Relaxor properties of Ba(Zr,Ti)O$_3$ ceramics

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BaZr$_x$Ti$_{1-x}$O$_3$ is a possible candidate as environmental friendly electroceramic material (Pb-free ferroelectric) due to its high dielectric and piezoelectric constants and ferroelectric properties in a temperature range which can be tuned by the composition. Its properties change from full ferroelectric behavior (x=0; BaTiO$_3$) with a sharp ferro-para phase transition to the full relaxor state (for $0.10 \leq x \leq 0.35$), when the structure is pseudo-cubic and the transition has a strong diffuse character and a frequency-relaxation in the kHz range. In the present work, the cross-over composition BaZr$_{0.1}$Ti$_{0.9}$O$_3$ was investigated. The ceramics have been prepared via solid state reaction; optimum parameters for calcination and sintering in order to obtain pure perovskite phase and a good densification have been found. The temperature dependence of the dielectric constant shows a diffuse phase transition with a small shift of the temperature corresponding to the maximum permittivity of (1-2) ^{o}C in the frequency range of 1 Hz÷1 MHz. The losses are smaller than 30% for temperatures below 130 ^{o}C, with a slight increasing at low frequency and high temperatures. The real part of the permittivity follows the Curie-Weiss law with frequency-dependent constants. The dielectric spectroscopy data show at least two relaxation processes: a thermally-activated one characteristic to low-frequency range f<100 Hz and a temperature-independent one at f$\geq$100 Hz.

1. Introduction

Perovskite oxides derived from BaTiO$_3$ has are well-known for their use in applications for: multilayer ceramic capacitors (as a high dielectric constant ceramics having the specifications X7R, Y5V), materials in electronic, electrostriction and pulse generating devices, transducers, infrared detectors, tunable devices for microwave electronics etc. [1-3]. In addition, BaTiO$_3$ is an environment-friendly dielectric system with similar performances as showed by many Pb-based electroceramics. Its properties can still be improved by doping or by forming solid solutions with other systems or by controlling its microstructural characteristics (porosity level, grain size, secondary phases, etc.). The solid solution BaTiO$_3$–BaZrO$_3$ is also of great interest due to its different character of the dielectric response which can be tuned by composition. The dielectric data reported for BaZr$_x$Ti$_{1-x}$O$_3$ ceramics [4, 5] suggest a normal ferroelectric behavior for 0<x<0.1, a diffuse phase transition in the range 0.1<x<0.20 and non-ferroelectric character for x>0.20. Therefore, these limits are very sensitive to the preparation method, to the presence of possible secondary phases and to the microstructural aspects.

The relaxor materials are a special class of ferroelectrics characterized mainly by [6]: (a) diffuse phase transition (DPT) extended in a large range of temperatures, around the temperature T$_m$ for which the dielectric constant assumes its maximum value; (b) a non-Debye dielectric dispersion for T<T$_m$ and frequency-independent dielectric constant for T>T$_m$; (c) Curie-Weiss dependence of the permittivity far above T$_m$ and strong deviations from this law for T$\geq$T$_m$; (d) the majority of relaxors have at low temperatures a pseudo-cubic phase and the transition relaxor-paraelectric is not accompanied by structural modifications detectable by diffraction methods; (e) the relaxors do not posses a macroscopic polarization, but local non-zero polarizations P$_i \neq 0$ associated to some nanopolar regions.

The present work is reporting the results of a dielectric study aimed to find the relaxor-like properties in the Ba(Zr$_x$Ti$_{1-x}$)O$_3$ ceramics prepared by solid state reaction, having the nominal composition x=0.10.

2. Experimental details

BaZr$_x$Ti$_{1-x}$O$_3$ (BZT) ceramics were prepared by solid-state reaction technique using the following chemical reaction:

