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# Dielectric Relaxation Phenomenon in Ferroelectric Perovskite-related Structures

A. Peláiz-Barranco<sup>1</sup> and J. D. S. Guerra<sup>2</sup>

<sup>1</sup>*Facultad de Física-Instituto de Ciencia y Tecnología de Materiales, Universidad de La Habana. San Lázaro y L, Vedado. La Habana 10400,*

<sup>2</sup>*Grupo de Ferrolétricos e Materiais Multifuncionais, Instituto de Física, Universidade Federal de Uberlândia. 38400-902, Uberlândia – MG,*

<sup>1</sup>*Cuba,*

<sup>2</sup>*Brazil*

## 1. Introduction

The dielectric relaxation phenomenon in ferroelectric materials reflects the delay (time dependence) in the frequency response of a group of dipoles when submitted to an external applied field. When an alternating voltage is applied to a sample, the dipoles responsible for the polarization are no longer able to follow the oscillations of the electric field at certain frequencies. The field reversal and the dipole reorientation become out-of-phase giving rise to a dissipation of energy. Over a wide frequency range, different types of polarization cause several dispersion regions (Figure 1) and the critical frequency, characteristic of each contributing mechanism, depends on the nature of the dipoles. The dissipation of energy, which is directly related to the dielectric losses, can be characterized by several factors: *i*- the losses associated to resonant processes, characteristics of the elastic displacing of ions and electrons, and *ii*- the dipolar losses, due to the reorientation of the dipolar moment or the displacing of the ions between two equilibrium positions.

For ferroelectric materials the dielectric relaxation mechanisms are very sensitive to factors such as temperature, electric field, ionic substitution, structural defects, etc. The defects depend on either intrinsic or extrinsic heterogeneities due to special heat treatments, ionic substitutions, grain size additives, and grain boundary nature. On the other hand, structural defects may cause modifications of the short and/or long-range interactions in ferroelectric materials. From this point of view, apart from the localized dipolar species, free charge carriers can exist in the material. Several physical processes cause the decay of the electrical polarization: dipolar reorientation, motion of the real charges stored in the material and its ohmic conductivity. The former is induced by thermal excitations, which lead to decay of the resultant dipolar polarization. The second process is related to the drift of the charges stored in the internal field of the sample and their thermal diffusion. With the increase of the temperature, the dipoles tend to gradually disorder owing to the increasing thermal motion and the space charges trapped at different depths are gradually set free. Thus, the electrical conductivity in ferroelectric materials affects the physical properties because of there will be a competition between the ferroelectric phase and free charge carriers.

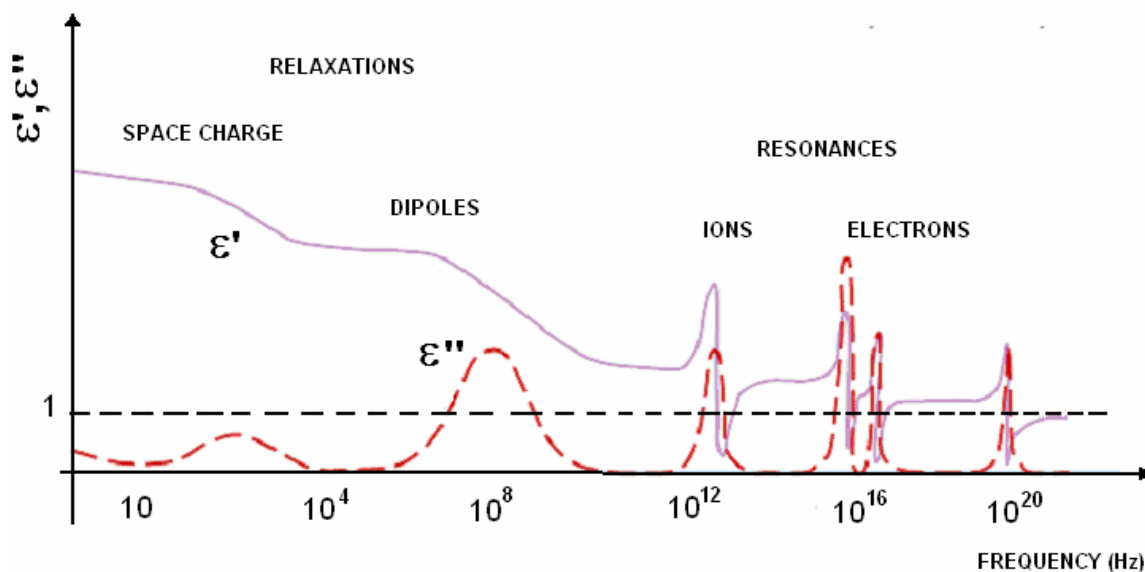


Fig. 1. General representation of relaxation and resonance types

The oxygen vacancies are always related to dielectric relaxation phenomenon, as well as to the electrical conductivity for ferroelectric perovskite-related structures, considering that these are the most common mobile species in such structures (Jiménez & Vicente, 1998; Bharadwaja & Krupanidhi, 1999; Chen et al., 2000; Islam, 2000; Yoo et al., 2002; Smyth, 2003; Verdier et al., 2005). For  $\text{ABO}_3$ -type perovskite structures, the  $\text{BO}_6$  octahedra play a critical role in the demonstration of the ferroelectric properties. It has been reported that the ferroelectricity could be originated from the coupling of the  $\text{BO}_6$  octahedra with the long-range translational invariance via the A-site cations (Xu, 1991). In this way, the breaking of the long-range translational invariance results in the dielectric relaxation phenomenon. The degree of the coupling between neighboring  $\text{BO}_6$  octahedra will be significantly weakened by introducing defects, such as vacancies. On the other hand, for the layered ferroelectric perovskites (Aurivillius family,  $[\text{Bi}_2\text{O}_2]^{2+}[\text{A}_{n-1}\text{B}_n\text{O}_{3n+1}]^{2-}$ ), the oxygen vacancies prefer to stay in the  $\text{Bi}_2\text{O}_2$  layers, where their effect upon the polarization is considered to be small, instead of the octahedral site, which controls the polarization. The origin of the dielectric behavior for these materials have been associated to a positional disorder of cations on A- or B-sites of the perovskite layers that delay the evolution of long-range polar ordering (Blake et al., 1997; Ismunandar & Kennedy, 1999; Kholkin et al., 2001; Haluska & Misture, 2004; Huang et al., 2006).

For at least several decades, the dielectric response of ferroelectric materials (polycrystals, single crystals, liquids, polymers and composites) has been of much interest to both experimentalists and theorists. One of the most attractive aspects in the dielectric response of ferroelectric materials is the dielectric relaxation phenomenon, which can show the direct connection that often exists between the dipolar species and the charge carriers in the materials. Researchers typically fit the complex dielectric permittivity data according to a relaxation theoretical model, which is representative of the physical processes taking place in the system under investigation.

The complex dielectric permittivity ( $\epsilon$ ) can be expressed as:

$$\epsilon(\omega) = \epsilon'(\omega) - i\epsilon''(\omega) \quad (1)$$

where  $\omega$  is the angular frequency;  $\epsilon'$  is the real component, which is in phase with the applied field;  $\epsilon''$  is the imaginary component, which is in quadrature with the applied field. Both components of the complex dielectric permittivity are related each other by the Kramers-Kronig relations.

The Debye's model (Debye, 1929), which considers not-interacting dipoles, proposes the following expression for the complex dielectric permittivity:

$$\epsilon(\omega) = \epsilon_{\infty} + \frac{\epsilon_s - \epsilon_{\infty}}{1 + i\omega\tau} \quad (2)$$

where  $\tau$  is the relaxation time,  $\epsilon_s$  is the static dielectric permittivity (at very low frequencies) and  $\epsilon_{\infty}$ , the dielectric permittivity at high frequencies.

