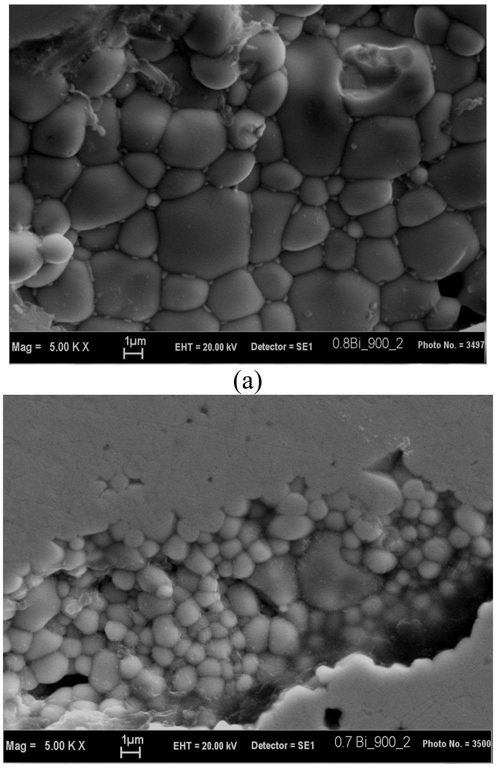
Fig. 3 presents the microstructures of the calcined powders, while Fig. 4 and Fig. 5 are showing the SEM micrographs of the ceramics surfaces after sintering in air and in oxygen atmosphere, respectively, for both compositions x=0.20 and x=0.30. While the calcined powders have almost similar particle size, as visible in the Fig. 3 a-b, for both the ceramics sintered in air and in oxygen atmosphere, the better microstructures, with a good homogeneity, high density and perfect triple junctions were obtained for the composition x=0.20. The presence of $BaTiO_3$ influenced the microstructure (Fig. 4 and Fig. 5), by changing the grain growth process. A higher average grain size (almost double) was found for x=0.20 by comparison with x=0.30 composition.



(a)

(b)

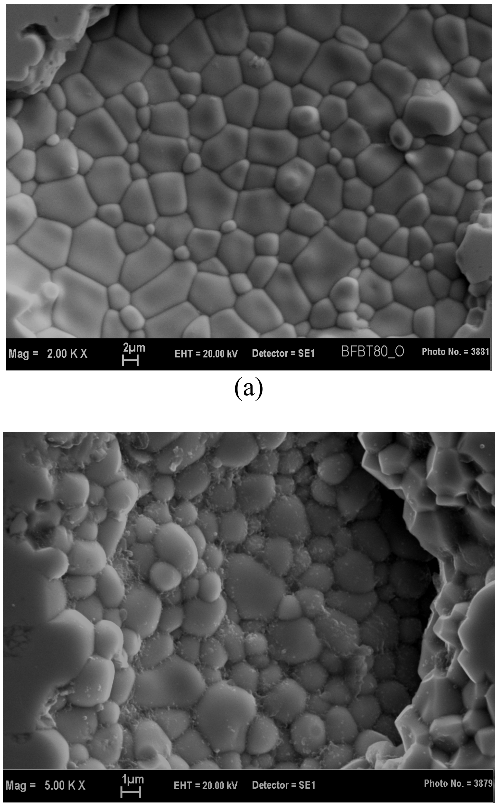
Fig. 3. SEM micrographs of the (1-x)BiFeO$_3$ – xBaTiO$_3$ solid solutions after calcination at 750°C/8h, having the compositions: (a) x=0.20, (b) x=0.30 (bar: 200 nm).



(a)

(b)

Fig. 4. SEM micrographs of the (1-x)BiFeO$_3$ – xBaTiO$_3$ solid solutions after sintering at 900°C/2h in air, with the compositions: (a) x=0.20, (b) x=0.30 (bar: 1μm).