$$BaCO_3 + (1-x)TiO_2 + x\,ZrO_2 \rightarrow$$
$$Ba(Zr_xTi_{1-x})O_3 + CO_2\uparrow \qquad (1)$$
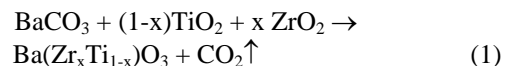
High-purity starting materials (BaCO$_3$, TiO$_2$, and ZrO$_2$) were weighed and wet-mixed with distilled water. After drying, the powders were calcined at 1000 ^{o}C for 2 hours (see the scheme of the preparation – Fig. 1). The phase purity in the calcined powders was checked by X-ray diffraction (XRD, Philips, Model PW 1710). The diffraction patterns were collected using Co K$_\alpha$ radiation (0.179 nm), a secondary graphite monochromator, a step size of 2θ=0.03^o and a sampling time of 10 s. The phase and crystallographic microstructure of the ceramics were examined also by Scanning Electronic Microscopy (SEM, Philips, Model 515) analysis.
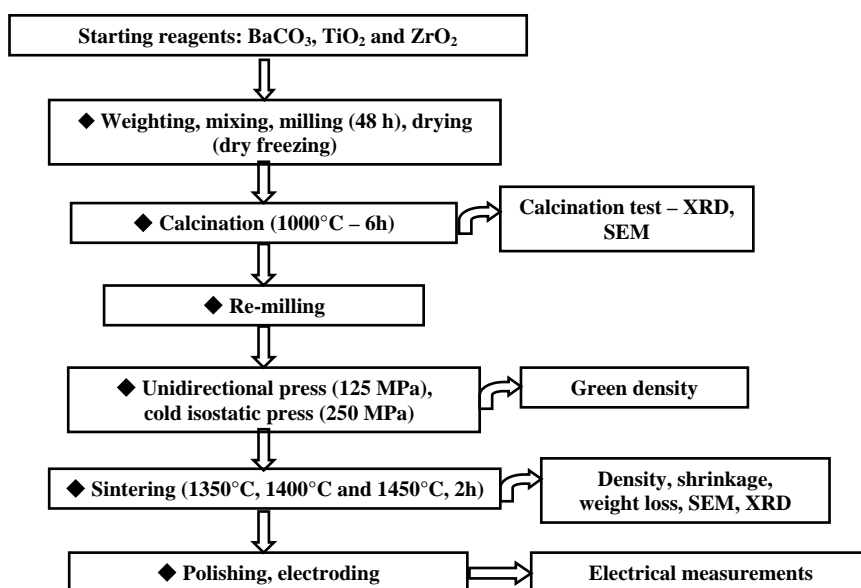
Fig. 1. Scheme of the preparation of BZT ceramics.

The calcinated powders were milled again and compacted in cylinders (length 2-3 cm, $\phi = 1$ cm) by cold isostatic pressing at 1500 bar. The samples were sintered at different temperatures (1350-1450 ^{o}C) for 2 hours. Apparent densities were measured by the immersion method in water. The phase purity and the microstructures of the ceramic samples after various sintering steps were also checked by XRD and SEM analysis. Ag-Pb electrodes were deposited on the plane-parallel polished surfaces of ceramics followed by annealing in air at 500 ^{o}C for 12h. The impedance spectroscopy system composed by an impedance analyzer (Solartron, SI 1260, 0.5 V 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 $(1-10^6)$Hz and temperatures ranging from 20 to 200 ^{o}C.

3. Results and discussion

3.1 Crystalline symmetry and microstructure of BaZr$_x$Ti$_{1-x}$O$_3$ ceramics (x = 0.10)

The XRD analysis proves that the powders after calcinations at 1000 ^{o}C for 6 h show the presence of the major titanate phase with cubic or pseudo-cubic symmetry and some wt % of orthorhombic BaCO$_3$, (Fig. 2). Slow step scanning XRD analysis performed at various temperature calcinations steps revealed that BaTiO$_3$ (BT) starts forming from 700 ^{o}C and BaZrO$_3$ (BZ) from 800 ^{o}C. Above 1350 ^{o}C, BZT phase increases rapidly due to the inter-diffusion between BT and BZ. After sintering at 1350 ^{o}C the pure perovskite phase was fully formed (Fig. 2).
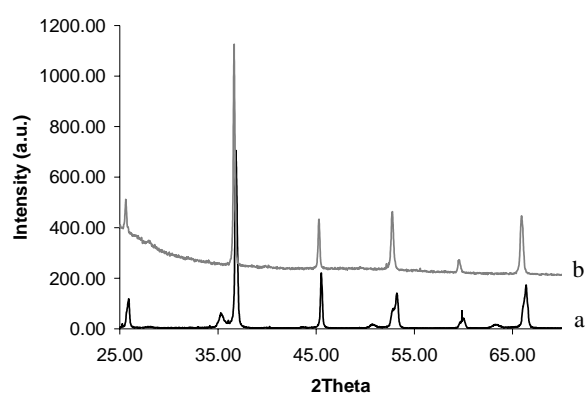

Fig. 2. XRD patterns of BaZr$_{0.1}$Ti$_{0.9}$O$_3$ ceramics: a) after calcination at 1000 ^{0}C and b) after sintering at 1350 ^{0}C.

