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Phase transition and PTCR effect in erbium doped BT ceramics

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ABSTRACT

In this work the dielectric behaviour and main features of the phase transition of $BaTiO_3$ and $Ba_{0.99}Er_{0.01}TiO_3$ ceramics were carefully investigated. The temperature and frequency dependences of the dielectric properties of erbium doped $BaTiO_3$ ceramics were measured in the 25–225 °C and 100 Hz to 10 MHz ranges, respectively. From this study, a dielectric anomaly in the ferroelectric–paraelectric phase transition of the $Ba_{0.99}Er_{0.01}TiO_3$ ceramic was observed. The features of the samples phase transition were analysed by using Curie–Weiss, Santos–Eiras' and order parameter local phenomenological models. In the $BaTiO_3$ system, all models showed a normal phase transition, while was not possible to establish the character of the phase transition in the $Ba_{0.99}Er_{0.01}TiO_3$ system. The relaxation parameters of conductive processes for the study ferroelectric materials, analysed in the time domain, did not show any influence on the ferroelectric–paraelectric phase transition. Finally, it was demonstrated that the anomaly observed on the phase transition of the erbium doped $BaTiO_3$ ceramics is associated with the processes that results in the PTCR effect.

1. Introduction

Barium titanate ($BaTiO_3$ or simply BT) is a classical perovskite-type compound. This system is a well-known ferroelectric and piezoelectric material below the Curie temperature $T_C \approx 120$ °C [1–5] and it has been one of the most studied ferroelectrics over last decades, not only from the fundamental point of view but also for its huge number of applications [1–8]. The $BaTiO_3$ ceramic system shows a diffuse dielectric anomaly in the temperature range of 400–700 °C [9,10]. Several origins have been associated to this dielectric anomaly (or relaxation process), among them a conductive process [9,10]. Leyet et al. have been investigated the conduction mechanism of $BaTiO_3$ ferroelectric ceramics over wide temperature and frequency ranges [10], which was performed based on the relaxation dynamics method of the conductive process, using a temporal distribution function obtained from the dielectric modulus formalism [10]. As a main result, they obtained that the BT system shows a conductive relaxation process in the low frequencies-high temperatures region. Moreover, the thermal evolution of the relaxation parameters revealed that there is no influence of the relaxation process on the paraelectric–ferroelectric phase transition.

In systems like $PbNb_2O_6$ and $PbZr_{0.6}Ti_{0.4}O_3$ with a paraelectric–ferroelectric transition temperature above 300 °C, it has been found that a conductive process is overlapped with the ferroelectric–paraelectric phase transition. In this case, some changes take place in the dielectric response of the material that is reflected in the temperature behaviour of the relaxation parameters [10,11].

The mechanism of the dopant incorporation into barium titanate as well as the influence of some transition-metal and large rare-earth ions in the structural and electrical properties of the $BaTiO_3$ ceramics has been extensively investigated [12,13]. Among them, Erbium (Er^{3+}) has been widely used due to its great technological interest [12]. Simultaneous substitution has been observed in both BT cation sites as the of Er^{3+} content increase, with higher preference for the barium site [12]. However, when erbium concentrations below 2% are introduced in $BaTiO_3$ ceramics it is not observed a shift in X-ray diffraction peaks and the maximum dielectric permittivity value remain constant [12,14]. It has been previously reported that with the erbium cation incorporation into the BT crystalline lattice, according to the formula $(Ba_{1-x}Er_x)TiO_3$ (BET), a n type semiconductor behaviour is induced and a positive temperature coefficient resistivity (PTCR) effect appear in this system [15,16]. This suggests that electronic compensation governs completely the electric behaviour of Erbium doped BT ceramics, affecting its dielectric behaviour.

