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O García-Zaldívar[1]**, A Peláiz-Barranco**[1]**, F Calderón-Piñar**[1]**, A Fundora-Cruz**[1]**, J D S Guerra**[2,5]**, D A Hall**[3] **and M E Mendoza**[4]

[1] Facultad de Física—Instituto de Ciencia y Tecnología de Materiales, Universidad de La Habana, San Lázaro y L, Vedado 10400, La Habana, Cuba
[2] Departamento de Física e Química, Universidade Estadual Paulista, 15385-000, Ilha Solteira-SP, Brazil
[3] School of Materials, University of Manchester, Manchester, M1 7HS, UK
[4] Instituto de Física, Universidad Autónoma de Puebla, AP J-48, 72570, Puebla, Mexico

E-mail: santos@dfg.feis.unesp.br

Abstract
The relaxor behavior of lanthanum modified lead zirconate titanate (PLZT) ferroelectric ceramics, for a La/Zr/Ti ratio of $x/60/40$, has been analyzed. An approximation to the dynamical behavior of the polar nano-regions (PNRs) has been discussed, taking into account a relaxation model, which considers a distribution function for the relaxation times. A good agreement between theoretical and experimental results was obtained. The behaviors of the mean relaxation time and its standard deviation with temperature were discussed, considering the correlation between the polar nano-regions and the freezing temperature. The temperature dependence of the polarization showed an anomalous behavior around a temperature, which was associated with the freezing temperature, according to the proposed model in the present work.

1. Introduction

Ferroelectric materials are commonly characterized by high dielectric permittivity values [1]. Usually, for the well known 'normal' ferroelectrics the temperature of the maximum real dielectric permittivity (T_m) corresponds to the paraelectric–ferroelectric (PE–FE) phase transition temperature (T_C) [2]. For 'normal' PE–FE phase transitions, T_m does not show any frequency dependence and the ferroelectric and paraelectric states are determined by thermodynamic coordinates, such as temperature and pressure, instead of the measurement frequency. On the other hand, there are some kinds of ferroelectric materials, so-called relaxor ferroelectrics, which have received especial attention in the last years

because of the observed intriguing and extraordinary dielectric properties [3–10], which remain not clearly understood nowadays. For instance, some remarkable characteristics of the dielectric response of relaxor materials can be summarized as follows: (i) they are characterized by wide peaks in the temperature dependence of the dielectric permittivity, (ii) the temperature of the corresponding maximum for the real (ε') and imaginary (ε'') component of the dielectric permittivity (T_m and $T_{\varepsilon'' \max}$, respectively) appears at different values, showing a frequency dependent behavior, and (iii) the Curie–Weiss law is not fulfilled for temperatures around T_m. Therefore, the temperature of the maximum real dielectric permittivity, which depends on the measurement frequency, cannot be associated with a PE–FE phase transition; indeed, it is possible to affirm that there is not a crystallographic phase transition.

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[5] Author to whom any correspondence should be addressed.