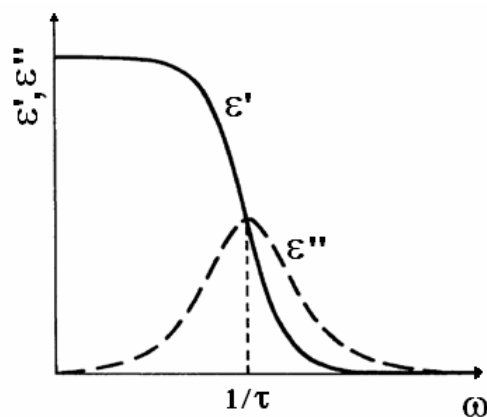


Fig. 2. Frequency dependence for the real and imaginary components of the dielectric permittivity from the Debye's model

This was the first model proposed to evaluate the dielectric relaxation. However, the experimental results in polar dielectric materials have showed that corrections to that simple model are necessary. The Cole-Cole's model (Cole & Cole, 1941) introduces a correction considering a distribution function for the relaxation time (expression 3).

$$\epsilon(\omega) = \epsilon_{\infty} + \frac{\epsilon_s - \epsilon_{\infty}}{1 + (i\omega\tau)^{\alpha}} \quad (3)$$

From that model, the real ( $\epsilon'$ ) and imaginary ( $\epsilon''$ ) parts of the dielectric permittivity (Cole & Cole, 1941) can be written as:

$$\epsilon'(\omega) = \epsilon_{\infty} + \left(\frac{\Delta\epsilon'}{2}\right) \left\{ 1 - \frac{\sinh(\beta z)}{\cosh(\beta z) + \cos\left(\beta \frac{\pi}{2}\right)} \right\} \quad (4)$$

$$\epsilon''(\omega) = \left(\frac{\Delta\epsilon'}{2}\right) \frac{\sin\left(\beta \frac{\pi}{2}\right)}{\cosh(\beta z) + \cos\left(\beta \frac{\pi}{2}\right)} \quad (5)$$

where  $z=\ln(\tau)$ ,  $\Delta\epsilon'=\epsilon_s-\epsilon_{\infty}$ , and  $\beta=(1-\alpha)$ , where  $\alpha$  shows the deformation of the semicircle arc in the Cole-Cole plot, i.e. it is the angle from the  $\epsilon'$  axis to the center of the semicircle arc.

The temperature dependence for the relaxation time follows the Arrhenius dependence given as:

$$\tau = \tau_o \exp\left(\frac{E_a}{k_B T}\right) \quad (6)$$

where  $E_a$  is the activation energy of the relaxation process,  $k_B$  is the Boltzmann's constant,  $T$  is the temperature and  $\tau_o$  is the pre-exponential factor. By using this dependence, the activation energy value of the dielectric relaxation process can be calculated and the mechanism, or mechanisms, associated to it be evaluated.

On the other hand, it has been previously commented that for ferroelectric materials (for dielectrics in general) the charge carriers have to be taking into account in the dielectric relaxation mechanisms. When an electric field is applied to the material, there is the known reorientation of the dipoles but also the displacement of the charge carriers. Therefore, the electrical conductivity behavior should be considered.

In order to evaluate the frequency dependent conductivity, the Universal Relaxation Law (Jonscher, 1996) can be used, where the electrical conductivity can be expressed as:

$$\sigma(\omega) = \sigma_{dc} \left[ 1 + \left( \frac{\omega}{\omega_H} \right)^n \right] + A\omega \quad (7)$$

where  $\sigma_{dc}$ ,  $\omega_H$ ,  $n$  and  $A$  are the dc conductivity, the onset frequency of the ac conductivity (mean frequency of the hopping process), the exponent and the weakly temperature dependent term, respectively. The first and the second terms of the equation (7) refer to the universal dielectric response (UDR) and to the nearly constant loss (NCL), respectively.

The power-law frequency dependent term (UDR) originates from the hopping of the carriers with interactions of the inherent defects in the materials, while the origin of the NCL term (the linear frequency dependent term) has been associated to rocking motions in an asymmetric double well potential (Nowick & Lim, 2001). For NCL term, the electrical losses occur during the time regime while the ions are confined to the potential energy minimum (León et al., 2001).

Both the dc conductivity and the hopping frequency are found to be thermally activated following an Arrhenius dependence (equations 8 and 9), being  $U_{dc}$  and  $U_H$  the activation energies of the dc conductivity and the hopping frequencies of the carriers, respectively, and  $\sigma_o$  and  $\omega_o$  the pre-exponential factors. It has been interpreted by using different theoretical models (Funke, 1993; Ngai, 1993; Jonscher, 1996) as indicating that the ac conductivity originates from a migration of ions by hopping between neighboring potential wells, which eventually gives rise to dc conductivity at the lowest frequencies.

$$\sigma_{dc} T = \sigma_o \exp\left(-\frac{U_{dc}}{k_B T}\right) \quad (8)$$

$$\omega_H = \omega_o \exp\left(-\frac{U_H}{k_B T}\right) \quad (9)$$

The objective of the present chapter is conducted to discuss the dielectric relaxation phenomenon in ferroelectric perovskite-related structures considering the relaxation mechanisms and the influence of the vacancies on them, so that the results can be more easily understood, from the physical point of view. Examples are given from the previously reported work of the present authors, as well as from the literature, with preference to the formers.

## 2. Ferroelectric $\text{ABO}_3$ perovskites.

Perovskite type oxides of general formula  $\text{ABO}_3$  are very important in material, physics and earth sciences because they exhibit excellent physical properties, which make them especial candidates for a wide application range in the electro-electronic industry (Lines, 1977). They are known for their phase transitions, which may strongly affect their physical and chemical properties. Perovskite structure-type oxides exist with all combination of cation oxidation states, with the peculiar characteristics that for  $\text{ABO}_3$  compounds one of the cations, traditionally the A-site ion, is substantially larger than the other one (B-site). This structure seem to be a particularly favorable configuration, because it is found for an extremely wide range of materials, where its basic pattern is frequently found in compounds that differ significantly from the ideal composition. From a direct review of the current literature, it has been established as well that important defects in the perovskite structure are directly related to vacancies of all three sub-lattices, electrons, holes, and substitutional impurities (Lines, 1977). Such a chemical defects strongly depend on the crystal structure as well as on the chemical properties of the constituent chemical species. The structure influences the types of lattice defects that may be formed in significant concentrations, and also influences the mobilities of the defects and hence of the chemical species. These mobilities determine whether or not defect equilibrium can be achieved within pertinent times at several temperatures, and at which temperature, during the cooling process of the material, these defects become effectively quenched. The charges and size of the ions affect the selection of the most favored defects, and their ability to be either oxidized or reduced determines the direction and amount of non-stoichiometry and the resulting enhanced electronic carrier concentrations. The volatility of a component, for instance, can also affect the equilibration and defect choice. This aspect is of particular importance for Pb-based compounds, due to the volatility of PbO during the synthesis of a specified material, which commonly achieves very high treatment temperatures (Xu, 1991). Thus, for perovskites structure-type systems, the partial substitution of A- or B-site ions promotes the activation of several conduction mechanisms (carrier doping).

In the last few years, extensive studies have been carried out by doping at A- and/or B-site by various researchers. It has been suggested that the introduction of different elements, which exhibit the dissimilar electronic configuration each other, should lead to dramatic effects associated with the electronic configuration mismatch between the ions located at the same A- or B-site. In this way, dielectric dispersions related to a conductivity phenomenon, which obeys the Arrhenius's dependence, have been reported for  $\text{Ba}_{1-x}\text{Pb}_x\text{TiO}_3$  ceramics (Bidault et al., 1994). Dielectric anomalies at the high-temperature region have been studied for  $(\text{Pb},\text{La})\text{TiO}_3$ ,  $\text{BaTiO}_3$  and  $(\text{Pb},\text{La})(\text{Zr},\text{Ti})\text{O}_3$  systems (Keng et al., 2003). The authors have showed that the dielectric anomalies are related to the competition phenomenon of the dielectric relaxation and the electrical conduction by oxygen vacancies.



On the other hand, the dielectric spectra of  $(\text{Ba}_{0.85}\text{Sr}_{0.15})\text{TiO}_3$  ceramics have been studied in the paraelectric phase showing the contribution of the dc conduction to the dielectric relaxation (Li & Fan, 2009). For  $\text{KNbO}_3$  ceramics, the temperature and frequency dependence of the dielectric and the conductivity properties have been studied, showing that the dielectric relaxation can be attributed to the hopping of oxygen vacancies in the six equivalent sites in the perovskite structure (Shing et al., 2010).