The SEM analysis showed a good homogeneity of the microstructure (grain size of 1-2 μm) and some porosity (as presented in Fig. 3). The relative density determined by the Archimedes method was found around 90%.
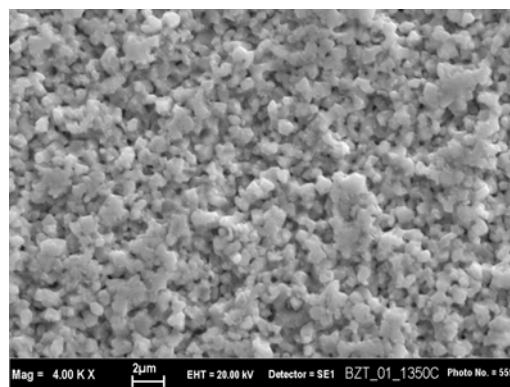

Fig. 3. SEM micrograph of the polished surface of BaZr$_{0.1}$Ti$_{0.9}$O$_3$ ceramic sintered at 1350 ^{o}C.

3.2. Dielectric properties of BaZr$_x$Ti$_{1-x}$O$_3$ ceramics (x = 0.10)

As shown in Fig. 4 a, the dielectric constant of the BaZr$_{0.1}$Ti$_{0.9}$O$_3$ ceramics is quite high (around 3900 at room temperature and a maximum of 5100), by considering the porosity effects in these materials. The temperature dependence of permittivity determined at f = 16.8 Hz shows a thermal hysteresis (difference between the dielectric response on heating/cooling cycles in the ferroelectric range T<T$_m$); the temperatures corresponding to the maximum permittivity are: T$_m$(h)=89.3 ^{o}C and T$_m$(c)=86.7 ^{o}C respectively. The ferro-para phase transition is evidenced by the maximum of the permittivity which has a diffuse character (DPT). The imaginary part of the permittivity at fixed frequency also reveals by anomalies the existence of the phase transition (Fig. 4 b). A strong increase of the imaginary part of the dielectric constant is presented above the temperature of around 130 ^{o}C.
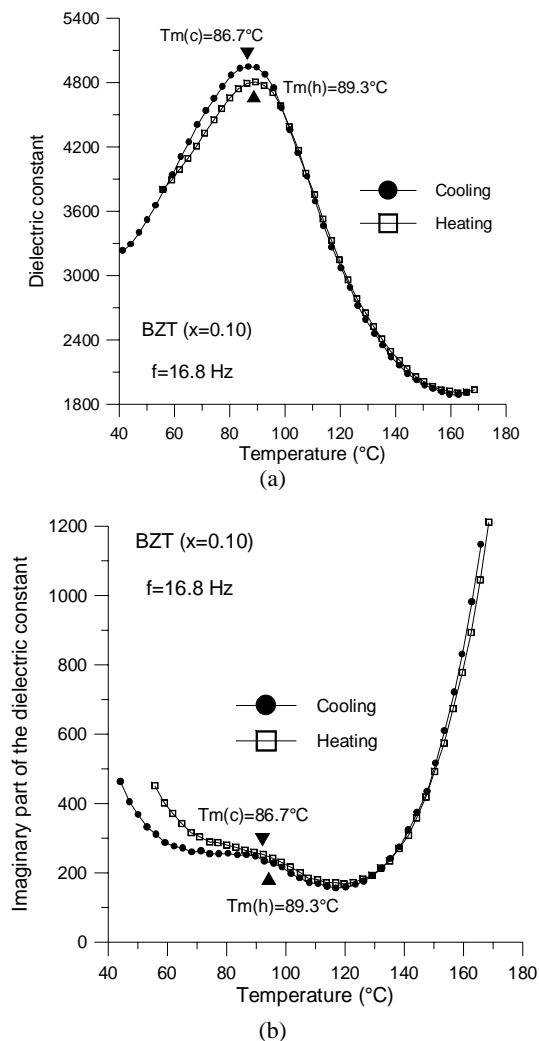

Fig. 4. The real and imaginary part of the dielectric constant vs. temperature obtained for BaZr$_{0.1}$Ti$_{0.9}$O$_3$ ceramics at f = 16.8 Hz on a heating/cooling cycle.

The influence of the frequency on the permittivity and losses in BaZr$_{0.1}$Ti$_{0.9}$O$_3$ ceramics is illustrated in Fig. 5.