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Lead zirconate titanate (PZT) system is a typical ferroelectric showing a 'normal' PE–FE phase transition [11]. Nevertheless, the partial substitution of Pb^{2+} or Zr^{4+}/Ti^{4+} by different elements, such as La^{3+}, contributes to enhancing such relaxor characteristics [12, 13]. In fact, for some lanthanum concentrations, the distortion of the crystalline lattice in the PZT system due to ion displacement could promote the formation of the so-called polar nano-regions (PNRs), which have been studied from the temperature dependence of the optical refraction index, using elastic diffuse neutron and x-ray scattering techniques [14–16]. In order to explain the dielectric behavior of relaxor ferroelectrics, several models have been proposed. The basic ideas have been related to the dynamics and formation of the PNRs. In this way, Smolenskii proposed the existence of compositional fluctuations on the nanometer scale, taking into account a statistical distribution for the phase transition temperature [17]. On the other hand, Cross extended the Smolenskii's theory to a superparaelectric model associating the relaxor behavior to a thermally activated ensemble of superparaelectric clusters [18]. Viehland *et al* have showed that cooperative interactions among these superparaelectric clusters could produce a glass-like freezing behavior, commonly exhibited in spin-glass systems [19]. Later, Qian and Bursill analyzed the possible influence of random electric fields on the formation and dynamics of the polar clusters [20], which can originate from nano-scaled chemical defects. They have also proposed that the relaxor behavior can be associated with a dipolar moment in an anisotropic double-well potential, taking into account only two characteristic relaxation times. According to this model, the dispersive behavior is produced by changes in the cluster size and the correlation length (defined as the distance above which such PNRs become noninteractive regions) as a function of the temperature, which provides a distribution function for the activation energy. However, despite their very attractive physical properties, the identification of the nature of the dielectric response in relaxor systems still remains open and requires additional theoretical and experimental information, which can be very interesting to contribute to the explanation of the origin of the observed anomalies. The objective of the present work is to carefully investigate the dielectric and ferroelectric properties of lanthanum modified lead zirconate titanate ceramics ($Pb_{1-3/2x}La_x(Zr_{0.60}Ti_{0.40})O_3$, with $x = 8$ and 10 at.%). The present work proposes the fulfilment of dielectric studies, considering an approximation to the dynamical behavior of the PNRs by using a relaxation model, which, to the best knowledge of the present authors, has been scarcely reported in the literature and considers a distribution function for the relaxation times, contributing to a better understanding concerning the nature of the relaxor behavior. Two PLZT compositions, for the $x/60/40$ ratio, have been selected in order to validate the proposed model.

2. Physical model

The nature of the relaxor behavior, as aforementioned, is determined by the existence of PNRs, which possess different relaxation times [16, 20]. The relaxation time (τ) represents the time response of such PNRs or polarization mechanisms to change with the applied electric field. However, this process does not occur instantaneously. Indeed, there exists certain inertia, which is the cause of the pronounced dielectric relaxation in relaxor ferroelectrics. The polar nano-regions appear below a certain temperature, the so-called the Burns' temperature (T_B) [21], which is typically hundreds degrees above the temperature of the maximum real dielectric permittivity (T_m). On cooling, the number, size (some of them) and the interaction of the PNRs increase [22]. The increase of such interactions promotes the freezing of some regions around certain temperatures below T_m, known as the freezing temperature (T_f).

Two fundamental polarization mechanisms been reported, which have been associated with the dynamics of the PNRs; (i) dipole reorientation [15, 16] and (ii) domain wall vibrations [20]. Both mechanisms have a characteristic time response, which depends on the temperature and size of the PNRs. If the contributions of an ensemble of these regions are considered, the macroscopic polarization function, at fixed temperature, can be expressed by [23]:

$$P(t) = P_{01}\,\mathrm{e}^{-\frac{t}{\tau_1}} + P_{02}\,\mathrm{e}^{-\frac{t}{\tau_2}} + P_{03}\,\mathrm{e}^{-\frac{t}{\tau_3}} + \cdots = \sum_i P_{0i}\,\mathrm{e}^{-\frac{t}{\tau_i}}$$
(1)

where τ_i is the relaxation time of the ith PNR and P_{0i} takes the form of equation (2), in analogy with the Debye single relaxation time model, which takes into account a distribution function of relaxation times [23]:

$$P_{0i} = \frac{\varepsilon_s - \varepsilon_\infty}{\tau_i} g(\tau_i)$$
$$g(\tau_i) = \frac{2\sigma}{\pi} \frac{1}{4(\ln\frac{\tau_i}{\tau_0})^2 + \sigma^2}.$$
(2)