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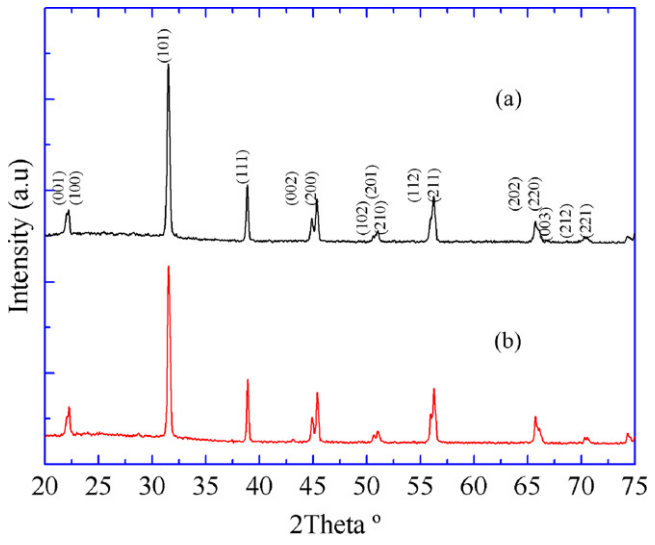

Fig. 1. Room temperature X-ray diffraction patterns of (a) BT and (b) BET samples sintered at 1275 °C and 1300 °C, respectively.

The aim of this work is to investigate the influence of conductivity process and PTCR effect on the ferroelectric–paraelectric phase transition erbium doped $BaTiO_3$ ceramics. For this purpose, several phenomenological models have been used.

2. Experimental procedure

A polymeric precursor synthesis method was used to obtain pure BT and erbium modified barium titanate (BET) ceramics [15]. For this purpose, high-quality precursors materials (i.e., barium acetate (99.9% – Synth), erbium oxide (99.9% – Alfa Aesar), titanium tetra-isopropoxide (97% – Alfa Aesar)) and organic and inorganic solvents (i.e., glycol-ethylene (98% – Synth), nitric acid (65% – Dinamica) and citric acid (99.5% – Synth)), were used to prepare BT and BET ceramics. Disc shaped samples with 10 mm in diameter and 1 mm thick were obtained by uniaxial and isostatic cold pressing. The resulting *green* pellets were sintered at 1275 °C and 1300 °C for 2 h. Afterwards, the sintered samples were slowly cooled down to room temperature. Details of the samples preparation could be found elsewhere [15].

X-ray diffraction analysis was carried out by a Rigaku diffractometer equipped with CuK_α radiation. X-ray patterns were measured in continuous mode for 20°–75° in 2θ and the resulting spectra were used to determine the lattice parameters.

Scanning electron microscopy (SEM) images were recorded by Jeol field emission scanning electron microscope, working at 15 kV at 11 mA, while the average grain size was calculated by using a professional line intercept method program.

Computer assisted dielectric characterization was performed as a function of temperature, using a HP 4194A Impedance Gain Phase Analyser. The measurements were obtained in a the temperature range of 24–225 °C and a wide frequency interval of 100 Hz to 10 MHz.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of the BT and BET samples sintered at 1275 °C and 1300 °C for 2 h, respectively. There is no visible shift in the peak positions and difference in their respective intensities, being isostructural with an early reported BT tetragonal perovskite structure [17]. Table 1 shows the structure parameters of the BT and BET obtained ceramics and BT* reported ceramics [17]. Based on the theoretical densities calculated from the structural parameters shown in Table 1, it was determined relative densities higher than 95% for both BT and BET samples. Table 1 also shows the average grain size values of the pure and erbium doped BT ceramics, revealing there is practically no differences between the grain sizes of the samples. More details about the microstructure of the ceramics have been reported in reference [15].

Table 1
Structural parameters of the BT and BET prepared samples together with BT tetragonal reference (ICSD #15453) and their calculated average grain sizes.

Sample	a (Å)	b (Å)	c (Å)	Grain size (μm)
BT	3.994 (3)	3.994 (3)	4.030 (2)	4.2
BET	3.994 (5)	3.994 (5)	4.034 (3)	4.0
BT*	3.988	3.988	4.012	–

* Ref. [17] (ICSD 15453).