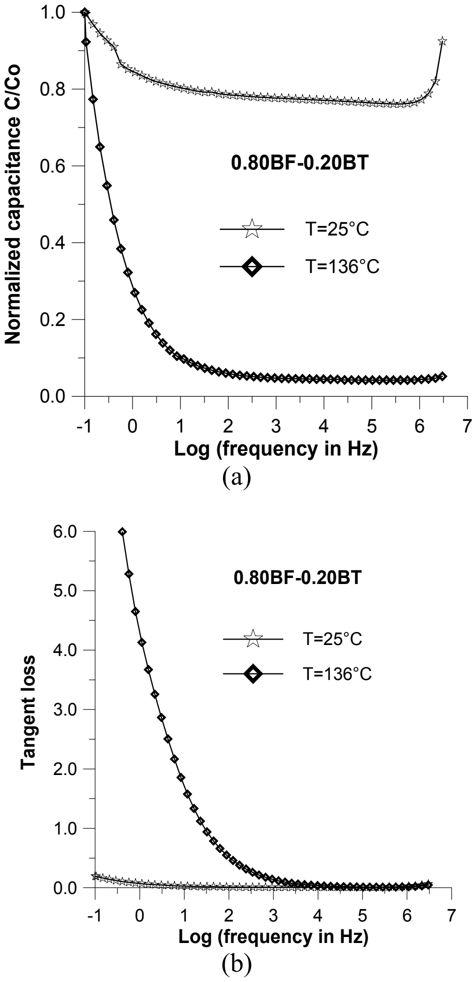
(a)

(b)

Fig. 5. SEM micrographs of the (1-x)BiFeO$_3$ – xBaTiO$_3$ solid solutions after sintering at 900°C/2h in oxygen atmosphere, having the compositions: (a) x=0.20 (bar: 2μm), (b) x=0.30 (bar: 1μm).

3.2 Dielectric properties

As mentioned before, the dielectric and ferroelectric characteristics of the BiFeO$_3$- based ceramics are poor even in the pure phase, due to their low resistivity causing leakage phenomena and high dielectric losses. Even for a high purity single-crystal at low temperature (80 K), a low spontaneous polarization of 3.5 μC/cm^2 along the (001) was determined, indicating a value of only 6.1 μC/cm^2 along the (111) direction [13]. Therefore, the saturation of the loop was not observed even at high fields of 55 kV/cm. Saturated ferroelectric hysteresis loops were observed recently at room temperature in the single-phase BiFeO$_3$ ceramics obtained by rapid liquid phase sintering [2], with values of the spontaneous polarization, remanent polarization and coercive field of 8.9 μC/cm^2, 4.0 μC/cm^2, and 39 kV/cm, respectively, under an applied field of 100 kV/cm [2]. The high conductivity and leakage found especially at higher temperatures were considered firstly caused by the high difficulty to produce single phase of BiFeO$_3$ (so that even very small impurities segregated at boundaries could have a doping effect and transform the dielectric into a semiconductor). On the other hand, even in very pure BiFeO$_3$, due to the spontaneous change of the oxidation state of Fe (3+/2+), oxygen vacancies are formed as a result of the electrical neutrality requirement, giving rise to thermal activated hoping conductivity.

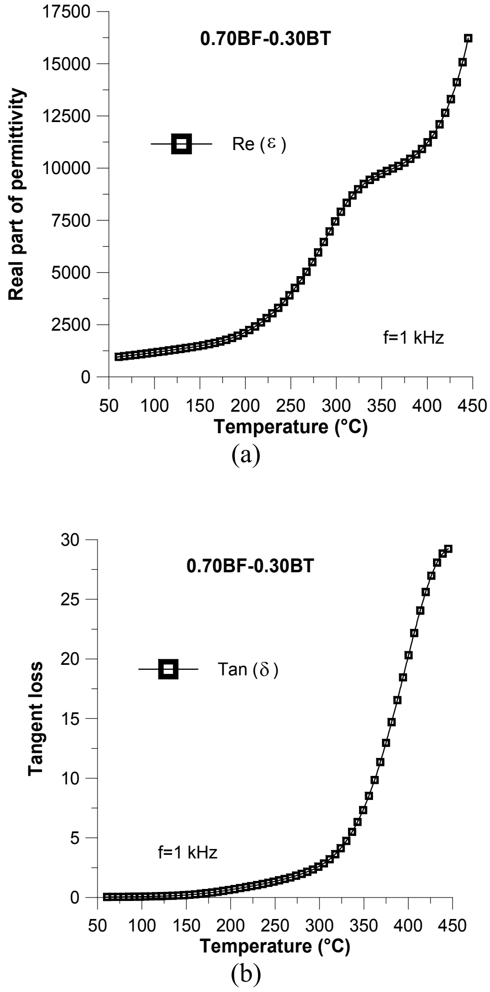


(a)