This section will show some experimental and theoretical results, for  $\text{ABO}_3$ -type perovskite structure systems, where the  $\text{BO}_6$  octahedra play a critical role in the demonstration of the ferroelectric properties. First, it will be presented the  $(\text{Pb}_{1-x}\text{La}_x)(\text{Zr}_{0.90}\text{Ti}_{0.10})_{1-x/4}\text{O}_3$  ceramic system (hereafter labeled as PLZT  $x/90/10$ ), with  $x = 2, 4$  and  $6$  at%, whose results have been discussed in the framework of the analysis of the effect of oxygen vacancies on the electrical response of soft doping  $\text{Pb}(\text{Zr,Ti})\text{O}_3$  ceramics in the paraelectric state (Peláiz-Barranco et al., 2008a; Peláiz-Barranco & Guerra, 2010). On the other hand, the frequency and temperature dielectric response and the electrical conductivity behavior around the ferroelectric-paraelectric phase transition temperature will be presented in the  $(\text{Pb}_{0.88}\text{Sm}_{0.08})(\text{Ti}_{1-x}\text{Mn}_x)\text{O}_3$ , with  $x = 0, 1$  and  $3$  at.% (named as PSTM- $x$ ) ferroelectric ceramic system (Peláiz-Barranco et al., 2008b). In this case, the contribution of the conductive processes to the dielectric relaxation for the studied frequency range has been discussed considering also the oxygen vacancies as the most mobile ionic defects in perovskites, whose concentration seems to increase with the manganese content.

## 2.1 $(\text{Pb}_{1-x}\text{La}_x)(\text{Zr}_{0.90}\text{Ti}_{0.10})_{1-x/4}\text{O}_3$ ceramic system.

Figure 3 shows the temperature dependence of the real ( $\epsilon'$ ) and imaginary ( $\epsilon''$ ) parts of the dielectric permittivity (A and B, respectively), for the studied PLZT  $x/90/10$  compositions, at  $20$  kHz. The dielectric properties results revealed no frequency dependent dispersion of the dielectric parameters and a non-diffusive phase transition for all the studied compositions. However, it can be observed that the temperature corresponding to the maximum in real and imaginary dielectric permittivities ( $T_m$ ) is strongly dependent on the lanthanum content. Additional anomalies in  $\epsilon'(T)$  were observed in the paraelectric phase range for low frequencies, characterized by an increase of the dielectric parameter with the increase of the temperature (Peláiz-Barranco et al., 2008a; Peláiz-Barranco & Guerra, 2010). Moreover, this anomaly is more pronounced when the lanthanum content increases. As shown in the temperature dependence of the imaginary part of the dielectric permittivity (Figure 3(B)), very high values of this parameter are observed at the corresponding temperature range, even at not low frequencies. Such results lead to infer that the anomalous behavior in the real dielectric permittivity with the increase of the temperature, and the high values of  $\epsilon''$ , are attributed to the same mechanism, that is to say, to the conductivity losses (Peláiz-Barranco et al., 2008a). It can be also noted that, for the PLZT  $4/90/10$  and  $6/90/10$  compositions, the maximum imaginary dielectric permittivity, which is associated to the paraelectric-ferroelectric phase transition (Figure 3(B) inset), can not be easily observed as in the case of the PLZT  $2/90/10$  composition. The observed behavior for the PLZT  $4/90/10$  and  $6/90/10$  compositions has been associated to the quickly increase of the losses factor above the phase transition temperature ( $T_m$ ), which is more pronounced for such compositions than for the PLZT  $2/90/10$  composition.

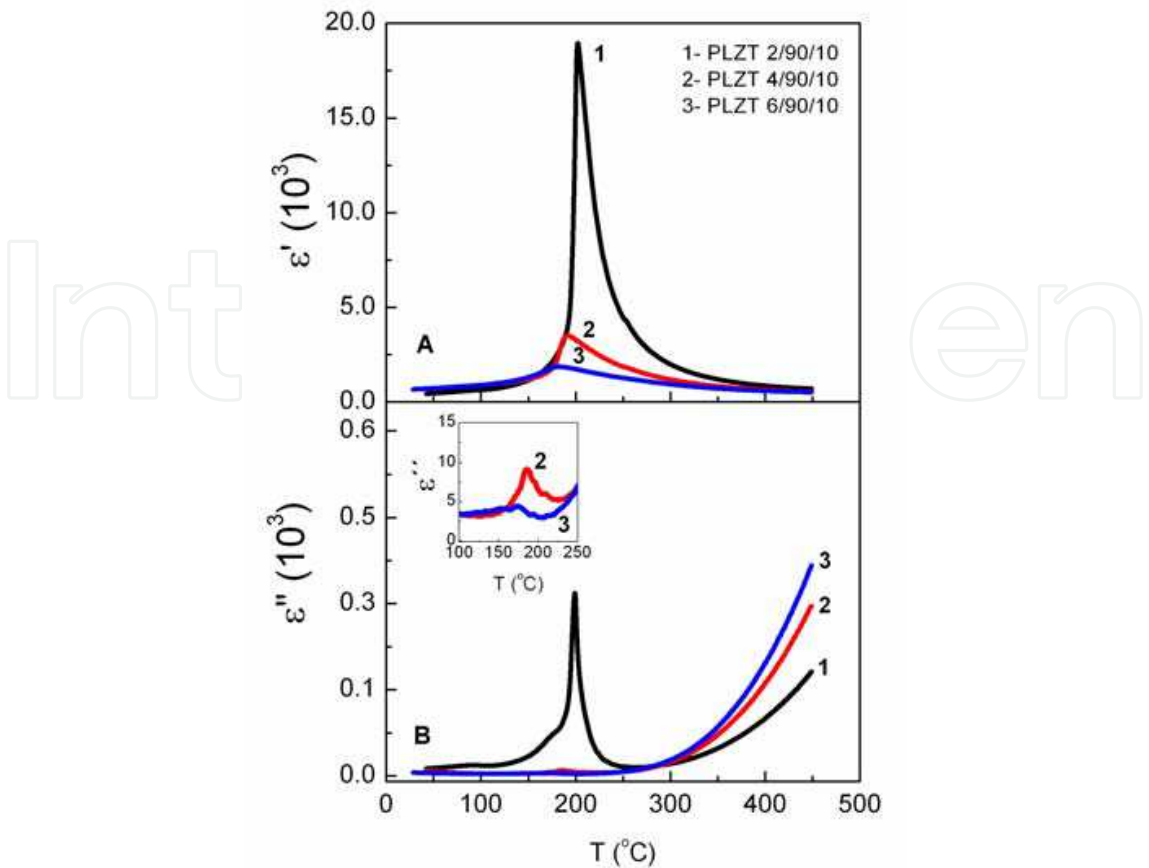


Fig. 3. Temperature dependence of the real ( $\epsilon'$ ) and imaginary ( $\epsilon''$ ) parts of the dielectric permittivity for the PLZT  $x/90/10$  ( $x = 2, 4$  and  $6$  at%) compositions, at 20 kHz

With the increase of measurement frequency, the observed behavior in the paraelectric phase gradually decreases, and almost disappears in the studied temperature range. Figure 4 shows the temperature dependences of  $\epsilon'$  and  $\epsilon''$  (A and B, respectively) for the PLZT 4/90/10 composition, at several frequencies. As can be seen, the high temperature anomaly almost disappears for the higher frequencies, showing that it could be related to a low-frequency relaxation process. It is well known that in perovskite ferroelectrics the oxygen vacancies could be formed in the process of sintering due to the escape of oxygen from the lattice (Kang et al., 2003). Thus, this anomaly could be correlated with a low-frequency relaxation process due to oxygen vacancies. Conduction electrons could be created by the ionization of oxygen vacancies, according to the expressions (10) and (11), where  $V_O$ ,  $V'_O$  and  $V''_O$  represent the neutral, single- and doubly-ionized oxygen vacancies, respectively.



The positions of the electrons depend on the structure characteristics, temperature range, and some other factors. It was, however, shown that the oxygen vacancies lead to shallow the electrons level. These electrons are easy to be thermally activated becoming conducting electrons. To elucidate the physical mechanism of this behavior in the paraelectric state, the electrical conductivity has been analyzed in the paraelectric phase (Peláiz-Barranco et al., 2008a).