In these relations $g(\tau_i)$ is a distribution function for the logarithms of the relaxation times, which has been assumed to be a Lorentz rather than a Gaussian distribution function; τ_0 and σ are the mean relaxation time and the standard deviation, respectively. According to the Debye model, the frequency dependence of the complex dielectric permittivity can be expressed as:

$$\varepsilon^*(\omega) = \varepsilon' - \mathrm{i}\varepsilon'' = \varepsilon_\infty + \int_0^\infty P(t)\,\mathrm{e}^{-\mathrm{i}\omega t}\,\mathrm{d}t$$
(3)

where ε_s and ε_∞ are the low (static) and high (optical) dielectric permittivity, respectively, ω the measurement frequency ($\omega = 2\pi f$), and $P(t)$ the decay polarization function. Substituting equations (1) and (2) into equation (3), the real and imaginary component of the dielectric permittivity for the multi-relaxation times approximation can be obtained and expressed as in equation (4). It is important to point out that equation (4) has been derived from the discrete expression (1), taking into account the values of the relaxation times (τ_i) close to each other [23].
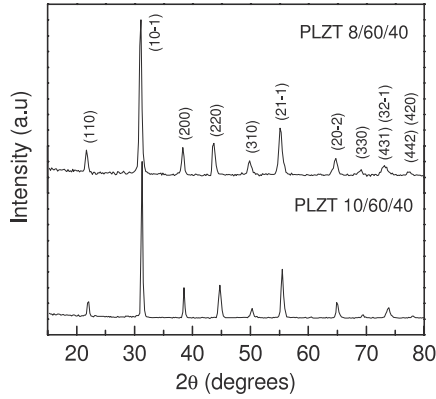
Figure 1. X-ray diffraction patterns at room temperature for the PLZT 8/60/40 and PLZT 10/60/40 compositions.

$$\varepsilon'(\omega, T) = \varepsilon_\infty + (\varepsilon_s - \varepsilon_\infty)\frac{2\sigma}{\pi}$$

$$\times \int_{-\infty}^{+\infty} \frac{1}{(4z^2 + \sigma^2)(1 + \omega^2\tau_0^2 \exp(2z))}\, \mathrm{d}z$$

$$\varepsilon''(\omega, T) = (\varepsilon_s - \varepsilon_\infty)\frac{2\sigma}{\pi}$$

$$\times \int_{-\infty}^{+\infty} \frac{\omega\tau_0 \exp(z)}{(4z^2 + \sigma^2)(1 + \omega^2\tau_0^2 \exp(2z))}\, \mathrm{d}z. \tag{4}$$

It has been considered in equation (4) that $z = \ln \tau/\tau_0$. By using the experimental results of $\varepsilon'(\omega, T)$ and $\varepsilon''(\omega, T)$ for two frequencies in equation (4), the temperature dependence of dielectric parameters, such as, τ_0, ε_s and σ can be obtained as a solution of the equations system. After that, by using the theoretical results of $\tau_0(T)\varepsilon_s(T)$ and $\sigma(T)$ in equation (4), the theoretical dependences of $\varepsilon'(\omega, T)$ and $\varepsilon''(\omega, T)$ can be obtained for the studied frequency and temperature ranges. The parameter ε_∞ has been considered negligible because of the high values of the dielectric permittivity obtained for ferroelectric systems [1].