The dielectric constant of the system decreases with the increasing the frequency in the investigated range of (7.2 Hz – 569 kHz). A small shift of (1-2)^{o}C towards higher values of the temperature T$_m$ corresponding to the maximum value of the permittivity ε$_{max}$ is visible with increasing the frequency. A relaxation of the dielectric constant in the ferroelectric place gives the idea that the present sample is close to the relaxor state. Below 130 ^{o}C the dielectric losses tanδ<30% and they are even smaller at the room temperature (tanδ<2%). The strong increase of the losses towards 1 (Fig. 5, b) together with the apparent increasing of the dielectric constant (Fig. 5, a) at low frequencies and temperatures around 150°-170 ^{o}C are caused by space charge effects that give a thermally-activated conductivity.
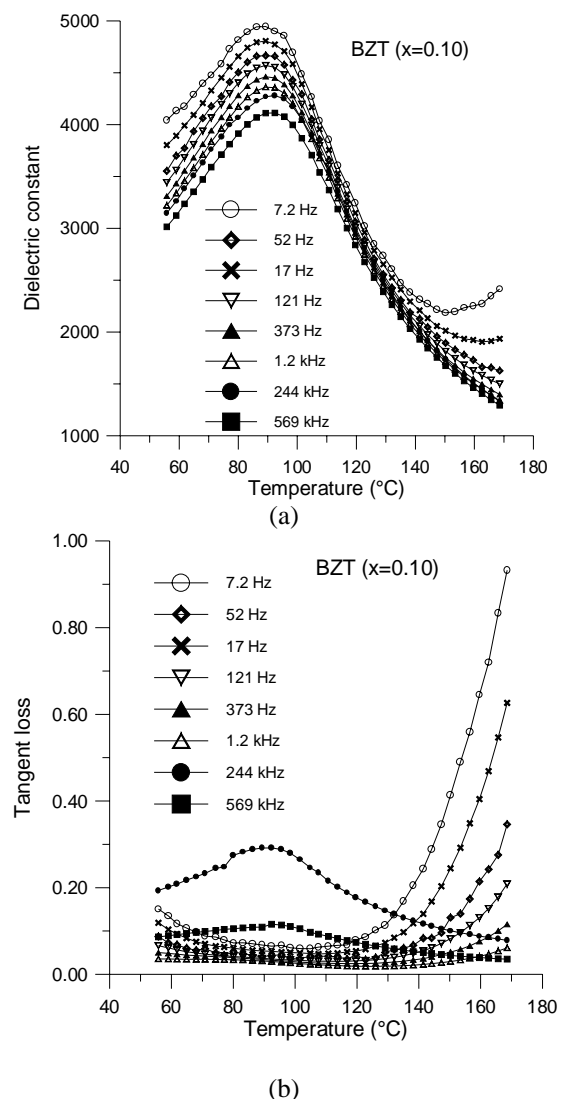

Fig. 5. Dielectric constant (a) and tangent loss (b) at different frequencies vs. temperature determined for Ba(Zr$_{0.1}$Ti$_{0.9}$)O$_3$ ceramic sintered at 1350 ^{o}C for 2h.

The linear regression analysis of the temperature dependence of the reciprocal dielectric data (presented in Fig. 6) shows that the material closely follows the Curie-Weiss law (2) far away from the Curie region (T>>T$_m$),

particularly visible at higher frequency, where the space charges do not have any relaxation.