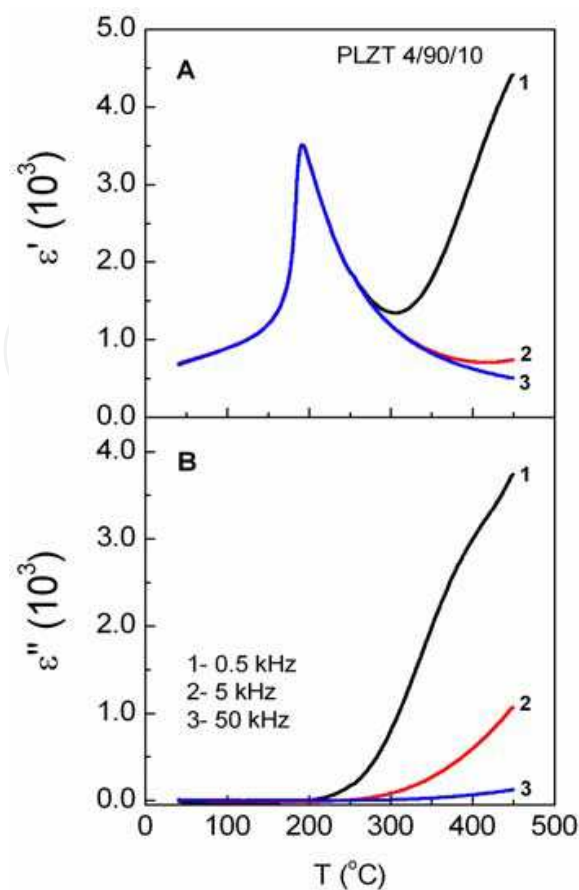


Fig. 4. Temperature dependence of the real ( $\epsilon'$ ) and imaginary ( $\epsilon''$ ) parts of the dielectric permittivity, at several frequencies for the PLZT 4/90/10 composition

By using the Jonscher’s relation expressed on the equation (7), the frequency dependence of the electrical conductivity for the studied compositions was analyzed in the paraelectric state, at several temperatures (Peláiz-Barranco et al., 2008a). The temperature dependence of the dc conductivity and the hopping frequency also followed an Arrhenius’ behavior, according to the equations (8) and (9), respectively. The obtained activation energy values for both cases are shown in the Table 1.

Composition	$U_{dc}$ (eV)	$U_H$ (eV)
PLZT 2/90/10	0.56	1.21
PLZT 4/90/10	0.49	1.15
PLZT 6/90/10	0.46	0.99

Table 1. Activation energy values for dc conductivity contribution,  $U_{dc}$ , and the hopping process,  $U_H$ , for the studied compositions (Peláiz-Barranco et al., 2008a)

According to the obtained results, some considerations can be taken into account in order to explain the observed behaviors. It is well known that during the synthesis and process of the ceramic system, i.e. the powders calcinations and the sintering stages, especially for the  $Pb(Zr,Ti)O_3$  system (PZT), there exists a high volatility of lead oxide because of the high temperatures operation. Such lead volatilization provides both fully-ionized cationic lead ( $V''_{Pb}$ ) vacancies and anionic oxygen vacancies ( $V''_O$ ). On the other hand, following the Eyraud’s model (Eyraud et al., 1984; Eyraud et al., 2002), it is assumed that the lanthanum

valence, as doping in the PZT system, has a strong influence in the ionization state of extrinsic lead and oxygen vacancies. In order to compensate the charge imbalance, one  $\text{La}^{3+}$  ion occupying a  $\text{Pb}^{2+}$  site (on the A-site of the perovskite structure) generates one half of singly ionized lead vacancies ( $V'_{\text{Pb}}$ ) rather than one doubly ionized vacancy ( $V''_{\text{Pb}}$ ). Thus, in the studied PLZT  $x/90/10$  compositions it should be considered different types of defects, related to  $V'_{\text{Pb}}$ ,  $V''_{\text{Pb}}$ ,  $V'_\text{O}$  and  $V''_\text{O}$  vacancies, whose contribution depends on the analyzed temperature range. A very low concentration of neutral lead and oxygen vacancies are considered around and above the room temperature.

At low temperatures, the lead vacancies are quenched defects, which are difficult to be activated. They could become mobile at high temperatures with activation energy values around and above 2 eV (Guiffard et al., 2005). However, to the best of our knowledge the ionization state of lead vacancies remains unknown. On the other hand, it has been reported (Verdier et al., 2005; Yoo et al., 2002) that the oxygen vacancies exist in single ionized state with activation energy values in the range of 0.3–0.4 eV. For Pb-based perovskite ferroelectrics, activation energies values in the range of 0.6–1.2 eV are commonly associated to doubly-ionized oxygen vacancies (Smyth, 2003; Moos et al., 1995; Moos & Härdtl, 1996). For PLZT 4/90/10 and PLZT 6/90/10 compositions, the results have suggested that the dc conductivity could be related to single ionized states ( $V'_\text{O}$ ). For the PLZT 2/90/10 composition, a higher activation energy value suggests a lower oxygen vacancies concentration (Steinsvik et al., 1997), whose values are closer to those values associated to doubly-ionized oxygen vacancies ( $V''_\text{O}$ ) (Smyth, 2003; Moos et al., 1995; Moos & Härdtl, 1996). Thus, the dc conductivity is assumed to be produced according to the reaction given by the expression (11), decreasing the number of  $V'_\text{O}$ , which could contribute for the lower anomaly observed for the PLZT 2/90/10 composition. The released electrons may be captured by  $\text{Ti}^{4+}$  and generates a reduction of the valence, following the relation (12).



Thus, the conduction process can occur due to the hopping of electrons between  $\text{Ti}^{4+}$  and  $\text{Ti}^{3+}$ , leading to the contribution of both single and doubly-ionized oxygen vacancies and the hopping energy between these localized sites for the activation energy in the paraelectric phase region for the studied PLZT compositions.

Considering the oxygen vacancies as the most mobile defects in the studied PLZT compositions, it has been analyzed their influence on the dielectric relaxation processes (Peláiz-Barranco et al., 2008a; Peláiz-Barranco & Guerra, 2010). It is known that the spontaneous polarization originating from the ionic or dipoles displacement contributions is known to be the off-center displacement of  $\text{Ti}^{4+}$  ions, from the anionic charge center of the oxygen octahedron for the PLZT system (Xu, 1991). The presence of oxygen vacancies would distort the actual ionic dipoles due to the  $\text{Ti}^{4+}$  ions. The decay of polarizations due to the distorted ionic dipoles could be the cause for the dielectric relaxation processes. However, usually the activation energy values associated to the relaxations involving thermal motions of  $\text{Ti}^{4+}$  (Peláiz-Barranco & Guerra, 2010) are higher than those observed in the studied PLZT  $x/90/10$  compositions, showing that it should not be a probable process. The obtained  $U_\text{H}$  values have suggested that the hopping process could be related to the doubly-ionized oxygen vacancies motion (Smyth, 2003; Moos et al., 1995; Moos & Härdtl, 1996). The short-range hopping of oxygen vacancies, similar to the reorientation of the dipoles, could lead to the dielectric relaxation.

On the other hand, the frequency and temperature behavior of the complex dielectric permittivity was analyzed (Peláiz-Barranco & Guerra, 2010) considering the Cole-Cole model, given by equations (4) and (5). The main relaxation time, obtained by the fitting by using both equations, followed the Arrhenius dependence (equation (6)) in the studied temperature range. The activation energy values for the relaxation processes are shown in Table 2 (Peláiz-Barranco & Guerra, 2010). The results have been associated with ionized oxygen vacancies. Thus, following the previously discussion, the dielectric relaxation phenomenon could be related to the short-range hopping of oxygen vacancies.

Composition	Ea (eV)
PLZT 2/90/10	0.48
PLZT 4/90/10	0.40
PLZT 6/90/10	0.37

Table 2. Activation energy values of the relaxation process for the studied compositions (Peláiz-Barranco & Guerra, 2010)

2.2 (Pb<sub>0.88</sub>Sm<sub>0.08</sub>)(Ti<sub>1-x</sub>Mn<sub>x</sub>)O<sub>3</sub> ceramic system.