3. Experimental procedure

PLZT ceramic samples, with nominal composition $Pb_{1-3/2x}$ $La_x(Zr_{0.60}Ti_{0.40})O_3$, for $x = 8$ and 10 at.% (hereafter labeled as PLZT 8/60/40 and PLZT 10/60/40, for 8 and 10 at.% La^{3+}, respectively), were prepared by the traditional ceramic method [1], considering vacancies in the A sites of the perovskite structure. The corresponding high purity precursor oxides (>98%) were ball-milled and calcined at 800 °C for 2 h. Ceramic bodies were sintered at 1200 °C for 2 h in air atmosphere. X-ray diffraction analysis was performed at room temperature on powder samples by using a Philips X-PERT diffractometer and Cu Kα radiation. A pure rhombohedral phase, without additional secondary phases, was obtained for the studied compositions, as shown in figure 1. Silver painted electrodes were applied on the opposite faces of the sintered samples by a heat treatment at 590 °C. Dielectric measurements were carried out in a wide frequency and temperature range (1 kHz–1 MHz and
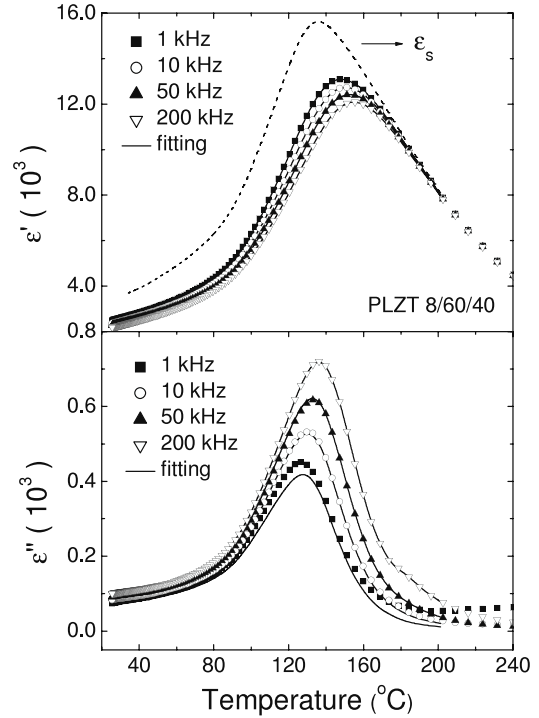

Figure 2. Temperature dependence of the real (ε') and imaginary (ε'') components of the dielectric permittivity at several frequencies for the PLZT 8/60/40 composition; the experimental and theoretical results are represented by symbols and solid lines, respectively. The dashed line is the representative curve of the static dielectric permittivity (ε_s).

27–400 °C, respectively) using an LCR meter AG4284A. Ferroelectric characterization was performed at 1 Hz and several temperatures by using a Sawyer–Tower circuit [24]. For the pyroelectric measurements, the samples were poled at 2 kV mm^{-1} and 70 °C for 20 min. The temperature dependence of the pyroelectric current was obtained by using a Keithley 617 programable electrometer.

4. Results and discussion

4.1. Dielectric response

Figures 2 and 3 show the temperature dependence of the real (ε') and imaginary (ε'') component of the dielectric permittivity (symbols), at several frequencies, for the studied PLZT 8/60/40 and PLZT 10/60/40 compositions, respectively. A relaxor characteristic behavior can be observed for both PLZT compositions; the maximum real dielectric permittivity (ε'_m) decreases, while its corresponding temperature (T_m) increases with the increase of the measurement frequency. On the other hand, it can be observed that ε'_m and the maximum of the imaginary component of the dielectric permittivity (ε''_{max}) do not appear at the same temperature. This latter fact can be related to the delay of the dielectric response for the relaxor ferroelectric behavior, with respect to the applied electric field.

The number of PNRs able to follow the applied external electric field switching decreases with the increase of the frequency, so that only such inertial-less regions
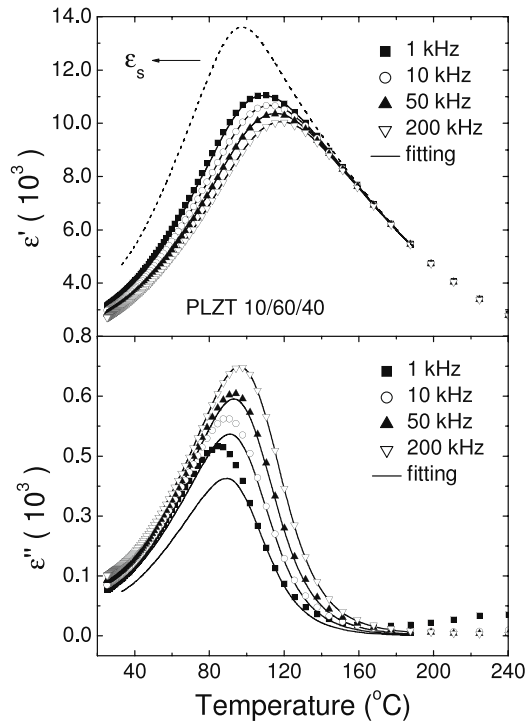
Figure 3. Temperature dependence of the real (ε') and imaginary (ε'') components of the dielectric permittivity at several frequencies for the PLZT 10/60/40 composition; the experimental and theoretical results are represented by symbols and solid lines, respectively. The dashed line is the representative curve of the static dielectric permittivity (ε_s).

