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Abstract

The relaxation dynamics of the conductive process present in PbNb$_2$O$_6$ piezoelectric ceramics was investigated. A relaxation function in the time domain, $\Phi(t)$, was found from the frequency dependence of the dielectric modulus (imaginary component, M'') by using a relaxation function in the frequency domain, $F^*(\omega)$. The best relaxation function, $F^*(\omega)$, was found to be a Cole–Cole distribution function, in which relaxation characteristic parameters, such as α and τ_{CC}, are involved. On the other hand, the relaxation function, $\Phi(t)$, obtained by the time domain method, was found to be a Kohlrausch–Williams–Watts (KWW) function type. The thermal evolution of the characteristics parameters of the KWW function (β and τ^*) was analysed. The values of the activation energy (E_a), obtained in the whole investigated temperature interval, suggest the existence of a relaxation mechanism (a conductive process), which may be interpreted by an ion hopping between neighbouring sites within the crystalline lattice. The results are corroborated with the formalism of the AC conductivity.

1. Introduction

Lead meta-niobate PbNb$_2$O$_6$ ferroelectric ceramics, hereafter labelled as PN, are promising materials for application in high-temperature piezoelectric transducers [1]. They exhibit very good piezoelectric properties with a high Curie temperature of around 843 K [2], low dielectric permittivity at room temperature and low quality factor [3]. The applicability range for this

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material has been significantly influenced by its microstructural characteristics [1, 4], which are conditioned as well by the employed processing and synthesis methods. Generally, PN ceramics are porous materials with relatively low densities showing cracks and bimodal grain size distribution [1]. A processing method that guarantees a relative density higher than 96%, as well as excellent piezoelectric properties, has been recently reported [5, 6]. These results have led to a increasing interest in the use of PN material in practical applications.

Others factors that greatly influence the piezoelectric response of ferroelectric materials are the temperature and frequency dependence of the piezoelectric and dielectric properties, such as the coupling factor (k), the quality factor (Q_m) and the dielectric permittivity (ε) [7]. On the other hand, the PN ferroelectric materials present a normal phase transition (NPT) [8], which has been fitted by the Santos–Eiras' phenomenological model [9]. It has been considered that the NPT is hardly affected by a conductive mechanism, which overlaps with the phase transition region (around T_m, the temperature of the maximum dielectric permittivity, which coincides with the Curie temperature, T_C, for normal ferroelectrics) and extents up to lower temperature interval (623 K) [8]. This conduction mechanism may contribute to affecting the piezoelectric response of the PN material. However, the true responsible mechanism related to the dielectric anomaly observed near the phase transition region in the PN system has remained until now not fully clarified. To the best of our knowledge, no works focusing the influence of the phase transition characteristics on the conductivity in ferroelectric materials, specifically in the PN system, can be found in the literature.

In order to investigate the conduction mechanisms, the relaxation processes have been the most powerful tools used. The analysis of these processes is normally carried out in the frequency domain [10, 11]. Nevertheless, it is also possible to study the dynamics of the relaxation processes only in the time domain. In this case, a relaxation function $\Phi(t)$, which is related to the relaxation characteristics of the material, can be defined [12], considering this process as the ions hopping from a crystallographic site to another neighbouring one [13, 14].

The Fourier transform method is the most commonly used mathematical technique to convert the experimental data from the frequency domain into the time domain [15]. In this case, the dielectric modulus, $M = 1/\varepsilon(\omega)$, is one of the most appropriate formalisms for the investigation of conductive relaxation processes. However, this method has its main disadvantage when the calculation is performed by numeric methods by using the experimental data measured in the frequency domain. Indeed, it is affected by numerical errors because of a finite distribution of points [15].

The aim of the present work is to investigate in detail the conduction mechanism on PN ferroelectric ceramics in a wide temperature and frequency range, as well as the influence of the phase transition on the conductive process. In this way, an analytical method that does not require the calculation of the Fourier transforms was used [16]. The relaxation dynamics of the conductive process will be investigated by using a temporal distribution function, which can be obtained by the dielectric modulus formalism.