$$\varepsilon^{-1}(T) = \frac{T - T_0}{C} \qquad (2)$$

Both the Curie-Weiss temperature T_0 and the Curie constant are frequency-dependent. For example, at the extreme frequencies in Fig. 6 ($f_1 = 7.2$ Hz and $f_2 = 569$ kHz) their values are: $T_{01} = 83$ °C, $C_1 = 1.73 \times 10^5$ grd^{-1} and $T_{02} = 90$ °C, $C_2 = 1.21 \times 10^5$ grd^{-1}, respectively. The precision in determining these values are strongly dependent on the accuracy of the dielectric constant data in the paraelectric region. The temperature where the reciprocal dielectric constant $\varepsilon^{-1}(T)$ starts to deviate from the Curie-Weiss law (around 100 °C) is often considered the onset temperature of local nanopolar order (Burns freezing temperature) [7, 8]. According to the present data, it results that in spite of its low Zr content, the BaZr$_{0.1}$Ti$_{0.9}$O$_3$ solid solution has a mixed character ferroelectric-relaxor. It is worth to mention that according to the Raman and structural data reported in Refs. 9-10, the Ba(Zr$_{0.1}$Ti$_{0.9}$)O$_3$ composition shoud present a succession of structural phase transitions: rhombohedral-orthorhombic-tetragonal-cubic with increasing tempe-rature. In addition, for the compositions x≤0.15, the BaZr$_x$Ti$_{1-x}$O$_3$ solid solutions should have full ferroelectric character with just a slightly diffuse ferro-para phase transition [10]. The dielectric properties found in the present ceramics are different than the mentioned ones. In the authors' opinion, the relaxations found in this study are caused by the small grain size (around 1-2 μm) which causes an additional increase of the local inhomogeneity inside the ceramic volume. This might induce the as-observed incipient relaxor behaviour in a composition for which full ferroelectric character was previously reported.
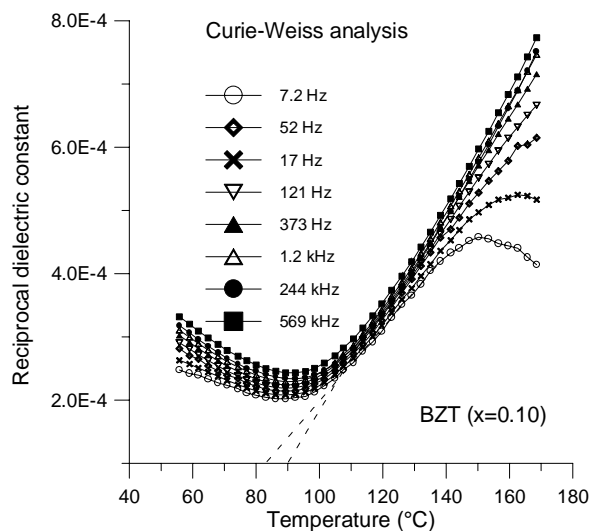

Fig. 6. The reciprocal permittivity vs. temperature for Ba(Zr$_{0.1}$Ti$_{0.9}$)O$_3$ at different frequencies.
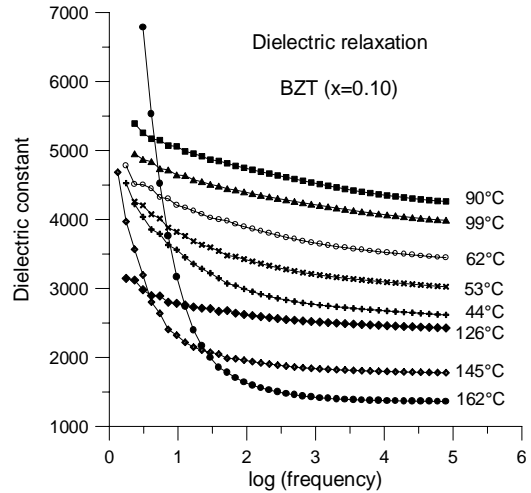

Fig. 7. Frequency dependence of the permittivity at a few temperatures.

No other relaxations except the mentioned one were found by measuring the dielectric constant *vs.* frequency, as presented in Fig. 7. A single relaxation process in the overall range of investigated temperatures ($44^0 \div 162^0$)C is typical for frequencies higher than 100 Hz. The role of space charge in creating at very low frequencies and high temperatures a small conduction effect is very well illustrated on the logarithmic plot of the permittivity versus frequency from Fig. 7. These are probably uncompensated charges created by the variation of the polarization within the ceramic volume which are located at the ceramic grain boundaries. The possible effect of the grain size or of other microstructural parameters in inducing relaxor effects in ferroelectric solid solution, as suggested in this preliminary study, is a very interesting topic to be further investigated in samples with different grain sizes and at various compositions.

4. Conclusions

The properties of BaZr$_{0.1}$Ti$_{0.9}$O$_3$ ceramics prepared via solid state reaction are reported. A single- perovskite phase was found by X-ray diffraction after sintering at 1350 °C (in spite that after calcination, some secondary phases were still present). A homogenous microstructure with grain size around 1-2 μm was obtained. The temperature dependence of the dielectric constant shows a diffuse phase transition with a small shift of the temperature corresponding to the maximum permittivity of (1-2) °C in the frequency range of 1Hz÷1MHz, indicating an incipient relaxor character (or a mixed relaxor-ferroelectric behavior). The real part of the permittivity strictly follows the Curie-Weiss law at high temperatures, with frequency-dependent constants. The dielectric spectroscopy data revgealed two relaxation processes: a thermally-activated one characteristic to low-frequency range f < 100 Hz, due to space charge effects, and a temperature-independent one for f ≥ 100 Hz.

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