Figure 4. Temperature dependence of the main relaxation time (logarithmic representation, $\ln \tau_0$) and its standard deviation (σ), for the studied compositions.

Table 1. Dielectric parameters for the PLZT 8/60/40 and PLZT 10/60/40 compositions, at several frequencies.

	PLZT 8/60/40			PLZT 10/60/40		
f (kHz)	ε'_{max}	T_m (°C)	$T_{\varepsilon'' \, max}$ (°C)	ε'_{max}	T_m (°C)	$T_{\varepsilon'' \, max}$ (°C)
1	13 099	148	127	11 054	109	85
10	12 730	151	131	10 674	112	90
50	12 415	153	132	10 357	115	93
200	12 094	155	137	10 045	118	97
500	11 866	157	139	9 828	121	99
1000	11 735	158	142	9 695	122	101

contribute to the dielectric permittivity (those regions whose activation energy is close to thermal energy, kT, k being the Boltzmann constant). Therefore, due to the cooperative nature, the real component of the dielectric permittivity decreases with the increase of the measurement frequency. As previously discussed, the observed maximum for the dielectric permittivity in relaxor systems is not related to a crystallographic transition. Indeed, such a maximum corresponds to rapid changes of the fraction of the frozen polar regions [22]. Hence, the shift up to higher temperatures of ε'_m with the increase of the frequency is a direct consequence of the delay in dielectric response of the frozen regions.

Table 1 shows some of the obtained dielectric parameters (ε'_m, T_m and $T_{\varepsilon'' \, max}$), at several frequencies, for the studied compositions. As observed, the increment of the lanthanum concentration promotes the decrease of T_m and ε'_m values. The Pb^{2+} substitution by La^{3+} ions in the perovskite structure weakens the long-range interactions [1], promoting a decrease of T_m when the lanthanum concentration increases.

By using equation (4) and the experimental data of figures 2 and 3, the temperature dependence of ε_s, σ and τ_0 was obtained. The results were obtained by numerical methods because there was no analytical solution for the equation system. The theoretical curves for ε' and ε'' were obtained for all the studied frequency range, and shown in the same figures 2 and 3 (solid lines), for the studied PLZT 8/60/40 and PLZT 10/60/40 compositions, respectively. The temperature dependence of the static dielectric permittivity (ε_s), which has
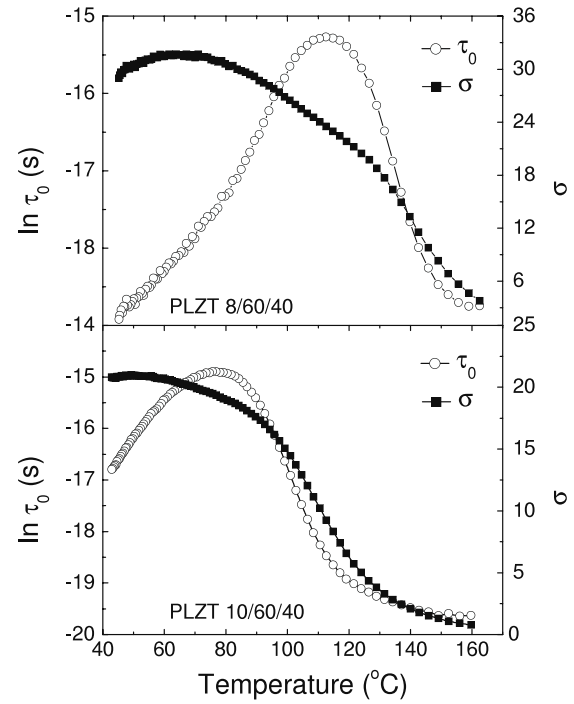
been obtained from the fitting of the experimental data and equation (4), is also shown in figures 2 and 3 (dashed lines). A good agreement between experimental and theoretical results for the studied compositions can be observed. It is important to point out that a little deviation between the experimental and theoretical results, observed at low frequencies for the temperature dependence of ε'', can be associated with the contribution of the electric conductivity to the dielectric response, which has not been considered in the proposed model.