Figure 5 depicts the temperature dependence of  $\epsilon'$  and  $\epsilon''$  for the PSTM- $x$  samples, for three selected frequencies, as example of the investigated behavior for the whole frequency range. Two peaks or inflections were observed for the real part of the dielectric permittivity at the studied frequency range. The first one, which was observed around 340°C for all the compositions, was associated to the temperature of the paraelectric-ferroelectric phase transition ( $T_m$ ), according to previous reports for these materials (Takeuchi et al., 1983; Takeuchi et al., 1985). For all the cases, the paraelectric-ferroelectric phase transition temperature ( $T_m$ ) did not show any frequency dependence, which is typical of ‘normal’ paraelectric-ferroelectric phase transitions (Xu, 1991). On the other hand, the imaginary dielectric permittivity showed a peak at the same temperature, to that observed for the real part of the dielectric permittivity ( $T_m$ ), confirming the ‘normal’ characteristic of the phase transition. In fact, not frequency dispersion of the temperature of the maximum dielectric permittivity was observed. However, a sudden increase of  $\epsilon''$  was obtained for temperatures around 400°C for all the studied compositions, which could be associated to high conductivity values that promote the increase of the dielectric losses.

The presence of two peaks in the temperature dependence of  $\epsilon'$  has been observed in (Pb<sub>0.88</sub>Ln<sub>0.08</sub>)(Ti<sub>0.98</sub>Mn<sub>0.02</sub>)O<sub>3</sub> (being Ln = La, Nd, Sm, Gd, Dy, Ho, Er) ferroelectric ceramics (Pérez-Martínez et al., 1997; Peláiz-Barranco et al., 2009a). In this way, for small-radius-size ions (Dy, Ho and Er) a strong increase of the tetragonality has been observed (Pérez-Martínez et al., 1997), even for values higher than those observed for pure lead titanate. Both peaks were associated to paraelectric-ferroelectric phase transitions concerning two different contributions to the total dielectric behavior of the samples; one, on which the rare earths ions occupy the A-sites and the other one where the ions occupy the B-sites of the perovskite structure (Pérez-Martínez et al., 1997). For high-radius-size ions (La, Nd, Sm and Gd) the analysis has shown that, even when it could be possible an eventual incorporation of the rare earth into the A- and/or B-sites of the perovskite structure, both peaks could not be associated to the paraelectric-ferroelectric phase transitions. In this case, the observed peak at lower temperatures has been associated to the paraelectric-ferroelectric phase transition, whereas the hopping of oxygen vacancies has been considered as the cause for the dielectric anomaly at higher temperatures (Peláiz-Barranco et al., 2009a).

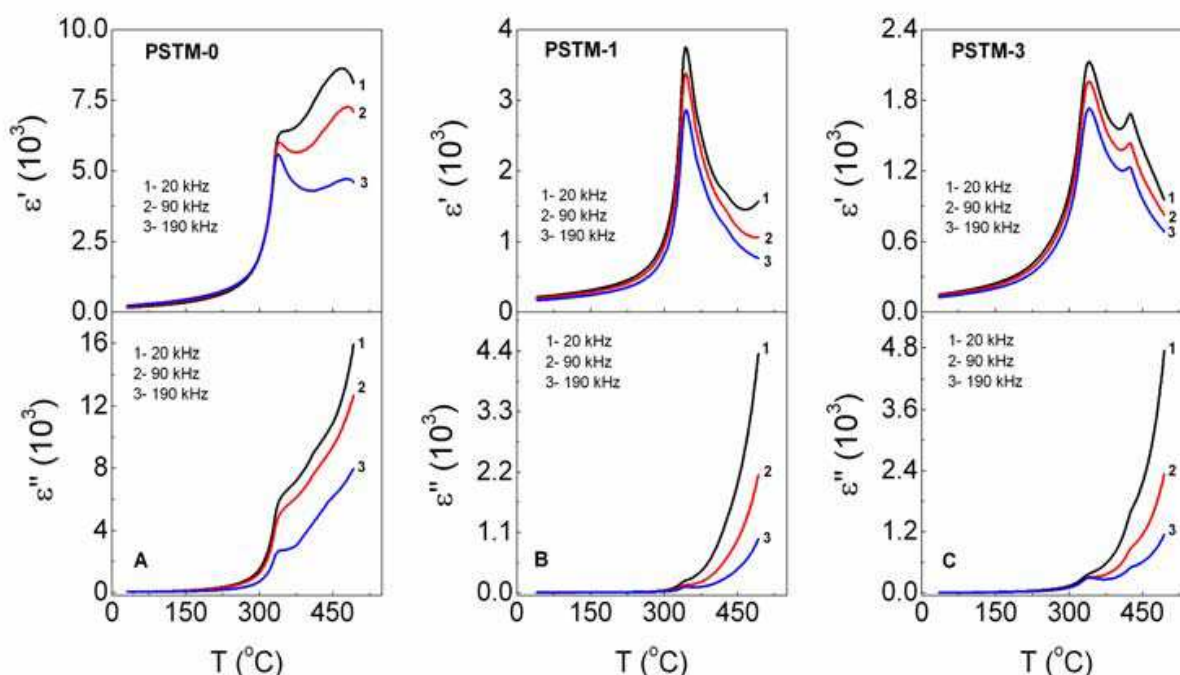


Fig. 5. Temperature dependence of the real ( $\epsilon'$ ) and imaginary ( $\epsilon''$ ) parts of the dielectric permittivity for the PSTM-0 (A), PSTM-1 (B) and PSTM-3 (C) compositions

Considering these results, two studies were carried out on these samples; the first one (Peláiz-Barranco et al., 2008b) concerning the dielectric relaxation phenomenon and the electrical conductivity behavior for temperatures around the paraelectric-ferroelectric phase transition (around 340°C); the second one concerning the electrical conductivity behavior around the second peak (Peláiz-Barranco & González-Abreu, 2009b).

The frequency dependence of the  $\epsilon'$  and  $\epsilon''$  for the studied PSTM- $x$  compositions below  $T_m$  (Peláiz-Barranco et al., 2008b) was analyzed by using the Cole-Cole model (equations (4) and (5)). The temperature dependence for the mean relaxation times, obtained from the fitting of the experimental data by using equations (4) and (5) revealed an Arrhenius' behavior, according to the equation (6). The obtained values for the activation energy were 0.89 eV, 0.81 eV and 0.62 eV, for the PSTM-0, PSTM-1 and PSTM-3 compositions, respectively, which clearly show that the dielectric relaxation processes in the studied samples are closely related to the oxygen vacancies, which have been reported as the most mobile ionic defects in perovskites (Poykko & Chadi, 2000). According to previously reported results (Steinsvik et al., 1997), the activation energy for  $ABO_3$  perovskites decreases with the increase of the oxygen vacancies content. As observed, the activation energy values for the studied samples decreases with the increase of the manganese content, which suggests an increase of oxygen vacancies concentration (Steinsvik et al., 1997). On the other hand, previous studies on electronic paramagnetic resonance (EPR) in earth rare and manganese modified lead titanate ceramics, have shown that a  $Mn^{4+}/Mn^{2+}$  reduction takes place during the sintering process (Ramírez-Rosales et al., 2001). As a consequence, oxygen vacancies have to be created to compensate for the charge imbalance. The increase of manganese content should promote a higher concentration of oxygen vacancies, which agrees with the decrease of activation energy values. Similarly to the results obtained for the PLZT  $x/90/10$  ceramics, the obtained activation energy values for the PSTM- $x$  compositions were found to be lower than those for relaxations involving thermal motions of  $Ti^{4+}$  (Maglione & Belkaoui, 1992). So that, the observed

relaxation process for the studied ceramics could be attributed to the decay of polarization in the oxygen defect-related dipoles due to their hopping conduction.

In order to better understand the conduction mechanism related to the observed relaxation process, the experimental data for the PSTM-*x* compositions were fitted by considering the equations (7), (8) and (9). Results of the dc conductivity ( $\sigma_{dc}$ ) and the hopping frequency ( $\omega_H$ ) are shown in the Figure 6, for temperatures below  $T_m$ . The solid lines on Figures 6(A) and 6(B), represent the fitting using the equations (8) and (9), respectively. The obtained activation energy values (for dc conductivity contribution,  $U_{dc}$ , and the hopping process,  $U_H$ ) are shown in the Table 3.