2. Experimental procedure

Ceramic powders of $PbNb_2O_6$ were prepared by the solid-state reaction method [5]. Analytical grade precursors PbO (Aldrich, 99.9%) and Nb_2O_5 (Aldrich, 99.4%), with 2 wt% PbO in excess, were mixed in a ball mill containing isopropyl alcohol and stabilized ZrO_2 cylinders, for 20 h. The mixture was dried and calcined at 1323 K for 3.5 h, and milled again for 22 h. In order to obtain the room-temperature (RT) orthorhombic ferroelectric phase, the PN powder was thermally treated at 1573 K for 1 h. After the thermal treatment, 3 wt% PbO in excess was added to the thermally treated powder, in order to compensate the further weight
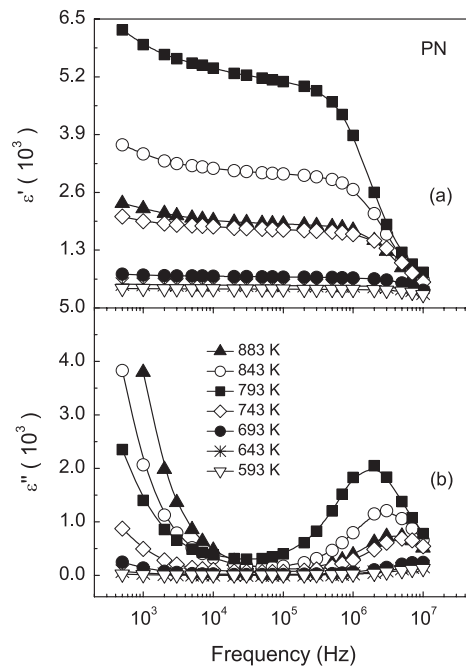
Figure 1. Frequency dependence of the (a) real, ε' and (b) imaginary, ε'' components of the dielectric permittivity as a function of the temperature.

losses during the sintering process. The powders were compacted by uniaxial (200 MPa) and isostatic (110 MPa) cold pressing, and sintered in air at 1543 K for 4.5 h, using heating and cooling rates of $7\,^{\circ}\text{C min}^{-1}$. X-ray diffraction analysis of the powders, obtained by using a Rigaku diffractometer with Cu Kα radiation, showed a single PN phase [5]. The samples were cut and polished, and after that heat-treated at 873 K for 20 min. Platinum electrodes were sputtered on the ceramic samples in the form of discs of 12.4 and 0.80 mm diameter and thickness, respectively. The dielectric characterization was performed as a function of the temperature by using an HP-4194A impedance gain phase analyser over a wide temperature and frequency range of 297–923 K and 20 Hz–10 MHz, respectively. The complex dielectric modulus ($M^* = 1/\varepsilon^*$) and the AC electric conductivity ($\sigma = \varepsilon''/\omega$) can be obtained from the temperature dependence of the real, ε', and imaginary, ε'', components of the dielectric permittivity ($\varepsilon^* = \varepsilon' - j\varepsilon''$).

3. Results and discussions

3.1. Frequency domain analysis

Figure 1 shows the frequency dependence of the real, ε', and imaginary, ε'', components of the dielectric permittivity. As observed in figure 1(a), the strength of the dielectric dispersion (characterized by the difference between the low- and high-frequency dielectric permittivity) increases with the increase of the temperature, traversing a maximum for a temperature around 793 K, which corresponds to the paraelectric–ferroelectric phase transition temperature (T_C), and then diminishes for higher temperatures values.
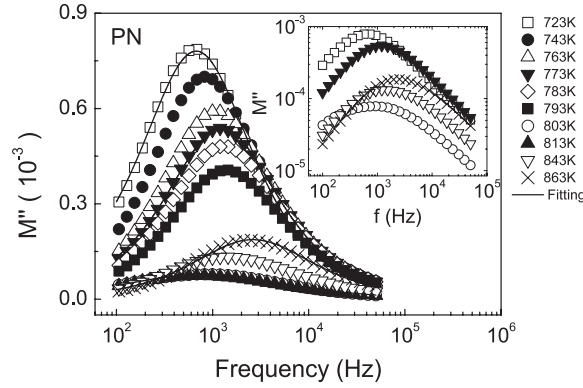
Figure 2. Frequency dependence of the imaginary component of the dielectric modulus for PN ceramics. The inset shows M'' versus frequency for the same sample at log–log scales. The solid lines represent the CC fitting for some selected temperatures around the paraelectric–ferroelectric phase transition temperature (723, 773, 803 and 863 K).