Figure 4 shows the temperature dependence of $\ln \tau_0$ and σ for the studied compositions. As can be seen, $\ln \tau_0$ increases with the increase of the temperature, passes through a maximum and then decreases for higher temperatures. Similar results have been previously reported by Lin *et al* [23]. According to the model, the logarithmic mean relaxation time ($\ln \tau_0$) has approximately the same tendency as that of $\sigma(T)$, which can be understood as a consequence of the increased inertia of the dipolar clusters as they become more correlated with each other upon cooling. This observation also could

reflect a dynamic change in the well potential for the shifting ions. However, the reduction in $\ln \tau_0(T)$ at lower temperatures possibly could reflect a freezing phenomenon of some clusters that are saturated in correlation, which leads to the frustration of cooperative interactions and, hence, leaves only relatively unstrained or smaller clusters available to couple with the electric field. Also, one could speculate that such clusters are the regions within the domain boundaries between the frozen regions.

In this way, the size and the interaction between PNRs increase on cooling from the high temperature region and its contribution to the dielectric permittivity becomes negligible below the freezing temperature (T_f) [22]. In this temperature range ($T < T_f$), the applied electric field is not strong enough to break such interactions and only the smallest regions can switch with the electric field, that is to say, there is a frustration of the cooperative effect. For temperatures above T_f, there are fluctuations between equivalent polarization states [18], leading to a decrease of the macroscopic polarization upon heating [25]. The applied electric field cannot reorient the ferroelectric dipoles because of the thermal fluctuation. The potential barrier between equivalent polarization states decreases with the increase of the temperature and the thermal energy promotes the spontaneous switching of the dipoles, even when an electric field is applied. The contribution to the dielectric permittivity is due to those PNRs, which can switch with the applied electric field. Thus, for temperatures slightly above T_f all the PNRs could contribute to the dielectric permittivity and a maximum value of the mean relaxation time could be expected. Therefore, it is possible to affirm that the temperature corresponding to the maximum of $\ln \tau_0$ can be related to the freezing temperatures, which in fact were found to be around 113 °C and 77 °C for the PLZT 8/60/40 and PLZT 10/60/40 compositions, respectively.

The standard deviation (σ), which can be interpreted as the correlation between the PNRs [20, 23], decreases upon heating and it is relatively small at high temperatures. When the temperature increases the thermal energy is high enough to break down the interaction between the PNRs. So that, a decrement of the correlation between the PNRs is promoted by an increase of the temperature and the standard deviation decreases up to a relatively constant value around the Burns' temperature (T_B) [21, 26], where the PNRs completely disappear.

The freezing temperature (T_f) was determined by using the Vogel–Fulcher relationship [27], as expressed by equation (5):

$$f = f_D \, e^{-\frac{E_a}{k(T_m - T_f)}} \tag{5}$$

where f_D is the Debye frequency, E_a is the activation energy and k the Boltzmann constant. Figure 5 shows the temperature dependence of the frequency ($\ln f$ versus $1/(T_m - T_f)$ curve) for the studied compositions, obtained from the fitting of the experimental data of figures 2 and 3 with equation (5). In order to maintain the standard representation, the temperature in figure 5 was expressed in kelvin. The fitting parameters E_a, f_D and T_f are listed in table 2. The results are in agreement with previously reported results in the literature [25]. No
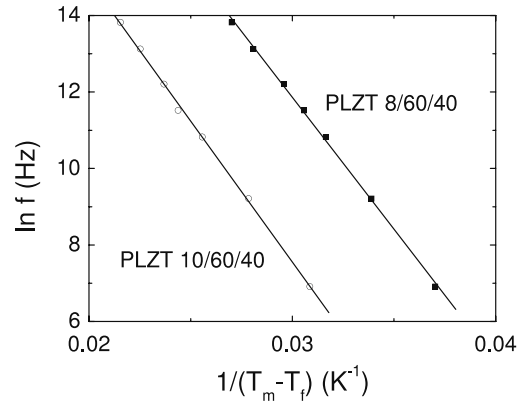

Figure 5. Temperature dependence of the frequency ($\ln f$ versus $1/(T_m - T_f)$ curve) for the studied compositions; solid lines represent the fitting of the experimental data by using the Vogel–Fulcher relation.