Fig. 2 shows the temperature dependence of the real (ε') and imaginary (ε'') part of the dielectric permittivity measured at 1 MHz for (a) BT and (b) BET samples. The real part of the dielectric permittivity maximum slightly increases from BT pure ceramic to BET ceramic, while the imaginary part of the dielectric permittivity observed in the BET sample is one order higher than that reported for BT ceramic. Moreover, the transition temperature remains practically constant for both samples, which is consistent with the reported by Hwang and Han, for BT ceramics doped with small erbium concentration [14]. The increase in the real part of the dielectric permittivity maximum could be the result of several factors, among them:

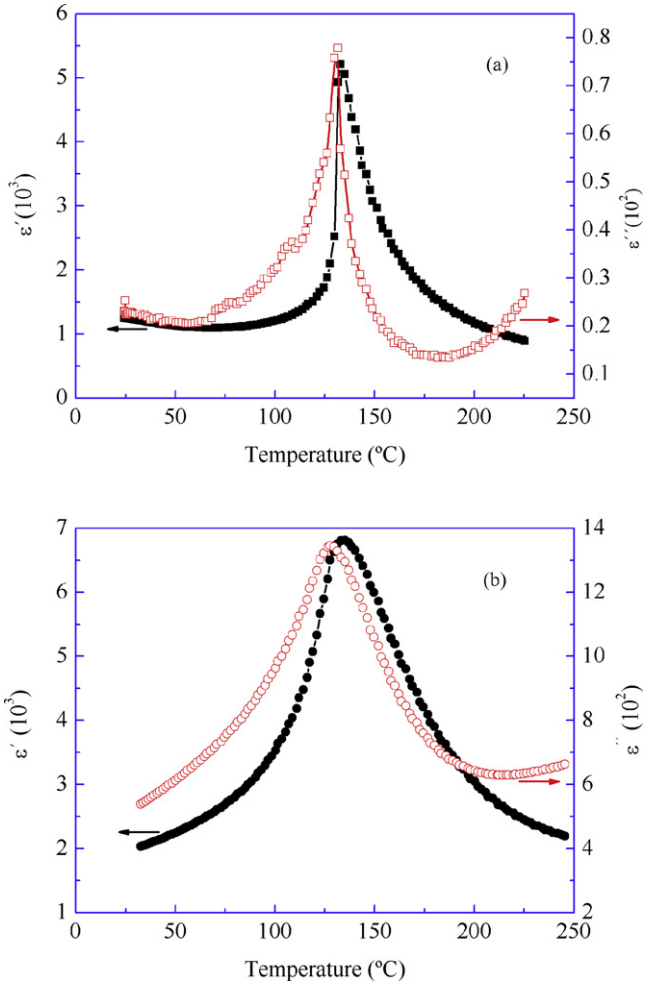

Fig. 2. Temperature dependence of the real and imaginary parts of the dielectric permittivity of (a) BT and (b) BET ceramics measured at 1 MHz.

Table 2
The parameters ε'_m, T_m, ξ and Δ for erbium doped an undoped BT ceramic system at 1 kHz, 10 kHz and 1 MHz.

Sample	ε'_m	T_m (°C)	Δ (°C)	ξ	Frequency
BT	5350	133	20.65 ± 0.26	1.09 ± 0.01	1 kHz
	5292	133	21.85 ± 0.11	1.13 ± 0.03	10 kHz
	5124	133	21.47 ± 0.26	1.11 ± 0.01	1 MHz
BET	19,606	133	119.12 ± 3.47	1.34 ± 0.03	1 kHz
	13,252	134	70.52 ± 1.01	1.36 ± 0.02	10 kHz
	6806	136	59.81 ± 0.40	1.42 ± 0.02	1 MHz

(i) The modifications in the grain size, resulting from the incorporation of the erbium in the structure [18]
(ii) the increase in the BT structural order, resulting from the incorporation of the erbium in the structure [12]
(iii) the apparition of a conductive process due to an increase in the number of Ba and Ti defects, resulting from the incorporation of the erbium in the BT structure and also due to the formation highly conductive erbium titanate pyrochlore phases [14]
(iv) the formation of a PTCR effect induced by the erbium incorporation in the BT structure [16].