Composition	$U_{dc}$ (eV)	$U_H$ (eV)
PSTM-0	1.19	0.98
PSTM-1	0.94	0.90
PSTM-3	0.81	0.71

Table 3. Activation energy values (for dc conductivity contribution,  $U_{dc}$ , and the hopping process,  $U_H$ ) for the studied compositions, obtained from the fitting of the experimental data by using the equations (8) and (9) (Peláiz-Barranco et al., 2008b)

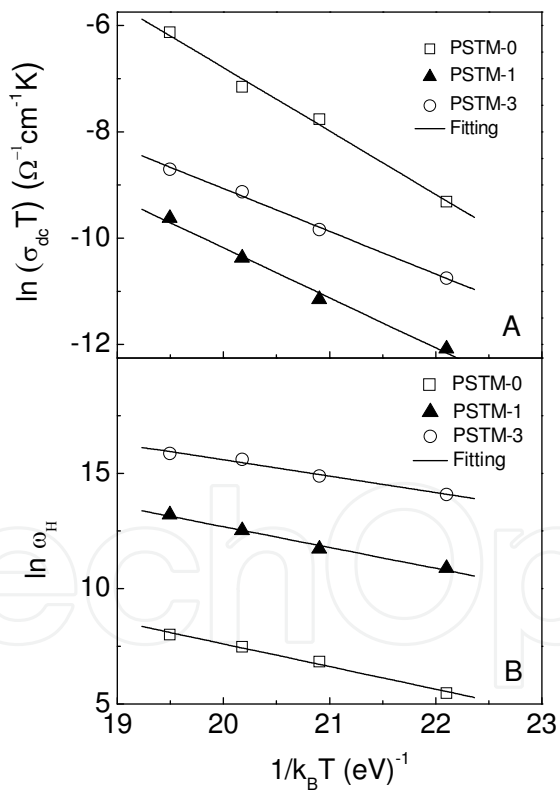


Fig. 6. Arrhenius' dependence for the dc conductivity ( $\sigma_{dc}$ ) and the hopping frequency ( $\omega_H$ ) (A and B, respectively), below  $T_m$ , for the studied PSTM-*x* compositions

As can be seen, the activation energy values for the dc conductivity are very close to the activation energy values of the ionic conductivity by oxygen vacancies in perovskite type ferroelectric oxides (Jiménez & Vicente, 1998; Bharadwaja & Krupanidhi, 1999; Chen et al., 2000; Smyth, 2003). Thus, it can be concluded that oxygen vacancies are the most likely



charge carriers operating in these ceramics below  $T_m$ . At room temperature, the oxygen vacancies exhibit a low mobility, whereby the ceramic samples exhibit an enhanced resistance. However, with rising temperature, they are activated and contribute to the observed electrical behavior. In addition, the dielectric relaxations occurring at low frequency are related to the space charges in association with these oxygen vacancies, which can be trapped at the grain boundaries or electrode-sample interface.

On the other hand, the activation energy values for the hopping processes ( $U_H$ ) are not very far from the  $U_{dc}$  values, showing that the hopping processes could be related to the movement of the oxygen vacancies. The short-range hopping of oxygen vacancies, similar to the reorientation of the dipole, could lead to the relaxation processes.

For temperatures above  $T_m$ , i.e. in the paraelectric phase, it was carried out the same analysis in the studied samples (Peláiz-Barranco et al., 2008b). The electrical conduction was associated with the doubly ionized oxygen vacancies and the relaxation processes were related to the distorted ionic dipoles by the oxygen vacancies.

Concerning the second peak (Peláiz-Barranco & González-Abreu, 2009b), a detailed study of the electrical conductivity behavior was carried out by using the Jonscher's formalism. The electrical conduction was associated to the doubly-ionized oxygen vacancies and its influence on the relaxation processes was analyzed.

### 3. Bi-layered ferroelectric perovskites.

The materials of the Bi-layered structure family were first described by Aurivillius in 1949. The corresponding general formula is  $[\text{Bi}_2\text{O}_2]^{2+}[\text{A}_{n-1}\text{B}_n\text{O}_{3n+1}]^{2-}$ , where A can be  $\text{K}^+$ ,  $\text{Sr}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Pb}^{2+}$ , etc.; B can be  $\text{Ti}^{4+}$ ,  $\text{Nb}^{5+}$ ,  $\text{Ta}^{5+}$ ,  $\text{W}^{6+}$ , etc., and n is the number of corner sharing octahedral forming the perovskite like slabs, which is usually in the range 1-5. The oxygen octahedra blocks, responsible for ferroelectric behavior, are interleaved with  $(\text{Bi}_2\text{O}_2)^{2+}$  layers resulting in a highly anisotropic crystallographic structure where the c parameter, normal to  $(\text{Bi}_2\text{O}_2)^{2+}$  layers, is much greater than a and b parameters of the orthorhombic cell. For this family, ferroelectricity is strongly depending on the crystallographic orientation of the materials, being the aim of continuing research (Lee et al, 2002; Watanabe et al., 2006). It is well-known that these have the majority polarization vector along the a-axis in a unit cell and that the oxygen vacancies prefer to stay in the  $\text{Bi}_2\text{O}_2$  layers, where their effect upon the polarization is thought to be small, and not in the octahedral site that controls polarization.

The layered perovskites are considered for nonvolatile memory applications because of the characteristics of resistance to fatigue (Chen et al., 1997). The frequency response of  $\text{SrBi}_2\text{Ta}_2\text{O}_9$  and  $\text{SrBi}_2\text{Nb}_2\text{O}_9$  ceramics has been studied considering the bulk ionic conductivity to evaluate the electrical fatigue resistance. The results have showed much higher conductivity values than those of the PZT perovskite ferroelectrics, which has been considered as the cause of the good fatigue resistance. There is an easy recovery of the oxygen vacancies from traps, which limits the space charge generated during the polarization reversal process.

An interesting feature of these materials is that some of them allow cation site mixing among atoms positions (Mahesh Kumar & Ye, 2001), especially between the bismuth and the A-site of the perovskite block (Blake et al., 1997). For example, it has been reported (Ismunandar & Kennedy, 1999) that both  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$  can occupy the Bi sites in  $\text{ABi}_2\text{Nb}_2\text{O}_9$  (A=Sr,Ba). For the studied materials, the degree of disorder is related to the change in the cell volume, which is much lower than that reported in  $\text{PbBi}_2\text{Nb}_2\text{O}_9$ . For  $\text{SrBi}_2\text{Ta}_2\text{O}_9$  (Mahesh



Kumar & Ye, 2001), the substitution of  $\text{Fe}^{3+}$  for  $\text{Sr}^{2+}$  increases the ferroelectric-paraelectric transition temperature and provides a higher resistivity value. However, the substitution of  $\text{Ca}^{2+}$  for  $\text{Bi}^{3+}$  in the bismuth layers increases the electrical conductivity.

The Aurivillius family exhibit a dielectric behavior characteristic for ferroelectric relaxors (Miranda et al., 2001; Kholkin et al., 2001), e.g. i) marked frequency dispersion in the vicinity of temperature ( $T_m$ ) where the real part of the dielectric permittivity ( $\epsilon'$ ) shows its maximum value, ii) the temperature of the corresponding maximum for  $\epsilon'$  and the imaginary part of the dielectric permittivity ( $\epsilon''$ ) appears at different values, showing a frequency dependent behavior, iii- the Curie-Weiss law is not fulfilled for temperatures around  $T_m$ . The materials have attracted considerable attention due to their large remanent polarization, lead-free nature, relatively low processing temperatures and other characteristics (Miranda et al., 2001; Kholkin et al., 2001; Lee et al., 2002; Nelis et al., 2005; Huang et al., 2006; Watanabe et al., 2006). The origin of the relaxor behavior for these materials has been associated to a positional disorder of cations on A or B sites of the perovskite blocks that delay the evolution of long-range polar ordering (Miranda et al., 2001).

For  $\text{BaBi}_2\text{Nb}_2\text{O}_9$  ceramics (Kholkin et al., 2001), it has been studied the frequency relaxation of the complex dielectric permittivity in wide temperature and frequency ranges. The reported relaxation time spectrum is qualitative difference from that of conventional relaxor ferroelectrics; this shifts rapidly to low frequencies on cooling without significant broadening. It has been discussed considering a reduced size of polarization clusters and their weak interaction in the layered structure.

For bismuth doped  $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$  ceramics, it has been showed that the  $\text{Bi}^{3+}$  doping decreases the maximum of the real part of the dielectric permittivity, whose temperature also shifts to lower temperatures for the lower  $\text{Sr}^{2+}$  concentrations (Zhou et al., 2001). A relaxor behavior has been reported for these ceramics, suggesting a random electric field as the responsible of the observed behavior.