As can be seen in figure 1(b), a typical low-frequency dispersion (up to 10 kHz), characteristic of the high-temperature region, was observed. This behaviour, which is characteristic of a conductive process (associated to a DC conduction), is observed not only for temperatures above the transition temperature, but also for temperatures below T_C. It is important to point out that the observed anomalies for ε' and ε'' in the higher-frequency region were discussed in a previous work [8] and will not be the central point of the present work. Therefore, the main focus will be directed to the investigation of the dynamics of the observed conductive process in the low-frequency region, and how it is affected by the paraelectric–ferroelectric phase transition. That is why the dielectric modulus formalism, which was obtained from the dielectric permittivity measurements, is used.

Figure 2 shows the frequency dependence of the imaginary dielectric modulus (M'') in the temperature range 723–863 K. The experimental results obtained for the imaginary dielectric modulus were fitted by using the Cole–Cole (CC) distribution function (equation (1)) [11], which resulted in the best fitting with a coefficient of determination (or correlation coefficient) higher than 0.99.

$$F_{CC}^*(\omega) = [1 + (i\omega\tau_{CC})^\alpha]^{-1}. \tag{1}$$

The characteristic parameters τ_{CC} (the Cole–Cole characteristic relaxation time) and α (an empirical parameter between 0 and 1) were obtained from the fitting of the experimental curves by using the equation (1), and its temperature dependence will be discussed later. ω is the measurement frequency ($\omega = 2\pi f$). A shift of the frequency of the maximum imaginary dielectric modulus (f_m) towards higher frequencies and a decrease of the maximum imaginary dielectric modulus values were observed, with the increase of the temperature up to 793 K, which corresponds to the paraelectric–ferroelectric phase transition temperature (T_C) for the studied PN ceramics. However, it is noticeable that the f_m variation is less pronounced than that observed for purely ionic conductors, as reported in the literature [15, 16], while the maximum dielectric modulus is hardly temperature dependent, which is associated with the ferroelectric characteristics of the PN materials, related to the paraelectric–ferroelectric phase transition near the T_C. On the other hand, for temperatures higher than T_C an anomalous behaviour was observed for the maximum value of the dielectric modulus, which increases with the increase of the temperature. f_m also shows a higher variation with the increase of the frequency with respect to that observed for temperatures below T_C.
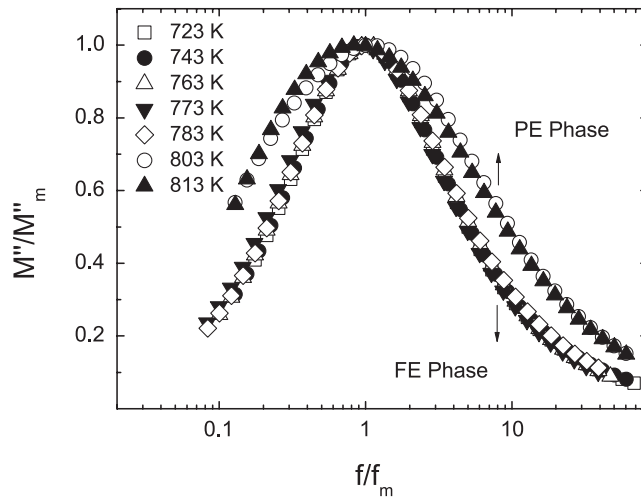
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Figure 3. Normalized frequency dependence (f/f_m) of the imaginary component of the dielectric modulus (M''/M''_m) for the PN ceramics in the temperature range 723–813 K.

For temperatures higher than T_C, in the paraelectric phase, the macroscopic electric polarization of the system disappears, while the activation of new charge carriers can be induced by thermal agitation. The creation and mobility of these charge carriers lead to an increase of the electric conductivity and, consequently, to the increase of the dielectric modulus in the high-temperature region. Therefore, for temperatures higher than the paraelectric–ferroelectric phase transition, the PN ceramics studied have similar characteristics to those of a typical ionic conductor material. On the other hand, a linear behaviour of the frequency dependence of M'', for frequencies far above and below the f_m, was observed when plotted in logarithmic scales, as shown in the inset of figure 2 for some selected temperatures, which evidences a frequency potential-type dependence of the imaginary dielectric modulus as reported by Jonscher [10].