There are no appreciable modifications in the grain size of the BT ceramic when it is doped with 1% of erbium, as reported in Table 1 and the X-ray analysis of the sample confirm that there is not formation of an erbium titanate secondary phase. On the other hand, it is known that rare-earth like yttrium, holmium and erbium decrease the BT transition temperature, which is not consistent with an increase in the $BaTiO_3$ structural order [14,19,20]. Based on the above-mentioned, there are only two viable factors that can increase of the dielectric constant for BET ceramic, the apparition of conductive processes and/or the formation of a PTCR effect, resulting from the incorporation of erbium in the BT structure.

On the other hand, the increase of the imaginary dielectric permittivity maximum for BET ceramic is also compatible with the formation of a conductive process and/or the formation of a PTCR effect due to the incorporation of erbium in the BT structure.

Fig. 3 shows the temperature dependence of the inverse of the real part of the dielectric permittivity measured at 1 kHz, 10 kHz and 1 MHz, for both BT and BET ceramics. A normal Curie–Weiss dependence was observed for the BT ceramic above the transition temperature (T_m) (Fig. 3a), which is characteristic of a normal ferroelectric–paraelectric phase transition [21]. However, for BET ceramic there is a shift in the transition temperature to higher T_m values as the driving frequency increases. This frequency dielectric dispersion observed in the BET is not characteristic of a normal ferroelectric phase transition. This fact is associated with conductive process caused by the incorporation of the Er^{3+} ion in the BT crystalline structure, as suggested by Buscaglia et al. [12].

The study of the ferroelectric–paraelectric phase transition for both samples was carried out by using the Santos–Eiras phenomenological equation [22,23]:

$$\varepsilon' \frac{\varepsilon'_m}{1 + ((T - T_m)/\Delta)^{\xi}} \quad (1)$$

where ε'_m is the dielectric permittivity maximum, T_m temperature of the real part dielectric maximum, ξ indicates the character of the paraelectric–ferroelectric phase transition (i.e., $\xi \approx 1$ indicates a "normal" paraelectric–ferroelectric phase transition) and Δ is the peak broadening, which defines the diffuseness degree of the ferroelectric–paraelectric phase transition.

In Table 2 are reported the experimental (ε_m, T_m) and fitting parameters (ξ and Δ) of the 1 kHz, 10 kHz, and 1 MHz dielectric curves for BT and BET samples. The results confirm that the ferroelectric–paraelectric phase transition of the BT ceramic

