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Relaxor ferroelectric behavior: An approach considering both the dipolar and electrical conductivity contributions

C. Carreras-Casas*, O. García-Zaldívar*,‡, A. Peláiz-Barranco*, Y. González-Abreu*,
F. Calderón-Piñar* and J. D. S. Guerra†

*Grupo de Materiales Ferroicos
Facultad de Física-Instituto de Ciencia y Tecnología de Materiales
Universidad de La Habana, La Habana 10400, Cuba

†Grupo de Ferroelétricos e Materiais Multifuncionais
Instituto de Física, Universidade Federal de Uberlândia
Uberlândia, Minas Gerais, 38408-100, Brazil

‡osmany.garcia@gmail.com

The relaxor behavior of PLZT ferroelectric ceramics has been analyzed in a wide frequency and temperature ranges, below and above the temperature for the formation of the so-called polar nano-regions (PNRs). An approximation to the dynamical behavior of the PNRs has been discussed using Cole–Cole's relaxation model and Jonscher's Universal Relaxation Law. The analysis considers both the dipolar contribution and those ones associated with DC and AC electric conductivities, this latter not being previously reported in the literature for relaxor materials. The effectiveness of the developed model has been verified from the agreement between the experimental data and the theoretical calculations. This study also offers an indirect method to predict the DC component of the electrical conductivity.

Keywords: Relaxor ferroelectrics; dielectric response modeling; conductivity; Cole–Cole.

1. Introduction

Ferroelectric systems are characterized by having a non-zero electric dipole moment, in the absence of an external electric field, below a certain critical temperature commonly known as the Curie temperature (T_C). Above T_C, the material is in a nonpolar paraelectric state (where the dipole moment is equal to zero), being this the ferroelectric-paraelectric (FE-PE) phase transition temperature.[1,2] Ferroelectrics are typical dielectric materials with a reversible polarization under the action of an external electric field. In general, FE systems show relatively high real dielectric permittivity values ($\varepsilon' \sim 10^3$–10^5), low dielectric losses ($\tan\delta \sim 10^{-3}$–10^{-2}) and enhanced piezoelectric and pyroelectric properties.[1–7] Roughly, FEs can also be classified into two groups as normal (conventional) and relaxor ferroelectrics,[1–7] according to the frequency behavior of the temperature at which the maximum of real and imaginary part of the dielectric permittivity (ε' and ε'', respectively) occurs. For the second group, relaxor-like characteristics reveal as a strong temperature and frequency dependence in the maximum of both ε' and ε'', leading to the well-known relaxor ferroelectrics.

In particular, relaxor ferroelectrics have received special attention due to their extraordinary dielectric properties.[1–7] Similar to conventional ferroelectrics, relaxors depict very high real dielectric permittivity values and low dielectric losses. However, different to conventional FEs, relaxors show particular and intriguing behaviors in the dielectric response, which reveal them promissory materials for practical applications. For instance, they present wide peaks in the temperature dependence of the dielectric permittivity, a slight difference between the temperatures of the corresponding maxima for ε' (T_m) and ε'' ($T_{\varepsilon''\text{max}}$) and a strong frequency dependence of both ε' (T_m) and ε'' ($T_{\varepsilon''\text{max}}$). Furthermore, for temperatures above T_m, the Curie–Weiss law is not fulfilled, so that T_m cannot be associated to a typical FE-PE phase transition.

From the fundamental point of view, the relaxor behavior in ferroelectrics has been ascribed to the existence of polar regions of nanometric scale (PNRs), which characterize by local short-range interactions.[1–4] Unlike for normal ferroelectrics, where a long-range dipolar interaction prevails and the system responds as a whole with a single relaxation time, relaxors are characterized by a relaxation times distribution due to the different response time of the PNRs. The correlated

‡Corresponding author.

PNRs appear well above T_m and below a certain temperature known as the Burns temperature (T_B).[8] Above T_B, the material remains in a higher symmetry paraelectric state and the Curie–Weiss law is then fulfilled.

At high temperatures, the PNRs can be considered as dipoles whose polarization directions thermally fluctuate between equivalent states. Under these conditions, the thermal energy is enough to overcome the energy barrier, which separates different polarization states. Therefore, the polarization is randomly oriented and the mean relaxation time (τ_0) is low. Thus, even when an intrinsic dipole moment exists in the material, there is no remnant polarization and no ferroelectric hysteresis loop can be obtained. This effect gives rise to the typical slim loops observed for relaxors. Upon cooling (from T_B), the number and size of the PNRs increase and so do the interactions between them.[1,2] As a consequence, the energy barrier between polar states, as well as the mean relaxation time, increases and in some temperature (far below T_B) the thermal energy is not enough to overcome the energy barrier. Therefore, no thermal switching of the polarization occurs. Such a temperature represents the so-called freezing temperature (T_F), below of which the system behaves like a normal ferroelectric.[1,2] Around T_m, between T_F and T_B, the maximum of the real permittivity takes place, which is not associated with a structural phase transition.