In figure 3 the frequency dependence of the imaginary dielectric modulus is shown for the normalized curves (M''/M''_m and f/f_m, where M_m and f_m are the maximum imaginary dielectric modulus and its respective frequency, respectively). As can be seen, for temperatures in the range 723–793 K all curves overlap each other, which indicates that the imaginary dielectric modulus becomes temperature independent. However, for the higher-temperature region the shape of the curves presents a broader peak around the frequency of the maximum dielectric modulus, which may be a consequence of the paraelectric–ferroelectric phase transition around T_C. For the highest-temperature region (in the paraelectric state) the contribution of the conductive processes are commonly intensified, directly affecting the dielectric properties of the PN material studied.

3.2. Time domain analysis

The Fourier transforms for the CC distribution function have not been established in the current literature. In order to describe the temporal response of this distribution function, it is common to use an analytical function distribution of relaxation times [17, 18] expressed in the form of equation (2).

$$g_{CC}(\ln \tau) = \frac{1}{2\pi} \frac{\sin(\alpha\pi)}{\cosh[\alpha \ln(\tau/\tau_{CC}) + \cos(\alpha\pi)]}. \tag{2}$$
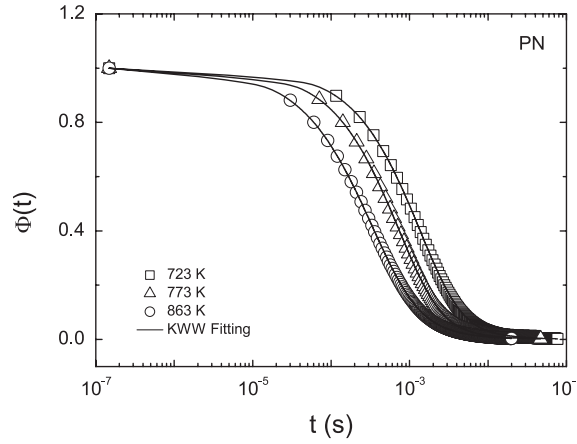
Figure 4. Time dependence of the distribution function $\Phi(t)$ in the temperature range 723–863 K. The solid lines represent the fitting with the KWW relaxation function in the time domain.

The relaxation distribution function, in the time domain, can be obtained from the analytical function distribution (equation (2)) and can be expressed by equation (3) [19, 20].

$$\Phi(t) = \int_0^\infty g_{CC}(\ln \tau) e^{-t/\tau}\, d\ln \tau. \tag{3}$$

Figure 4 shows time dependence of the relaxation distribution function for the PN ceramics in the temperature range 723–863 K. As observed, at the lower-time region up to around 10^{-5} s, $\Phi(t)$ remains nearly time independent. For times higher than 10^{-5} s, the $\Phi(t)$ function suddenly decreases with the increase of the time and remains again almost time independent for times higher than 10^{-2} s. On the other hand, a remarkable shift of the $\Phi(t)$ curves to lower values, with the increase of the temperature, was observed in the time range 10^{-5}–10^{-2} s.

In order to analyse the obtained behaviour it is necessary to investigate the thermal evolution of the relaxation function distribution parameters, which can be obtained from fitting with one of the distribution functions known in the literature [17]. Of them, the Kohlrausch–Williams–Watts (KWW) function, which is expressed by equation (4), was found to be the best adjustment distribution function.

$$f(t) = e^{-(t/\tau^*)^\beta}. \tag{4}$$

This function is normally known as 'stretched exponential', where the β and τ^* are the exponents that characterize the deformation and the characteristic relaxation time of the $f(t)$ function, respectively, for the time domain [21]. When β values are close to 0, there exists a strong correlation between the hopping ion (relaxing ion) and its neighbouring ions. By using the τ^* and β values involved in equation (4), it is possible to determine the average relaxation times $\langle \tau \rangle$ from equation (5), where Γ is the Euler gamma function [16].