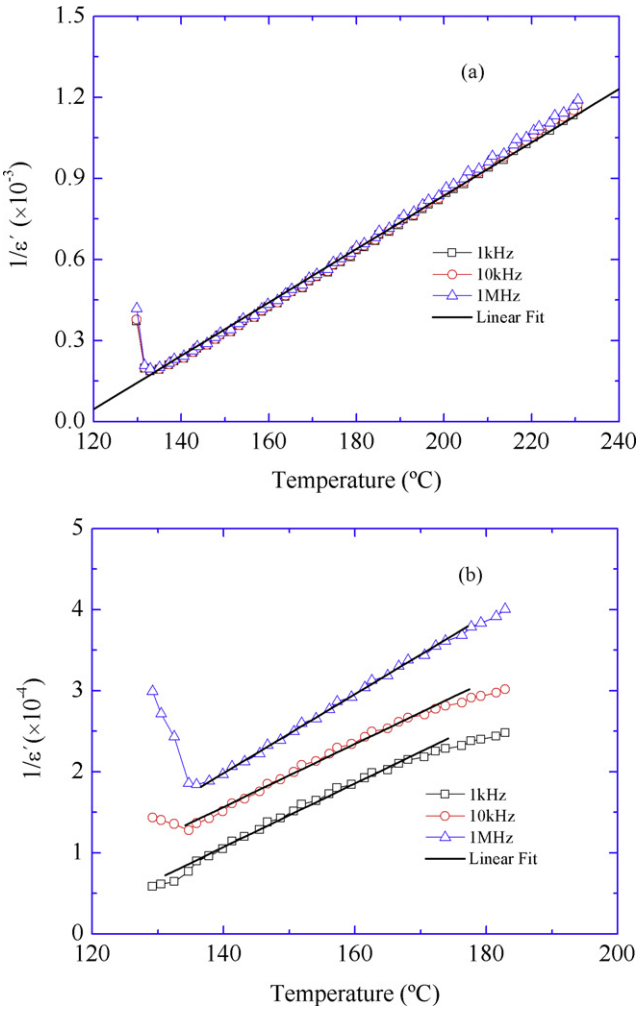

Fig. 3. Temperature dependence of the inverse of the real part of the dielectric permittivity of (a) BT and (b) BET ceramics measured at 1 kHz, 10 kHz and 1 MHz.

corresponds to a normal phase transition. On the other hand, the diffuseness degree values (Δ) of the BET phase transition are higher than BT, indicating that the Er^{3+} structural incorporation increase the diffuseness degree of the BT sample, which results in a BET diffuse phase transition (DPT). BET sample also shows high frequency dispersion in Δ and ξ values, which is not explicated by the Santos–Eiras model. The diffuse phase transition observed in BET sample can be caused for the incorporation of the erbium cation in the barium site, creating impurities and point defects and consequently bigger disorder in the domains structure of this material.

In order to obtain more information concerning to the evolution of the system from normal to diffuse ferroelectric, the Landau–Devonshire (LD) phenomenological cluster theory was used, which allows to carry out the evaluation of the local order parameter degree [24]. The temperature and the local order parameter dependences of the real component of the dielectric permittivity could be expressed as [24]:

$$\frac{1}{\varepsilon'} = \frac{T - T_m}{C} + \varepsilon_m \gamma q(T) \quad (2)$$

Eq. (2) provides a method for evaluation of the local order parameter $q(T)$, knowing that T_m and C are the Curie temperature and Curie constant, respectively; ε_m is the value that reaches ε' at T_m and γ is the Landau coefficient. This equation reveals that in this system the deviations of the low-field dielectric permittivity from Curie–Weiss behaviour above T_m occur due to the existence of a