The complex dielectric permittivity spectrum in the THz region was studied in  $\text{SrBi}_2\text{Ta}_2\text{O}_9$  films (Kadlec et al., 2004). The lowest-frequency optical phonon revealed a slow monotonic decrease in frequency on heating with no significant anomaly near the phase transitions. The dielectric anomaly near the ferroelectric phase transition was discussed considering the slowing down of a relaxation mode. It was also discussed the loss of a centre of symmetry in the ferroelectric phase and the presence of polar clusters in the intermediate ferroelastic phase.

For  $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$  ceramics (Bobić et al., 2010), the dielectric relaxation processes have been described by using the empirical Vogel-Fulcher law. The electrical conductivity behavior has suggested that conduction in the high-temperature range could be associated to oxygen vacancies.

The previous results correspond to part of the studies carried out in the last years concerning the dielectric and electrical conductivity behaviors of Bi-layered structure materials. However, a lot of aspects of these remain unexplored, especially concerning the dielectric relaxation phenomenon and the conductivity mechanisms. It has been the motivation of the present authors, and other colleagues, to study the dielectric relaxation in one of these systems.

### 3.1 $\text{Sr}_{1-x}\text{Ba}_x\text{Bi}_2\text{Nb}_2\text{O}_9$ ceramic system.

It has been previously commented that  $\text{SrBi}_2\text{Nb}_2\text{O}_9$  is a member of the Aurivillius family (Blake et al., 1997; Ismunandar & Kennedy, 1999; Haluska & Misture, 2004; Nelis et al., 2005;

Huang et al, 2006), consisting of octahedra in the perovskite blocks sandwiched by two neighboring  $(\text{Bi}_2\text{O}_2)^{2+}$  layers along the  $c$ -axis in a unit cell. The divalent  $\text{Sr}^{2+}$  cation located between the corner-sharing octahedra can be totally or partially replaced by other cations, most commonly barium (Haluska & Misture, 2004; Huang et al, 2006). The barium modified  $\text{SrBi}_2\text{Nb}_2\text{O}_9$  ceramics have showed that the incorporation of  $\text{Ba}^{2+}$  in the  $\text{Sr}^{2+}$  sites (A sites of the perovskite) provides a complex dielectric response showing a transition from a normal to a relaxor ferroelectric (Huang et al, 2006). On the other hand, it has been analyzed the barium preference for the bismuth site, which occur to equilibrate the lattice dimensions between the  $(\text{Bi}_2\text{O}_2)^{2+}$  layers and the perovskite blocks (Haluska & Misture, 2004).

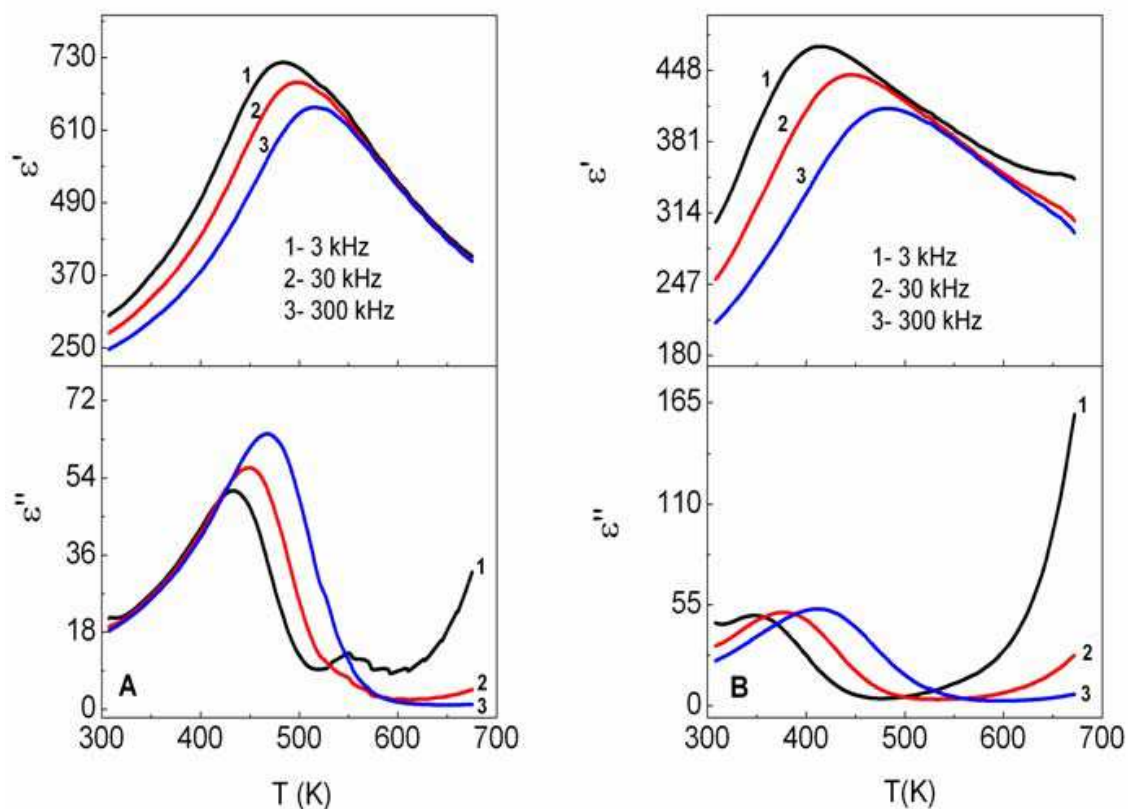


Fig. 7. Temperature dependence of the real ( $\epsilon'$ ) and imaginary ( $\epsilon''$ ) parts of the dielectric permittivity for A)-  $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Bi}_2\text{Nb}_2\text{O}_9$  and B)-  $\text{Sr}_{0.1}\text{Ba}_{0.9}\text{Bi}_2\text{Nb}_2\text{O}_9$ , at various frequencies

$\text{Sr}_{1-x}\text{Ba}_x\text{Bi}_2\text{Nb}_2\text{O}_9$  ferroelectric ceramics were analyzed in a wide frequency range (100 Hz to 1 MHz) for temperatures below, around and above the temperature where the real part of the dielectric permittivity showed a maximum value. Three compositions were considered, i.e.  $x=50, 70$  and  $90$  at%. Typical characteristics of relaxor ferroelectrics were observed in the studied samples (González-Abreu et al., 2009; González Abreu, 2010). Figure 7 shows the temperature dependence of the real ( $\epsilon'$ ) and imaginary ( $\epsilon''$ ) parts of the dielectric permittivity for  $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Bi}_2\text{Nb}_2\text{O}_9$  and  $\text{Sr}_{0.1}\text{Ba}_{0.9}\text{Bi}_2\text{Nb}_2\text{O}_9$ , at various frequencies, as example of the observed behavior in the studied frequency range for the three compositions. On the other hand, an important influence of the electrical conductivity mechanisms was considered from the temperature dependence of the imaginary part of the dielectric permittivity, which increases with temperature, especially for the lower frequencies.

The origin of the relaxor behavior for these ceramics has been explained by considering a positional disorder of cations on A or B sites of the perovskite blocks that delay the

evolution of long-range polar ordering (Miranda et al., 2001). For  $\text{Ba}^{2+}$  doped  $\text{SrBi}_2\text{Nb}_2\text{O}_9$  ceramics, a higher frequency dependence of the dielectric parameters has been observed than that of the undoped  $\text{SrBi}_2\text{Nb}_2\text{O}_9$  system (González Abreu, 2010). The results have been discussed by considering the incorporation of a bigger ion into the A site of the perovskite block. The  $\text{Ba}^{2+}$  ions not only substitute the  $\text{Sr}^{2+}$  ions in the A-site of the perovskite block but enter the  $(\text{Bi}_2\text{O}_2)^{2+}$  layers leading to an inhomogeneous distribution of barium and local charge imbalance in the layered structure.

Following the Cole-Cole model (Cole & Cole, 1941), the real and imaginary part of the dielectric permittivity were fitted by using equations (4) and (5) in a wide temperature range (González-Abreu et al., 2009; González Abreu, 2010). Figures 8 and 9 show the experimental data (solid points) and the corresponding theoretical results (solid lines) at a few representative temperatures for  $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Bi}_2\text{Nb}_2\text{O}_9$  and  $\text{Sr}_{0.1}\text{Ba}_{0.9}\text{Bi}_2\text{Nb}_2\text{O}_9$ , respectively, as example of the observed behavior in the studied temperature range for the three compositions.