(b)

Fig. 6 Frequency dispersion of the dielectric characteristics for the 0.80BF-0.20BT ceramic sintered in air, in the range (0.1Hz, 500MHz) at two temperatures: 25°C and 136°C: (a) Normalized capacitance, (b) Tangent loss.

By forming a solid solution with an insulator perovskite (like $BaTiO_3$), it was expected to obtain better dielectric characteristics. For the $(1-x)BiFeO_3-xBaTiO_3$ single-phase ceramics [8], the literature dielectric data show the presence of the dielectric relaxations with thermally-activated features. In the present case, the frequency dispersion of the dielectric characteristics shown in Fig. 6 for the composition x=0.20 sintered in air, in the range (0.1 Hz, 500 MHz) at two temperatures: 25°C and 136°C are presented. A similar dependence was found for the ceramics x=0.30. Very high losses above unity are characteristic to low frequency and higher temperatures, when the ceramic becomes conductive. Both compositions present features demonstrating a dispersion at low frequencies, particularly in the range $(10^{-1},10^{2})$ Hz, with a sharp variation both of the permittivity (normalized capacitance – Fig. 6 a) and of loss (Fig. 6 b). Only at frequencies above 100 Hz the ceramic has better dielectric properties (tan δ < 5-10%), but shows low permittivity for a ferroelectric material, of around 300-400 at room temperature. These frequency variations are even more rapid at the temperature T=136°C than at room temperature, demonstrating a thermally-activated dc-conductivity mechanism in these ceramics. These phenomena are most probably related to the high degree of local inhomogeneity (not related to the composition, which was proved by SEM-EDX analysis and microRaman as being uniform), but rather to a space charge effect (Maxwell-Wagner polarization) due to the local charge imbalance caused by the local oxygen non-stoichiometry.



(a)

(b)

Fig. 7. Temperature dependence of the dielectric properties at a fixed frequency f=1kHz, in the range (50, 450) °C for the 0.70BF-0.30BT ceramics sintered in air: (a) real part, (b) tangent loss.

A second relaxation was found in the dielectric constant (normalized capacitance - Fig. 6 a) at frequencies above 1 MHz only at room temperature in both ceramic compositions. Since no anomaly is present in the imaginary part of the permittivity and tangent loss and due to the fact that it completely disappears at higher temperatures, it results that such a relaxation might be related to the ferroelectric domain wall motions, normally active in this range of frequencies [14].

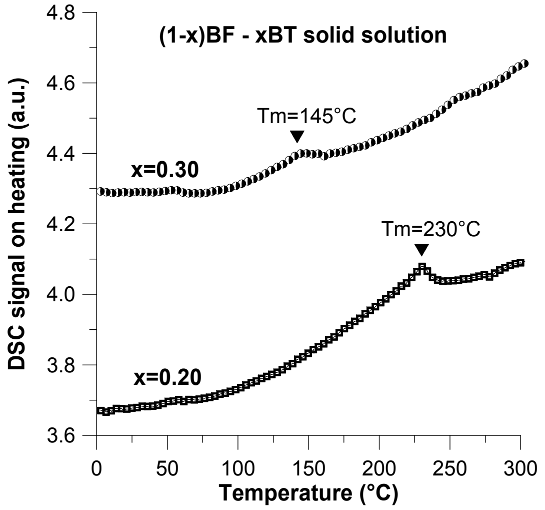


Fig. 8 Differential calorimetry data for (1-x)$BiFeO_3$-x$BaTiO_3$ ceramics showing endothermic peaks corresponding to the transition ferroelectric-paraelectric.