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

The temperature dependence of τ_{CC}, τ^* and $\langle \tau \rangle$ are shown in figure 5. As can be seen, the three relaxation time parameters present a similar behaviour to that obtained for the dielectric permittivity. A maximum of the relaxation times was observed at the same temperature, around 793 K, which corresponds with the paraelectric–ferroelectric phase transition temperature (T_C) for the PN ceramics studied. As observed, the obtained values for the relaxation time τ_{CC},
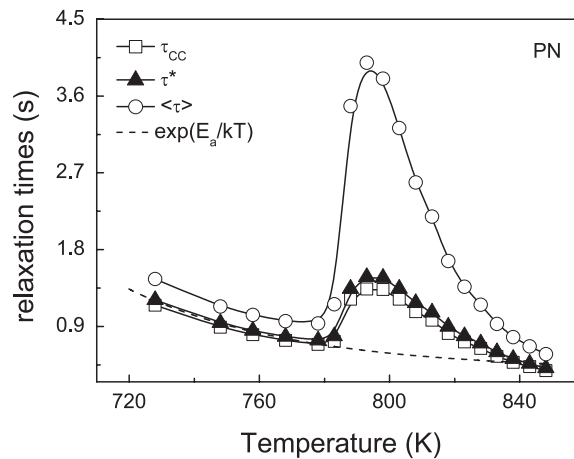
Figure 5. Temperature dependence of the relaxation times (τ_{CC}, τ^* and $\langle\tau\rangle$) for the PN ceramics.

characteristic of the frequency domain, and the relaxation time τ^*, characteristic of the time domain, remain almost similar in all the temperature region analysed. On the other hand, for temperatures far away from (above and below) the transition temperature the average relaxation time values, $\langle\tau\rangle$, were slightly higher than those obtained for τ_{CC} and τ^*. Nevertheless, for temperatures near the paraelectric–ferroelectric phase transition a notable difference of $\langle\tau\rangle$ with respect to τ_{CC} and τ^* was observed. This difference may be a consequence of the interaction effect between the relaxing ions and their neighbouring ones, which is involved in the average relaxation time, as reflected in equation (5), and not in the relaxation times τ_{CC} and τ^*. It is important to point out that the observed behaviour for all the relaxation times, at temperatures far beyond the phase transition temperature region, can be described by a decreasing exponential function (shown by a dashed line for τ^* in figure 5), which is in agreement with the results reported in the literature for ionic conductivity [21, 22].

Figure 6 shows the temperature dependence of the α and β parameters, which characterize the relaxation process in the frequency domain and the time domain, respectively. A similar behaviour for both α and β parameters was obtained in the whole temperature interval, showing a direct relation between them. At temperatures lower than T_C the β parameter remains almost constant, indicating that the interaction between the hopping ion and its neighbouring ions does not change (it is temperature independent). The strong decrease of the β parameter for temperatures near T_C indicates that the ions hopping to their neighbouring position is less likely to occur, because of the strong correlation between them and their neighbouring ions. This behaviour may be promoted by changes in the configuration of the crystallographic structure associated with the paraelectric–ferroelectric phase transition. For higher temperatures the β parameter starts to increase, indicating a slight correlation between the hopping ions and their neighbouring ions and consequently an increase of the conductivity of the material.

3.3. Conductivity analysis

Figure 7 shows the frequency dependence of the real component of the conductivity, which was obtained following the procedure described in the experimental section. As can be observed, for the temperature interval 723–793 K (ferroelectric region), σ' runs reveal similar behaviours increasing the conductivity with the increase of the temperature. In the lower-frequency region,
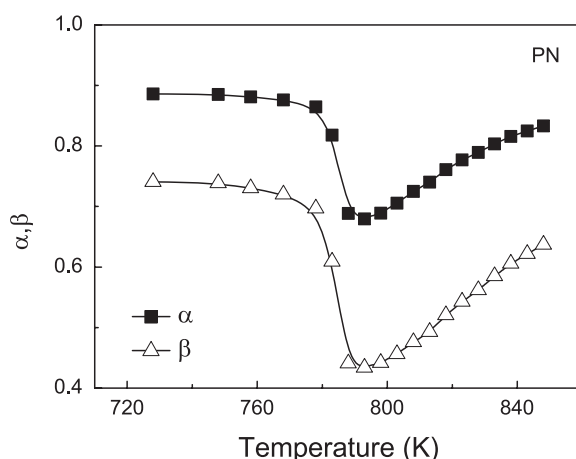
Figure 6. Temperature dependence of the α and β parameters, for the PN ceramics.
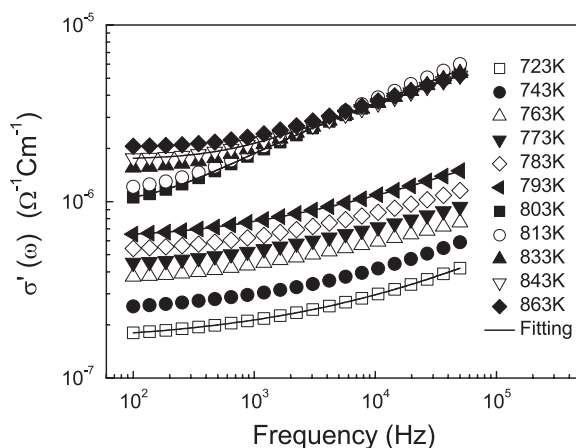