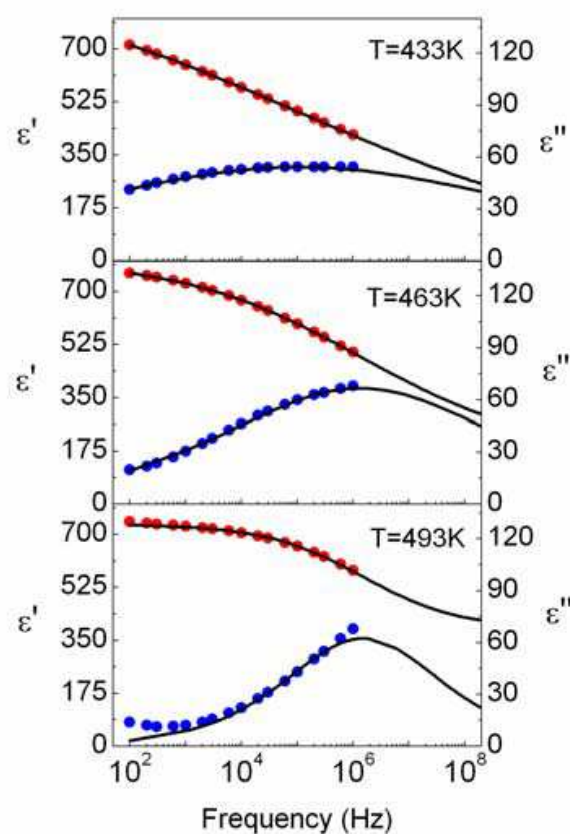


Fig. 8. Frequency dependence of the real  $\epsilon'$  (●) and imaginary  $\epsilon''$  (●) parts of the dielectric permittivity, at a few representatives temperatures, for  $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Bi}_2\text{Nb}_2\text{O}_9$ . Solid lines represent the fitting by using equations (4) and (5)

Two relaxation processes were evaluated for the studied compositions from the temperature dependence of the relaxation time (González-Abreu et al., 2009; González Abreu, 2010), which was obtained from the fitting by using the Cole-Cole model. The first one takes place around the temperature range where the high dispersion of the real part of the dielectric permittivity was observed (see Figure 7), i.e. below and around the region where the maximums of  $\epsilon'$  are obtained in the studied frequency range. The temperature dependence

of the relaxation time was found that follows the Vogel-Fulcher law (González-Abreu et al., 2009; González Abreu, 2010), which describes the typical temperature dependence of the relaxation time for relaxor ferroelectrics. From this point of view, it could be considered that the main origin of the first dielectric relaxation process could be associated to the relaxor-like ferroelectric behavior of the studied ceramics.

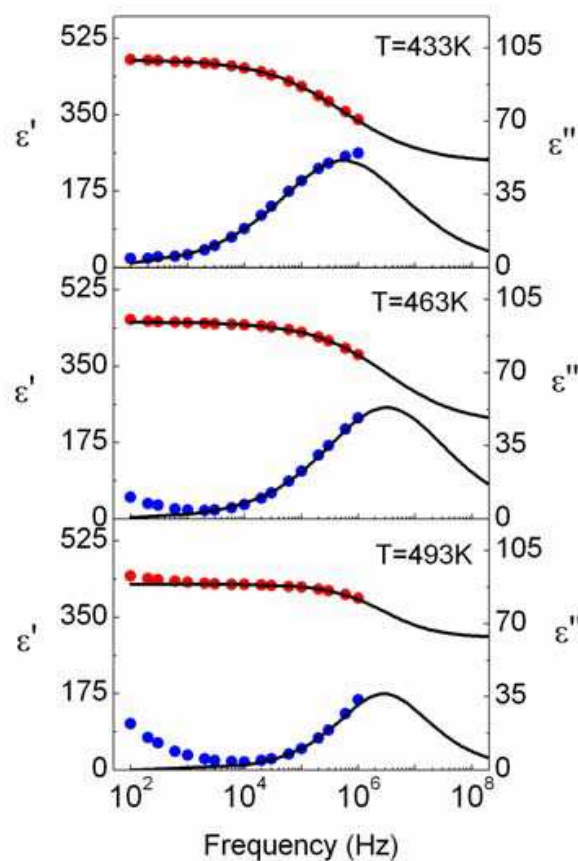


Fig. 9. Frequency dependence of the real  $\epsilon'$  (•) and imaginary  $\epsilon''$  (•) parts of the dielectric permittivity, at a few representatives temperatures, for  $\text{Sr}_{0.1}\text{Ba}_{0.9}\text{Bi}_2\text{Nb}_2\text{O}_9$ . Solid lines represent the fitting by using equations (4) and (5)

The temperature dependence of the relaxation time for second relaxation process was fitted by using the known Arrhenius law given by equation 6 (González-Abreu et al., 2009; González Abreu, 2010). This second process was observed for temperatures where an important contribution of the electrical conductivity mechanisms was considered from the temperature dependence of the imaginary part of the dielectric permittivity. It is known that  $\text{Ba}^{2+}$  ions could occupy the A-sites at the octahedra in the perovskite blocks and the bismuth site in the layered structure for  $\text{Sr}_{1-x}\text{Ba}_x\text{Bi}_2\text{Nb}_2\text{O}_9$  ceramics (Haluska & Mixture, 2004). The electrical charge unbalance caused by the trivalent  $\text{Bi}^{3+}$  ion substitution for the divalent  $\text{Ba}^{2+}$  ions is compensated by the creation of oxygen vacancies. Then, it could be suggested that the hopping of the electrons, which appears due to the ionization of the oxygen vacancies, could contribute to the dielectric relaxation and its long-distance movement contributes to the electrical conduction.

However, other important contribution should be considered. For relaxor ferroelectrics, microdomains can be observed even at temperature regions far from the region where the



maximums of  $\varepsilon'$  are obtained, i.e. far from the temperature of the relaxor behavior peak (Burns, 1985). Thus, it has been suggested that the dielectric relaxation process could result from the contribution of the interaction between the dipoles, which forms the microdomains existing at higher-temperature side of the relaxor peak, and the electrons that are due to the ionization of the oxygen vacancies.

#### 4. Summary

In this chapter, the dielectric relaxation phenomenon was discussed in ferroelectric perovskite-related structures considering the relaxation mechanisms and the influence of the vacancies on them. A schematic diagram illustrating the various relaxation processes in the frequency spectrum was showed and some important models used to analysis the dielectric relaxation were presented. Examples, which evidence relations between the relaxation phenomena and defects in the materials, were given.

#### 5. Acknowledgements

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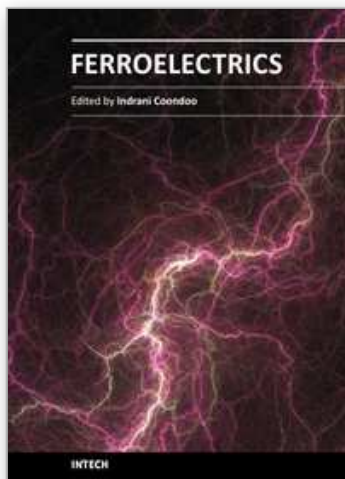
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Ferroelectric materials exhibit a wide spectrum of functional properties, including switchable polarization, piezoelectricity, high non-linear optical activity, pyroelectricity, and non-linear dielectric behaviour. These properties are crucial for application in electronic devices such as sensors, microactuators, infrared detectors, microwave phase filters and, non-volatile memories. This unique combination of properties of ferroelectric materials has attracted researchers and engineers for a long time. This book reviews a wide range of diverse topics related to the phenomenon of ferroelectricity (in the bulk as well as thin film form) and provides a forum for scientists, engineers, and students working in this field. The present book containing 24 chapters is a result of contributions of experts from international scientific community working in different aspects of ferroelectricity related to experimental and theoretical work aimed at the understanding of ferroelectricity and their utilization in devices. It provides an up-to-date insightful coverage to the recent advances in the synthesis, characterization, functional properties and potential device applications in specialized areas.

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Unit 405, Office Block, Hotel Equatorial Shanghai  
No.65, Yan An Road (West), Shanghai, 200040, China  
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Phone: +86-21-62489820  
Fax: +86-21-62489821

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