There are several ferroelectric materials belonging to the perovskites and Aurivillius' families, which exhibit a relaxor behavior. $Pb_{1-3x/2}La_x(Zr_{0.60}Ti_{0.40})O_3$ [PLZT–x] and $Sr_{1-x}Ba_xBi_2Nb_2O_9$ [SBBN–x] systems are classical examples, respectively, where the relaxor properties reveal only for specific compositions.[2,9] Previous works focused on the relaxor nature of the PLZT–x system, by using a multi-Debye relaxation model[2] and the Cole–Cole's (C–C) formalism,[10] have shown that both models fail at the lower frequency region and high temperatures (around and above T_m). In this region, the electrical conductivity mechanisms are commonly activated and their contribution to the dielectric permittivity cannot be neglected. The aim of the present work is to evaluate the dielectric behavior of the PLZT system, for a relaxor composition, by using C–C model and Jonscher's Universal Relaxation Law, considering both the dipolar contribution and the DC and AC electric conductivity.

2. Proposed Model

C–C has been extensively used to describe the dielectric behavior of (di)polar systems, including ferroelectrics, where the dielectric permittivity response deviates from the ideal Debye's relaxation.[10] The C–C formalism considers the existence of a relaxation time distribution function, different to the expected for the classical Debye's model, where the whole system responds with a single relaxation time.[11] However, from experimental measurements, because of ferroelectric systems are not ideal dielectrics, it can be observed that the dielectric response has both the dipolar and conductivity

contributions, being this later not considered by C–C model. Therefore, for some systems, the application of C–C model could lead to a misinterpretation of the dielectric behavior. It is particularly important for materials characterized by many defects, where the electrical conduction mechanisms are activated at temperatures far below T_m.

For such materials, considering the total contribution to the dielectric response (dipolar and conductive), the imaginary dielectric permittivity (using C–C model) it has been proposed to include the DC conductivity (σ_{DC}), according to Eqs. (1)–(3), where ε_s, ε_∞ and ω are the static dielectric permittivity, the dielectric permittivity at optical frequencies and the angular frequency $(\omega = 2\pi f)$, respectively. The α parameter is related to the width of the distribution function and τ_0 is the mean relaxation time.

$$\varepsilon' = \frac{(\varepsilon_s - \varepsilon_\infty)\left(\sin\left(\frac{\pi\alpha}{2}\right)(\tau_0\omega)^{1-\alpha} + 1\right)}{1 + (\tau_0\omega)^{2(1-\alpha)} + 2(\tau_0\omega)^{1-\alpha}\sin\left(\frac{\pi\alpha}{2}\right)} + \varepsilon_\infty, \quad (1)$$

$$\varepsilon'' = \frac{(\varepsilon_s - \varepsilon_\infty)(\tau\omega)^{(1-\alpha)}\cos\left[\frac{\pi\alpha}{2}\right]}{1 + (\tau\omega)^{2(1-\alpha)} + 2(\tau\omega)^{(1-\alpha)}\sin\left(\frac{\pi\alpha}{2}\right)} + \frac{\sigma_{DC}}{\varepsilon_0\omega}, \quad (2)$$

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'} = \frac{(\tau_0\omega)^{(1-\alpha)}\cos\left(\frac{\pi\alpha}{2}\right)}{1 + (\tau_0\omega)^{(1-\alpha)}\sin\left(\frac{\pi\alpha}{2}\right)} + \frac{\sigma_{DC}}{\varepsilon_0\varepsilon'\omega}. \quad (3)$$

It should be noted that C–C description can be reduced to Debye's model when $\alpha = 0$. Considering that C–C model is valid for interacting dipole moments systems, and taking into account that for relaxor ferroelectrics the polar regions disappear for temperatures above T_B, the final proposed model can be described according to Eq. (4). T_B, determined from the fulfillment of Curie–Weiss's law, has a value of $210\,°C \pm 5\,°C$. Below T_B, the corrected C–C model is proposed, and above this temperature the Jonscher Universal Response Law[12] is fulfilled. Equation (4) represents a general empirical expression that considers both the hopping (dipolar) and the conductivity contributions.