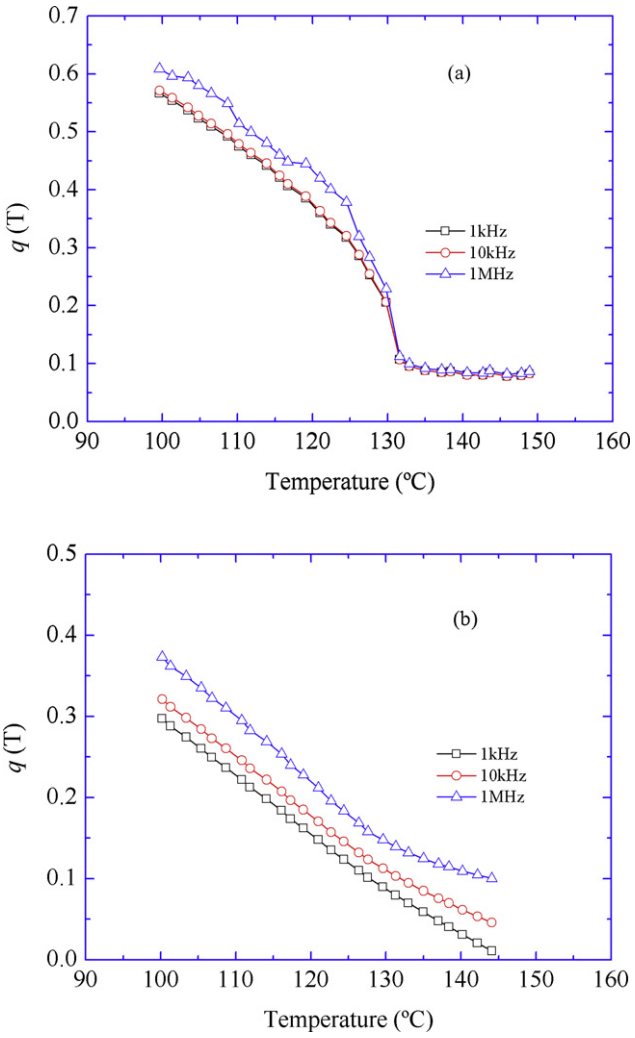

Fig. 4. Temperature dependence of the local order parameter of (a) BT and (b) BET ceramics measured at 1 kHz, 10 kHz and 1 MHz.

local order parameter different from zero. Thus, defining a temperature function $f(T) = \varepsilon^{-1}(T) - (T - T_m)/C$, it is possible to determine the local order parameter by using Eq. (3) [24]:

$$f(T) = \varepsilon_m \gamma q(T) \tag{3}$$

Fig. 4 shows the temperature dependence of the local order parameter ($q(T)$) obtained for both BT and BET samples. In BT ceramic the $q(T)$ change rapidly near to transition temperature and remain constant above the transition temperature ($T > T_m$), indicating a normal phase transition. In BET ceramics, for $T > T_m$, is observed a slowly increase in the local order parameter. This behaviour could be correlated with the influence of the conductivity process and the process that result in the PTCR effect on the local order parameter. However, for $T < T_m$, in this sample is observed a fast increases of the $q(T)$ with decreasing temperature that could be determined by the influence of a conductive process on the local order parameter. The results of local order parameter and Curie–Weiss temperature and Santos–Eiras model suggest that BT ceramic has a normal ferroelectric–paraelectric phase transition. However, it is impossible to determine the character of the BET dielectric transition based on the above-mentioned models. This behaviour could be associated with two processes: (i) an ionic conductivity and (ii) a PTCR effect taking places in the BET phase transition region.

(i) Ionic conductivity (Relaxation)

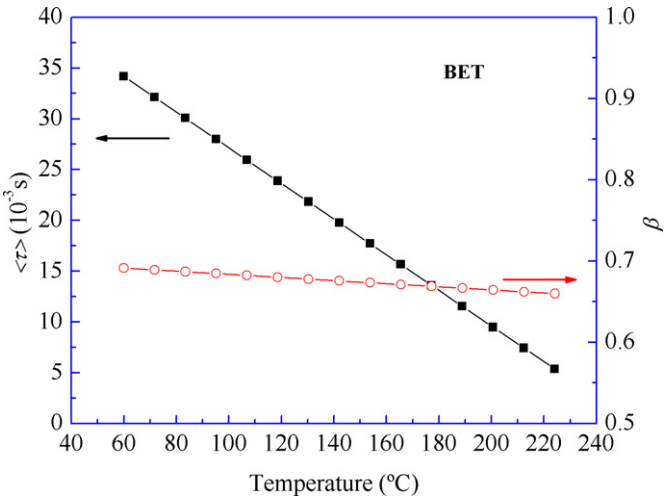

Fig. 5. Temperature dependence of the $\langle\tau\rangle$ and β parameters of BET ceramic.