Table 2. Fitting parameters corresponding to the Vogel–Fulcher relationship, for the PLZT 8/60/40 and PLZT 10/60/40 compositions.

	E_a (eV)	f_D (Hz)	T_f (K)
PLZT 8/60/40	0.05 ± 0.01	6.80×10^{13}	395 (122 °C)
PLZT 10/60/40	0.06 ± 0.01	7.63×10^{12}	349 (76 °C)

significant variation of the activation energy value can be observed with the increase of the lanthanum content, for the studied PLZT 8/60/40 and PLZT 10/60/40 compositions. It can be also noted that the calculated freezing temperature values are close to those observed for the maximum values of $\ln \tau_0$, as previously discussed, which validates the proposed model.

4.2. Hysteresis loops and pyroelectric behavior

Figure 6 shows the P–E curves (ferroelectric hysteresis loops) for three analyzed temperatures (below T_m), for the studied compositions. As can be seen, small remanent polarization (P_R) values were obtained for both PLZT 8/60/40 and PLZT 10/60/40 compositions, when compared to some other classical relaxor ferroelectrics [28], which indeed decreased with the increase of the temperature (see the inset of figure 6). It is important to point out that, due to the scarcely found ferroelectric hysteresis results in the literature for similar ceramic and/or single crystal PLZT 8/60/40 and PLZT 10/60/40 compositions, no further comparison of the obtained results in the present work can be carried out. That is why we have used the reported results of PLZT ceramics, whose composition is near the morphotropic phase boundary (x/65/35), in order to compare with those observed in the present work.

The lanthanum doping on PZT systems was known to reduce the crystalline lattice stress, which in turn increases the macroscopic polarization with respect to the pure PZT system. However, for high lanthanum concentrations, the disordering effects within the crystalline lattice become important. That is to say, the incorporation of La^{3+} ions and vacancies in the
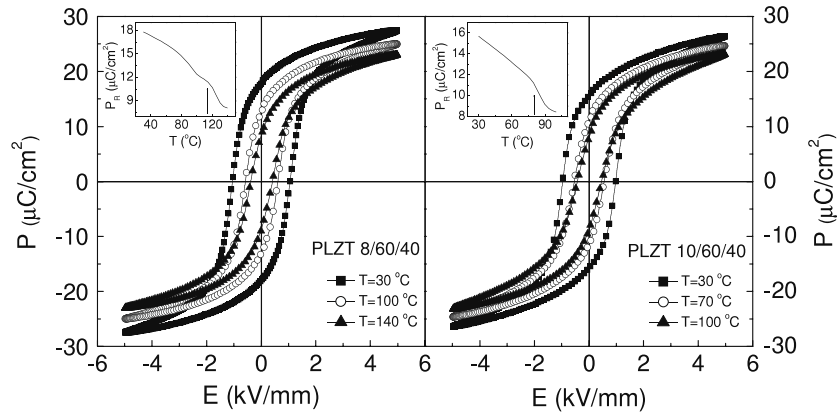
Figure 6. Ferroelectric hysteresis loops obtained at several temperatures, for the studied compositions; the insets show the temperature dependence of the remanent polarization (P_R).