Figure 7. Frequency dependence of the AC conductivity (double logarithmic scales) for the PN ceramics, at different temperatures. The solid lines represent the fitting curves with equation (6).

below 1 kHz, the conductivity is a weak function of frequency. From these dependences the DC conductivity σ_0 can be found by fitting the experimental data with equation (6) (solid lines in figure 7), where A is a temperature-dependent parameter and n the Jonscher parameter [10].

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

For higher frequencies a slight increase of the conductivity with the increase of the frequency is observed, which is a typical behaviour for ionic conductor materials. However, for temperatures higher than 793 K (paraelectric region), a different behaviour in the conductivity was observed, which becomes more evident for frequencies above 1 kHz. These different behaviours between the ferroelectric and the paraelectric regions may suggest that the conductivity is governed by different conduction mechanisms; however, it is noticeable that in the low-frequency region the high-temperature conductivities curves are practically frequency independent, as observed for the low-temperature region.

3.4. Discussion

The conductivity relaxation mechanisms are dynamic processes that involve the hopping of ions from a position to a vacant site in the crystallographic structure. From the existence of a maximum relaxation time, for temperatures around the paraelectric–ferroelectric phase transition temperature, it is possible to infer that in a ferroelectric material possessing a conductive effect below and above T_C the relaxation dynamics is greatly affected by the paraelectric–ferroelectric phase transition. This change could be reflected by quantitative changes in the relaxation time, shown by a strong increase of the relaxation time parameters for temperatures close to (below) T_C (figure 5). This result indicates that the ferroelectric dynamics affects the hopping of the ions involved in the relaxation process because of changes in the lattice dynamics, increasing the relaxation times. For temperatures above the transition temperature, the decreasing behaviour of the relaxation time can be associated to the fact that in the paraelectric state the ferroelectric materials tend again to an equilibrium state that involves a higher structural order. This analysis is also reflected in the temperature dependence of the β parameter as shown in the figure 6. In accordance with what has been proposed above, the relatively low values found for β, at temperatures close to T_C, also corroborates that the interaction between the hopping ions and the neighbouring ones within the crystallographic lattice increases, which may be a consequence of changes in the energy band structure across the paraelectric–ferroelectric phase transition. It is known that low values of the β parameter cause the major deviation in respect of the Debye-type relaxation [20]. The β parameter can also be interpreted as a result of the correlation of the ions' motion and, therefore, the motion of a hopping ion cannot be treated as an isolated event. For low β values the cooperative effect between the charge carriers increases; therefore, for low charge carrier concentration the conductivity is essentially characterized by independent hops. Nevertheless, for higher charge carrier concentration, the cooperative effect between the hopping ions increases [23]. Therefore, during the hops of the hopping ions through the crystalline lattice, the neighbouring ions relax in relation to the new occupied site to minimize the absolute potential energy. Thus, the energy barrier needed for an ion to return to its initial position increases with increasing of time.

For temperatures higher than 793 K, the β values increase with the increase of the temperature, indicating that the increase of the thermal motion can reduce the interaction between the hopping ion and its neighbouring sites and, consequently, cause an increase of the conductivity, as observed in figure 7. It is important to take into account that the correlation between hopping ions and neighbouring ones is a completely cooperative and random process. When the hopping ion moves into a vacant site, because of the reorganization of the neighbouring ions, in order to get a more stable configuration of the lattice, it cannot return to the original site and, therefore, it moves along the crystallographic lattice, promoting a conductive process of the charge carrier in a specific direction [21].

A similar analysis could be carry out by the Funke model [24]. It supposes that the motion of the hopping ion from a site to the nearest position leads to two processes after such a hop: (a) the ion can return to its original site, thus allowing the initial equilibrium state of the lattice, and (b) there can be a reorganization of the neighbouring ions, so that they can reach the minimum potential energy and, therefore, the hopping ion cannot return to the initial position. This reorganization process of the neighbouring ions is rightly characterized by the β parameter and, therefore, in this case the ions can only make successive forward hops.