$$\tan\delta = \begin{cases} \dfrac{(\tau_0\omega)^{(1-\alpha)}\cos\left(\frac{\pi\alpha}{2}\right)}{1 + (\tau_0\omega)^{(1-\alpha)}\sin\left(\frac{\pi\alpha}{2}\right)} + \dfrac{\sigma_{DC}}{\varepsilon_0\varepsilon'\omega}, & T \le T_B, \\[3em] \dfrac{\sigma_{DC}\left(1 + \left(\dfrac{\omega}{\omega_H}\right)^n\right)}{\varepsilon_0\varepsilon'\omega}, & T > T_B, \end{cases} \quad (4)$$

where ω_H is the characteristic frequency of the hopping processes and n is an exponential fitting parameter. Both σ_{DC} and ω_H are described by an Arrhenius type temperature dependence (typical of thermally activated processes presented in semiconductors and dielectrics) as represented by Eqs. (5) and (6), respectively. U_{DC} and U_H are the activation energies corresponding to the DC and hopping processes, respectively, σ_0 and ω_0 are the pre-exponential factors, k_B is Boltzmann's constant and T represents the absolute temperature. From this dependence, it is possible to analyze the type of the conduction mechanism that predominates for different temperature ranges, their respective activation energies, as well as the hopping species.

$$\sigma_{DC}T = \sigma_0 e^{-\frac{U_{DC}}{k_B T}}, \qquad (5)$$

$$\omega_H = \omega_0 e^{-\frac{U_H}{k_B T}}, \qquad (6)$$

From the fitting of the frequency dependence of $\tan\delta$ for each temperature, by using Eq. (4) in the whole temperature and frequency studied ranges, the parameters α, τ_0, ω_H, σ_{DC} and n can be determined as a function of temperature and then the temperature dependence of ε_s can be also obtained. After that, the theoretical values for the real and the imaginary components of the dielectric permittivity can be obtained for any temperature and frequency value by using Eqs. (1) and (2).

3. Experimental Procedure

PLZT ceramic sample, with nominal composition $Pb_{0.88}La_{0.08}(Zr_{0.60}Ti_{0.40})O_3$ (PLZT-8) was prepared by the traditional solid-state sintering method, considering vacancies in the A-site of the perovskite structure.[2] The corresponding high purity precursor oxides (>98%) were ball-milled and calcined at 800 °C for 2 h. The ceramic body was sintered at 1200 °C for 2 h in air atmosphere.

A pure rhombohedral phase, without any additional secondary phases, was obtained, and the observed strong dielectric dispersion has been investigated considering a multi-Debye relaxation model.[2] Silver painted electrodes were applied on the opposite faces of the sintered sample by a heat treatment at 590 °C. Dielectric measurements were carried out in a wide frequency and temperature range by using an AG4284A LCR meter, applying 1 V to the sample.

4. Results and Discussion

Figure 1 shows the temperature dependence of τ_0 and α for the studied PLZT-8 sample. The increase in τ_0 with the decrease of the temperature, below 200 °C, is a direct consequence of the PNRs freezing process. Therefore, it should be expected that τ_0 tends to infinity at T_F, below which temperature the PNRs are frozen. However, τ_0 reaches a maximum
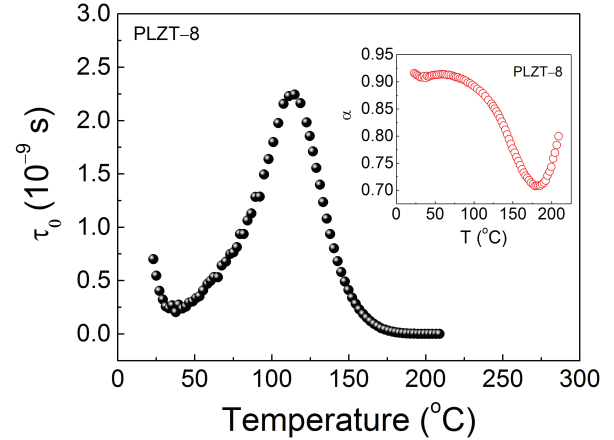

Fig. 1. Temperature dependence of τ_0 and α for the PLZT-8 sample.

value and decreases for lower temperatures. The relaxation time does not diverge at T_F because of the PNRs are not the only involved polarization mechanism.