lattice is known to break the long-range interaction between ferroelectrically active oxygen octahedra containing B-site cations. For high La^{3+} content, as in the case of the studied samples, the decoupling might be sufficiently strong to prevent a macroscopic transformation into a long-range ferroelectric state; rather, a state with locally polarized regions on a nanometric scale could be observed in the ceramics. The decoupling affects the total dipolar moment of the system and, consequently, directly affects the macroscopic polarization. As a result, the magnitude of the polarization decreases with the increase of the lanthanum content [1]. It is known, that in relaxor ferroelectric materials, nano-to macro-domain transition occurs [29]. In the absence of any external electric field, the domain structure of relaxor ferroelectrics contains randomly oriented polar nano-regions. However, when an electric field is applied, the nano-domains orient along the electric field direction in favor of the formation of macro-domains. This nano- to macro-domain transition has been confirmed from '*in situ*' switching by means of an electron beam inducing local stresses to align the domains [29]. On the other hand, it can be noted by a closer inspection of the inset in figure 6 that the temperature dependence of P_R shows an anomalous behavior around a temperature which is close to the previously discussed T_f.

Figure 7 shows the temperature dependence of the pyroelectric current (i_p) in a wide temperature range, for the studied compositions. The temperature dependence of the polarization was obtained from the experimental data of figure 7, and using equation (6), where A and dt/dT are the area of the samples and the heating rate, respectively.

$$ P = -\frac{1}{A}\frac{dt}{dT}\int_{T_0}^{T} i_p(T)\, dT. \tag{6} $$

As can be seen in the inset of figure 7, the polarization also showed notable changes for temperatures around the discussed freezing temperature. This behavior can be better observed by the temperature dependence of dP/dT and, together with those results obtained for P_R (inset in figure 6), confirms that the temperature of the maximum for the mean relaxation time, obtained by modeling the dielectric response using a
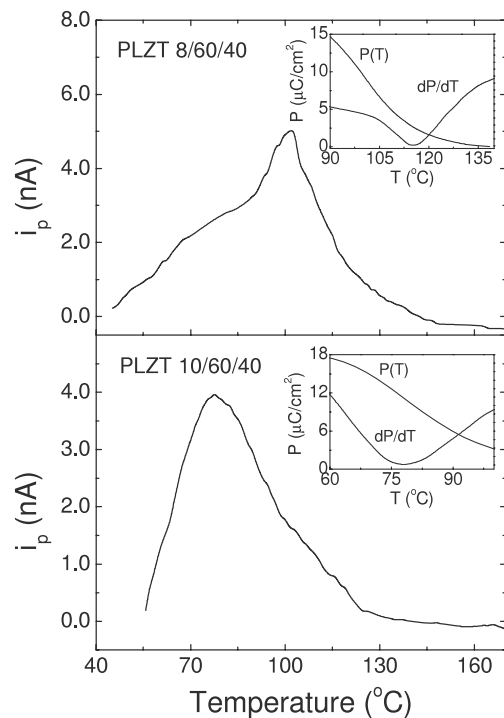

Figure 7. Temperature dependence of the pyroelectric current (i_p) for the studied compositions. The insets show the temperature dependence of the polarization, calculated from the pyroelectric current.

multi-Debye relaxation model, which considers a distribution function for the relaxation times, can be related to the freezing temperature of the studied compositions, validating the proposed model for relaxor ferroelectric systems.

5. Conclusions

The relaxor behavior of Pb$_{1-3/2x}$La$_x$(Zr$_{0.60}$Ti$_{0.40}$)O$_3$ ($x = 8$ and 10 at.%) ferroelectric ceramics, obtained by the standard ceramic method, has been investigated. The dielectric response was discussed by using a multi-Debye relaxation model, considering a distribution function for the relaxation

times, which in turn showed a good agreement between the theoretical and the experimental results. We discussed the contribution of the polar nano-regions (PNRs) to the dielectric permittivity and its dynamical behavior below and above the freezing temperature to explain the obtained behaviors of the mean relaxation time and its standard deviation. The temperature dependence of the polarization, obtained from the ferroelectric properties, showed changes in its behavior around a temperature that was associated with the freezing temperature from the modeling of the dielectric response by the proposed multi-Debye relaxation model. Results have also been confirmed by pyroelectric measurements, validating the proposed multi-Debye relaxation model for relaxor ferroelectric systems.

Acknowledgments

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