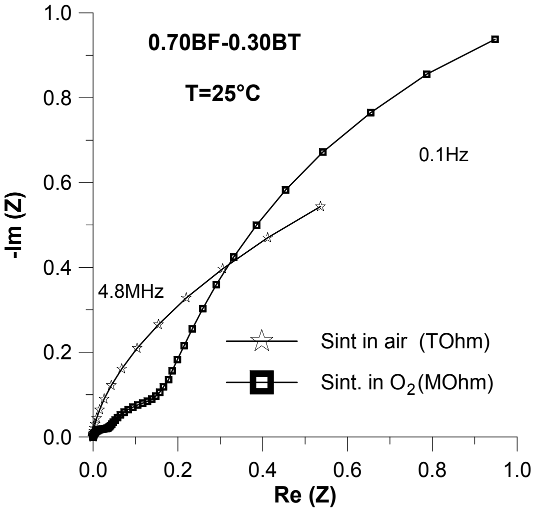


Fig. 9 Room temperature impedance spectra for the 0.70BF-0.30BT composition for two ceramics, showing the differences induced by the sintering in oxygen atmosphere by comparison with the sintering in air.

The temperature-dependence of the dielectric constant at a fixed frequency (Fig. 7) for the composition x=0.30 has a monotonous increasing from 1000 at the room temperature up to 10000 at 350°C at f=1 kHz, without presenting any anomaly at the expected ferroelectric-paraelectric transition temperature (~145°C for x=0.30). In fact, for both compositions analyzed here, the ferroelectric-paraelectric phase transition was confirmed by the DSC analysis (Fig. 8): ~145°C for x=0.30 and ~230°C for x=0.20). The present dielectric data were unable to clearly show this phase transition, due to the fact that other stronger extrinsic effects were superimposed on the ferroelectric polarization response. In any case, the dielectric data were reproducible at heating/cooling, showing that no degradation process takes place in the sample during the heating/cooling cycle. By increasing the temperature (up to 450°C, as shown in the Fig. 7 b), some anomaly of the real part takes place at around 330°C (not related to the phase transition), while the imaginary part is continuously increasing to high values. A similar dependence was also observed for the ceramic with composition x=0.20. Such anomalies and high losses at increasing temperature are signs of space charge effects in the present samples. Even in high purity ferroelectric or non-ferroelectric perovskites, some dielectric relaxations not related to the structural phase transitions were sometimes reported (not intrinsic). These are defect-related dielectric relaxation phenomena, i.e. extrinsic properties [15, 16] caused by many factors as: the presence of A-site vacancies in the perovskite ABO_3 unit cell [17], space charge electrons [15], oxygen vacancies [18, 19] or impurities [20]. In addition, all the magnetic materials contain transition elements as Fe, Mn, etc. that possess two or even more oxidation states. Additional charged defects can thus arise from the spontaneous transitions Fe^{3+}/Fe^{2+} in the ferrites, as in the present case, associated with local changes of the concentration of the oxygen vacancies preserving the electrical neutrality. These defects are strongly affecting the dielectric properties of the ceramics giving sometimes stronger contributions to the total polarization than the ferroelectric one.

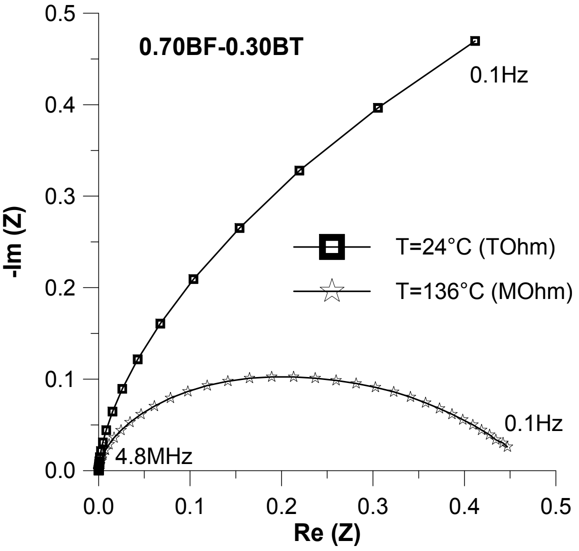


Fig. 10 Impedance spectra for the 0.70BF-0.30BT ceramics sintered in air, at two temperatures (24°C and 136°C), showing one component of impedance temperature-dependent.