At low temperatures, (below the temperature of the maximum τ_0) the contribution to the dielectric permittivity is governed by polarization mechanisms (ionic and electronic induced polarization) with relaxation times lower than those exhibited by PNRs, whereas the higher temperatures region is governed by the contribution of the PNRs. Therefore, it is possible to suggest that the maximum of τ_0 takes place at a temperature close to the freezing temperature (T_F).[2] T_F, determined from the temperature at which the maximum of τ_0 take place is around ~113 °C.

It is worth noting that there is a difference of about two orders of magnitude in the values of τ_0 between the present work and that of reported in Ref. 2. The difference can arise from the fact that dc conductivity was not considered in the previous model[2]; the contribution of conductivity to the dielectric response was "absorbed" by τ_0, σ and ε_s. In addition, the previously proposed model[2] is a generalization of an analytical Debye's model, while the model of the present work has an empiric nature. However, the difference lies in the values of τ_0 and not in its temperature behavior.

On the other hand, α shows very good correspondence with the previous reported model.[2] For low temperatures, it exhibits a very slight variation as the temperature increases, and then suddenly decreases for temperatures above T_F. It is known that α can be interpreted as the correlation between the PNRs, thus offering a measure of the interactions between them; i.e., the increase in α upon cooling is a consequence of the freezing process, whereas a decrease suggests a narrowing of the distribution function for the relaxation times, which means that the smaller α is, the relaxation times get closer to their mean value.[2] The further increment of α for higher temperatures ($T > 185$ °C) has not a physical meaning; it could be related with the proximity of T_B, at which PNRs completely
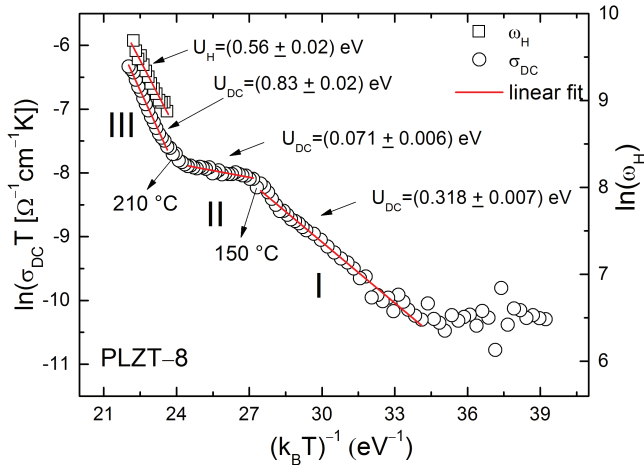
Fig. 2.   Arrhenius's behavior of σ_{DC}, for the PLZT-8 ceramic sample. The data extracted from the applied model are represented by symbols (open circles) while the solid-lines represent the fitting by using Eqs. (5) and (6).

disappear, so Jonscher's contributions begin to be significant respect to that of the C–C model in the temperature range of 185–210°C. In the current model, the overlapping of the C–C and Jonscher models is not considered, which could be leading to the anomalous behavior of α at high temperatures.

An important advantage of the proposed model is the possibility of obtain (indirectly) the electrical conductivity, which is generally difficult to be determined experimentally in ferroelectric ceramics due to their very low values and the influence of the impact of additional signal noises. Figure 2 shows the Arrhenius-like behavior of the direct component of the electrical conductivity (σ_{DC}) and the corresponding activation energy (U_{DC}) has been also included. The U_{DC} obtained values are associated to three typical regions, from which it is possible to evaluate the conduction mechanisms that predominate in the studied frequency range.

The first region (I) is related to the ionic conductivity due to the influence of single ionized oxygen vacancies,[13,14] whereas the U_{DC} value for the region II is associated to the presence of polarons in the material.[15] On the other hand, the ionic conductivity related to the region III can be associated to double ionized oxygen vacancies, which are typical in perovskite-type structure ferroelectrics.[16,17] Note that there is no discontinuity of the experimental results for σ_{DC} between region II and region III (below and above T_B, see Eq. (4)).

It is worth mentioning that the measured experimental data agree with the order of magnitude for the conductivity obtained from the proposed theoretical model (10^{-7}–$10^{-6}\ \Omega^{-1}cm^{-1}$). It can be seen, however, a remarkable dispersion of the conductivity towards the lower temperature region, which could be associated with the signal noise, typical of the very low current intensity values throughout the sample. The origin of the impact noise has been ascribed to

small fluctuations undergone by a stationary electric current as a result of the discrete nature of the charges.[18]

The temperature dependence of the hopping frequency (ω_H), not shown here, also depicted an Arrhenius' type behavior for temperatures higher than T_B (region III). The activation energy value for the hopping process (U_H) was found to be around 0.56 ± 0.02 eV. The conductivity related to the alternate current (AC) mechanism originates from the migration of the ions by hopping between neighboring potential wells, which eventually leads to the (DC) conductivity at lower frequencies. The DC activation energy (U_{DC}) was found to be around 0.833 ± 0.017 eV, which reveals to be higher than that obtained for the hopping process (U_H), indicating that, in the region III, the hopping mechanisms have higher probabilities to take effect.