In order to analyse the influence of the ionic conductive process on the behaviour of the BET ferroelectric–paraelectric phase transitions, it was used a dynamics relaxation model in the time domain. It is well-known that the conductivity relaxation method is a powerful tool to characterize conductivity processes in materials with ionic conduction [11,25,26], being this characterization usually carried out in the frequency domain, from complex admittance measurements [27]. However, in previous work [11], we demonstrated that it is possible to carry out an exhaustive study of the dynamics of the relaxation processes in the time domain. In this case, the complex electric modulus is associated with a relaxation distribution function, $F(\omega)$, from which an analytical time decay function, $\Phi(t)$, can be obtained by numerical integration [28]. The Kohlrausch–Williams–Watts (KWW) stretched exponential decay function, Eq. (4), generally gives the best fit when applied to non-Debye functions [11,26,28]:

$$\Phi(t) = \exp\left[-\left(\frac{t}{\tau^*}\right)^{\beta}\right] \tag{4}$$

In this equation, the parameter β characterizes the correlation between hopping ions, so that β values are close to zero for strongly correlated systems and $\beta = 1$ for random Debye-like hops, while τ^* is a characteristic relaxation time in the time domain. The average relaxation time, which is associated with the *dc* conductivity (σ_0) according to $\langle\tau\rangle = \varepsilon_\infty/\sigma_0$, in which ε_∞ refers to the permittivity at infinite frequency, can be obtained by using Eq. (5), in which Γ refers to the Euler gamma function [11,26,28],

$$\langle\tau\rangle = \frac{\Gamma(1/\beta)}{\beta}\tau^* \tag{5}$$

where $\langle\tau\rangle$ represents average relaxation time needed by the ion to carried out successive jumps that contribute to the conductivity.

Fig. 5 shows the thermal evolution of $\langle\tau\rangle$ and β parameters for the BET ceramic. In this case, $\langle\tau\rangle$ parameter follows a decay exponential function and β parameter displays nearly constant values in the whole temperature range. Both parameters show a behaviour very similar to that of materials with ion vacancies conduction [29,30], and it is not observed the influence of the ferroelectric–paraelectric phase transition on the relaxation parameters. Another method used to study the conductive processes is based on the direct current conductivity (σ_0). This could be determined from the frequency dependence of the alternating current conductivity.

Fig. 6 shows the alternating current conductivity behaviour of the BET sample at different temperatures (below and above T_m). DC

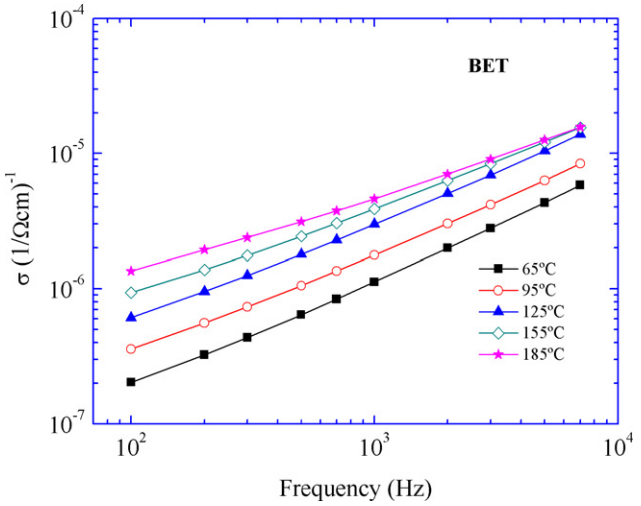

Fig. 6. Frequency dependence of the ac conductivity of BET ceramic samples measured at different temperatures.

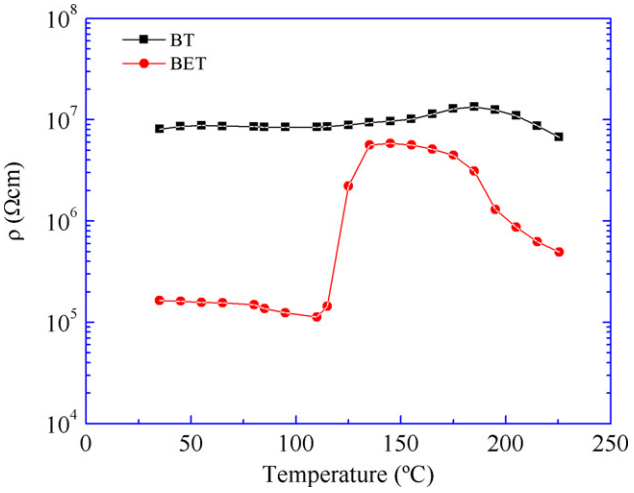

Fig. 7. Temperature dependence of the resistivity of BT and BET ceramic samples.

conductivity (σ_0) was obtained the by the fitting (below 1 kHz) of the experimental data with Eq. (6) [27]:

$$\sigma' = \sigma_0 + A\omega^n \tag{6}$$

where A is a temperature dependent parameter, ω the frequency and n the Jonscher's parameter.