In the case of bulk $BiFeO_3$ and even in the solid solutions with a good insulator like (1-x)$BiFeO_3$-x$BaTiO_3$ ceramics, it seems that such defects are impossible to be controlled within the overall sample's volume. In an attempt to reduce the dielectric phenomena associated to the oxygen vacancies and to further reduce the dielectric losses, a few samples with the same compositions were sintered in oxygen atmosphere, also. However, their impedance spectra showed an evident inhomogeneity as due to distinct components of the ceramic with different resistivity and permittivity characteristics, possible attributed to the grain bulk, grain boundary and ceramic-electrode interface. In the complex impedance plot, these regions are characterized by 3 distinct semicircles, as shown in the Fig. 9 (higher frequencies are closer to the axis origin), by comparison with the behavior of the ceramic sintered in air, showing only one component in the impedance arch, which is changing with the temperature according to the temperature dependence of the dielectric constant and losses of this composition (as shown in the Fig. 10). It results that after sintering, during the cooling in oxygen atmosphere, the system could not acquire in any local region the same degree of oxygen stoichiometry, giving rise to grain boundary effects (i.e. different concentrations of the oxygen vacancy causing various local dielectric and transport properties and consequently, multiple components on the complex impedance plot). This is showing that the oxygen vacancy level is not homogeneous inside the ceramic sample. This parameter is difficult to be controlled by normal ceramic processing in bulk ceramic samples and this is the main explanation for various dielectric responses reported in literature for this system [7, 8, 11]. By this treatment, the impedance response of the ceramic became even more complicated. Further post-annealing thermal treatments are expected to eliminate the oxygen deficiency inside the ceramic bulk and equilibrate the oxygen stoichiometry of (1-x)$BiFeO_3$-x$BaTiO_3$ ceramics.

It is known that dielectric properties of polycrystalline ceramics are very sensitive to the microstructural characteristics. It was initially considered that the small magnetoelectric response of the $BiFeO_3$ system, its high dielectric losses and the observed multiple relaxations are caused by the impossibility of obtaining pure perovskite phase by traditional ceramic processing, and by the poor homogeneity, high porosity determined by the limited sintering temperature and cracks resulting during the sintering. However, even in the solid solutions with $BaTiO_3$ for which a better sinterability and pure phase was obtained and in spite of many efforts aimed to improve the microstructures [8], the overall extrinsic contributions to the dielectric characteristics remained uncontrolled, so that finally the dielectric and ferroelectric properties were still poor. Similar dielectric properties, with more thermally activated dielectric relaxations and losses far above unity at low frequencies and higher temperatures were found in $BiFeO_3$-based solid solutions with $PbTiO_3$ [9], sintered in air or in oxygen atmosphere, in spite of their excellent phase purity, high density and homogeneous microstructures.

4. Conclusions

The properties of the $BiFeO_3$-based multiferroic were known from the literature as very contradictory. In spite of the high Curie temperature, poor dielectric and ferroelectric properties were reported, particularly for the $BiFeO_3$ in ceramic form (high losses, small polarization, high leakage). This is most probably due to the impossibility to control in the whole bulk volume the composition, stoichiometry and oxygen defect concentration as resulted from the spontaneous change of the oxidation state of Fe (3+/2+). In attempt to improve the dielectric characteristics, solid solutions with $BaTiO_3$ were realized in the present work. Excellent microstructural characteristics with high density and homogeneous microstructures and phase purity were obtained. The obtained solid solutions with ferroelectrics $BaTiO_3$ demonstrated much improved dielectric properties and high reproducibility, by comparison with other literature data. However, even in our case, multiple relaxations and thermally-activated dielectric processes extrinsic in nature, were found. Besides the mentioned dielectric relaxations, multiple components in the complex impedance plot were found for the ceramics sintered in oxygen atmosphere, demonstrating that different dielectric and conductive properties due to various oxygen stoichiometry inside the ceramic bulk were locally obtained in these ceramics. The present work confirms the complicated dielectric behavior of the $BiFeO_3$-based system. In any case, the debate related to the intrinsic/extrinsic nature of the functional properties of such materials is still far to be exhausted and more data are needed for improving the present understanding.

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