Figure 3 shows the temperature dependence of the real (ε') and imaginary (ε'') components of the dielectric permittivity, obtained at several frequencies, for the studied PLZT-8 ceramic. Experimental data are represented by symbols and the theoretical results obtained from the proposed model are represented by solid-lines. The temperature dependence of the theoretical static dielectric permittivity (ε_s) has been also included.

As observed, a very good agreement between the experimental and theoretical is achieved, which validates the proposed model to be applied for temperatures even higher than T_B. It is important to point out that this result was not possible to be obtained from the previous reported models. An alternative procedure, which allows to verify the quality of the proposed model is by considering the frequency dependence of the dielectric losses (tanδ), whose results are shown in Fig. 4 for the studied composition, at several typical temperatures: the room temperature (~28°C), a temperature around the "freezing" temperature (112°C), a temperature close the maximum real dielectric permittivity (150°C), a
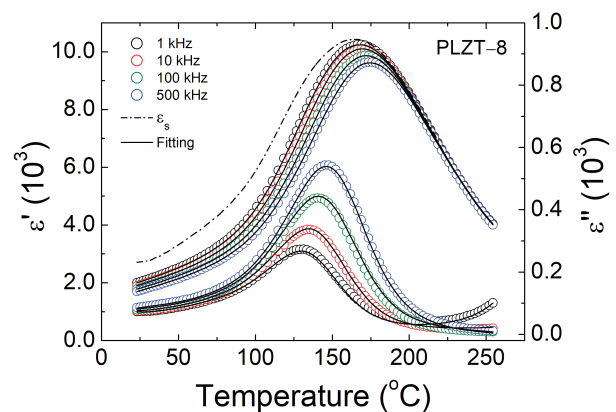

Fig. 3.   Temperature dependence of the real (ε') and imaginary (ε'') components of the dielectric permittivity, at several frequencies, for the PLZT-8 ceramic. The temperature dependence of the theoretical static dielectric permittivity (ε_s) is also included.
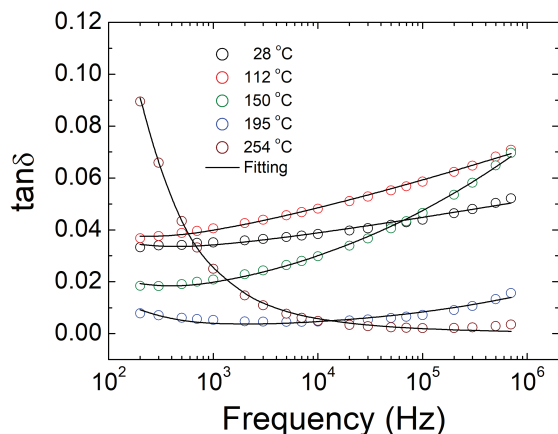
Fig. 4. Frequency dependence of the dielectric losses, at several temperatures, for the PLZT-8 sample.

temperature above T_m (195 °C) but lower than T_B, and a temperature higher than T_B (254 °C). As observed, a very good agreement between the experimental and theoretical data for all the analyzed temperatures has been obtained. Therefore, results reveal that the proposed model can be used in the entire analyzed range, which include not only the dipolar response region, but also those ones where the dielectric response is commonly dominated by additional conductive processes. These high conductivity regions include both DC mechanisms, characteristics at low frequencies, and AC processes, which are predominant in very high temperatures (i.e., higher than T_B), where the material is in a nonpolar paraelectric state and the C–C formalism is not applicable.

5. Conclusions

A model has been proposed to analyze the relaxor ferroelectric behavior in PLZT ceramics, considering both the dipolar contribution and those associated with DC and AC electrical conductivity, being the latter not previously reported in the literature for relaxor materials. The usefulness of the proposed model was verified from the excellent agreement between the experimental and theoretical data. This study, although indirectly, offers an alternative procedure to analyze the conduction mechanisms for these materials and contributes to a better understanding of the observed intriguing behaviors in relaxor ferroelectric systems, when analyzed in a wide temperature range.

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