Using the obtained σ_0 values and the Arrhenius expression it was determined the activation energy of the process. The activation energy of the conductive process present in the ferroelectric region is 0.28 eV, which is near to the activation energy of the first ionization of oxygen vacancies (V_0) [31], as described in Eq. (7).

$$V_0 \Leftrightarrow V_0' + e', \tag{7}$$

This result indicates that in the temperature range analysed ($T < T_m$), the conduction of free electrons result from the first-ionization of oxygen vacancies. These conductivity values can be associated with the existence of free electrons in the material due to the electrical compensation in the crystalline lattice, caused by the erbium substitutions in the Ba site of the crystalline structure.

In addition, the contribution of the conduction electrons (oxygen or ion vacancies) to dielectric polarization has been reported in many systems for both single crystals and polycrystalline ceramics [31]. In order to explain the higher permittivity in Er-doped BT ceramics is possible to use the Maglione and Belkaoumi model [32]. This model suggests an electron relaxation–mode coupling, i.e., the polarization was greatly enhanced by the interaction of the electrons (created by the ionization of oxygen vacancies) and the dielectric relaxation process. In this case, even with low concentration of the dipoles, the system could exhibit a very high permittivity. The above mentioned is the main source of the PTCR effect in these material.

(i) PTCR effect

The PTCR effect is characterized by an anomalous increase of resistivity, which has been observed in several kinds of materials [12,15]. If it is assumed that the discreet nature of the charges can be insignificant, the magnitude of the potential barrier can be calculated, solving the Poisson equation for the potential [33]. The resistivity temperature dependence for both BT and BET ceramics is shown in Fig. 7. In all the analysed temperature range, it can be observed that the resistivity behaviour of the BT ceramic do not obey the characteristic behaviour of the PTCR effect, while BET ceramic experiments a slight PTCR effect.

The DC resistivity is then expressed simply by:

$$\rho = \rho_0 \exp\left(\frac{\phi_0}{kT}\right) \tag{8}$$

where ρ_0 is the residual resistivity at infinite temperature, ϕ_0 the grain boundary potential barrier, k is the Boltzman constant and T is the absolute temperature of the sample. Based on Eq. (8), it is obtained the grain boundary potential barrier $\phi_0 = (0.32 \pm 0.01)$ eV. This value is similar to the reported by Miki et al. [34], which suggests an incorporation of the Er^{3+} in the BT unit cell and the existence of a PTCR effect in the BET sample.

Based on the results we could conclude that the processes that results in the PTCR effect are the responsible for the character ferroelectric–paraelectric phase transition observed in the BET sample. It is important to say that this result could be not determined by using classic phenomenological models.

4. Conclusions

The influence of conductivity process and PTCR effect on the ferroelectric–paraelectric phase transition erbium doped $BaTiO_3$ ceramics was analysed. Classical phenomenological models (Curie–Weiss, Santos–Eiras and LD) used for the characterization of the ferroelectric–paraelectric phase transition showed contradictory results when they are applied to a system where other processes are coexisting with the ferroelectric–paraelectric phase transition. Based on the thermal evolution of the relaxation parameters (β and τ) in the time domain, was established that the conduction process that appears in the high temperature and low frequency region in BET ceramic does not have any influence on the ferroelectric–paraelectric phase transition. Finally, it was found that the processes that result in the PTCR effect are the responsible for the character of the ferroelectric–paraelectric phase transition observed in BET ceramic.

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