In order to obtain the conduction mechanism, the classical procedure of the conductivity is commonly used. In this way, the converse temperature (T^{-1}) dependence of σ_0, which was obtained from the average relaxation time by using equation (7), is shown in figure 8 and clearly
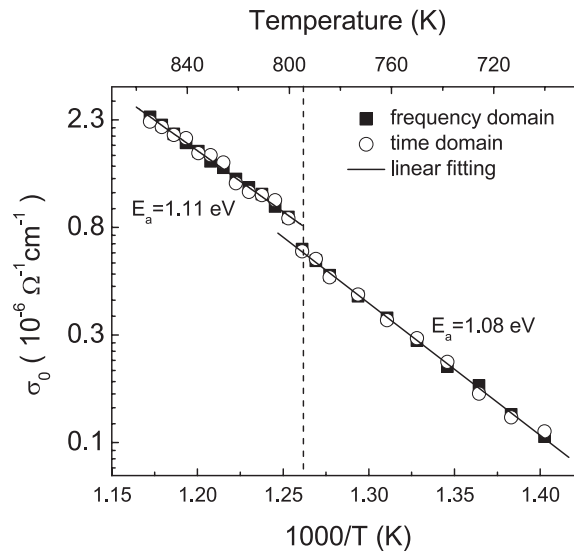
Figure 8. Arrhenius-type behaviour of the DC conductivity for the PN ceramics.

reveals an Arrhenius' behaviour for the PN samples. The results have been compared to that obtained from the time domain method [13], by using the relations (5) and (7), as shown in the same figure 8 by open symbols.

$$\sigma_0 = \varepsilon_\infty / \langle \tau \rangle. \tag{7}$$

As observed, a good correspondence for the obtained conductivity values, between both the frequency domain and time domain methods, reflects that they are equivalent methods, which allows us to characterize the relaxation process in solid materials by using either the frequency or the time domain method. However, the relaxation dynamics, which is the central focus of the present work, is better investigated by using the time domain method. The pre-exponential factors of the conductivity obtained from the Arrhenius-type behaviour were 1.24 Ω^{-1} cm^{-1} and 0.35 Ω^{-1} cm^{-1} for the ferroelectric and the paraelectric phases, respectively. These values of the pre-exponential factors are comparable to those found for other ferroelectric systems in the literature [27]. The activation energy (E_a) values obtained from the conductivity formalism are also shown in figure 8. Taking into account the measurement errors, similar values of the activation energies were obtained for temperatures below and above T_C (1.08 and 1.11 eV, respectively), which indicates the existence of a single conduction mechanism. Similar values for the activation energy have been obtained for other lead-based ferroelectric systems (i.e. PZT) [25, 26], where there exist doubly ionized oxygen vacancies due to the PbO losses through its volatility, which have been identified as the main cause for the bulk ionic conduction. Figure 1, however, shows a departure of the real permittivity data from a low-frequency plateau-like behaviour towards the lowest frequencies and high temperature. This suggests that, for a complete interpretation of the overall material's electrical response, an additional interfacial contribution, of either inter-granular or/and material-electrode interfaces origin, may be probably considered. Further measurements and data treatment to better elucidate this additional low-frequency effect are in progress.

4. Conclusions

The conduction mechanisms of PN ferroelectric ceramics and the influence of the phase transition on the conductive process were investigated in a wide temperature and frequency range. The relaxation dynamics in the time domain was investigated from the results obtained in the frequency domain formalism by using a relaxation distribution function, $F(\omega)$, for the dielectric modulus, which allowed us to obtain the temporal relaxation distribution function, $\Phi(t)$. The results were corroborated by the classical procedure of the conductivity. A Cole–Cole distribution function was found to be the best relaxation function for the frequency domain, while the KWW distribution was found to be the best relaxation function for the time domain method. The characteristic parameters τ^* and β (related to the relaxation processes in the time domain) show a maximum and a minimum, respectively, at a temperature close to the paraelectric–ferroelectric phase transition temperature, which evidences a high contribution of the conductive processes not only in the high-temperature region (far above T_C), but also in the ferroelectric phase, below T_C. This effect is clearly reflected by the thermal behaviour of the characteristic parameters (τ^* and β). The activation energy values of 1.08 and 1.11 eV, corresponding to the temperature region below and above T_C, respectively, indicate the existence of a single conduction mechanism, which is associated to the doubly ionized oxygen vacancies.

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