Journal of the European Ceramic Society 19 (1999) 2677–2683
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PII: S0955-2219(99)00039-4
0955-2219/99/$ - see front matter

AC Behaviour and Conductive Mechanisms of 2·5 mol% La_2O_3 Doped $PbZr_{0\cdot53}Ti_{0\cdot47}O_3$ Ferroelectric Ceramics

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(Received 15 October 1998; accepted 6 February 1999)

Abstract

Impedance spectroscopy (IS) is an effective characterization method for the investigation of many ceramic systems including the ferroelectric systems. It is employed to analyze the properties of the intragranular and interfacial regions, their interrelations, their temperature and frequency dependences and the DC and AC phenomena in order to separate the individual contributions from the total cell impedance. Using this technique and thermally stimulated current measurements we have studied the ac behavior and the conductive mechanisms in lanthanum-doped lead zirconate titanate, a donor-doped ferroelectric ceramic system. AC and DC conductivity components were found; a Jonscher power-law behavior was obtained and a strong low frequency dispersion was observed in a wide frequency range. A mixture of ionic–electronic conductive behavior was analyzed from the experimental results and the energy activation values obtained. © 1999 Elsevier Science Limited. All rights reserved

Keywords: impedance spectroscopy, electrical conductivity, ferroelectric properties, PZT.

1 Introduction

Impedance spectroscopy (IS) is a relatively powerful method of characterizing many of electrical properties of materials and their interfaces with electronically conducting electrodes.[1] It is employed to analyze the properties of the intragranular and interfacial regions, their interrelations, and their dependence on such controllable variables as temperature, frequency and applied static voltage. It is particularly characterized by the measurement and analysis of some of the impedance-related functions: impedance, admittance, modulus and permittivity, and the plotting of these functions in the complex plane. Such plotting can be very helpful in interpreting the small-signal AC response of the material being investigated. By using this technique, the DC and AC phenomena can be understood and the individual contributions can be separate from the total cell impedance.

Structural disordered materials exhibit some characteristic spectroscopic anomalies, i.e. unusual but typical frequency response in a variety of properties. All of them are at variance with the conception of a random hopping of mobile charge carriers. The feature is often referred to as 'universal dielectric response' when the permittivity and the conductivity are concerned.[2] By the way, the intergrain contribution (grain boundaries and interfaces) plays an important role in the properties of the material. It is possible that close to a grain boundary, the properties of the sample are controlled by imperfections, expected to be present there in higher concentration that in the center of the grain, leading to an additional contribution to the intergrain impedance. The internal space charge created at the boundaries may lead to a significant increase in the concentration of mobile defects. Different potential barriers will result in different frequency dependent contributions to the conductivity. Decomposition of the experimental overall conductivity into its components may be a problem. There is, however, a simple way to identify the constituents, namely by making use of their

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temperature dependence rather than their frequency dependence.

Ferroelectric ceramic materials are very particular systems whose temperature dependence shows a transition from an ordered state (ferroelectric phase) to a disordered state (paraelectric phase) at the Curie temperature (T_c), typical for each material. Below T_c, the ferroelectric ceramics exhibit their dipoles oriented by themselves and in the absence of an external field, and the only possible reorientation is the reversal of the domain. Above that temperature, the constituent particles do not have firmly assigned positions in the lattice and where the energies and positions of the individual particles are affected by their neighbors. The resulting situation leads to any alternative configurations of particles having very similar energies and transitions from one configuration to another may take place with very little energy input and with only very small adjustments of the positions of individual particles. Thus, spectroscopy anomalies could be observed in their electrical properties from temperature and frequency dependence. There still is not certain opinion regarding these behaviors in ferroelectric ceramic systems. The lanthanum-doped lead zirconate titanates (PLZT) are interesting ferroelectrics from the physical point of view.[3] Substitution of Pb^{2+} ions by La^{3+} ions creates vacancies in the A-site and also, could be created vacancies in the B-site of the perovskite ABO_3 structural lead zirconate titanate ferroelectric ceramics (PZT). The incorporation of La ions and vacancies in the lattice is believed to break the long-range interaction between ferroelectrically active oxygen octahedral interaction containing B-sites cations. Once a vacancy has been created, further motion of atoms is relatively easy by a neighboring atom hopping into the vacancy, which is therefore translated to another site, and so on.

In the present investigation, an introduced complex impedance in PZT-53 + 2·5 mol% La_2O_3 ferroelectric ceramic is employed to analysis the individual contributions of the bulk, grain boundaries, and electrode sample interface. The conductivity phenomenon is studied in order to obtain information about the mobile charge carriers.

2 Experimental Procedure

Lanthanum-doped lead titanate zirconate ceramic ($PbZr_{0{\cdot}53}Ti_{0{\cdot}47}O_3 + 2{\cdot}5$ mol% La_2O_3) ceramic samples were prepared by hot-pressing technique.[3,4] The starting powders of reagent grade were PbO, La_2O_3, ZrO_2 and TiO_2. The mixed oxides were milled and calcined simultaneously in a ball mill kept at 600°C for 2 h. The dried powders were mixed with polyvinyl alcohol and sintered at 1000 °C for 1 h under a pressure of 6 MPa. X-ray diffraction analysis of the powder samples showed a pure rombohedral phase[5] and a grain size of the order of 0·2 μm was obtained from the microstructural studies.[4]

Gold-painted electrodes were applied to the opposite faces of sintered samples to properly get electrical response from the studied material. The impedance spectra was measured by using a Hewlett Packard 4192A Impedance Analyzer, controlled by a PC, which covers a frequencies range between 5 Hz and 13 MHz. Measurements were made isothermally with an applied voltage of 1 V, from room temperature to 700 °C. The thermally stimulated current measurements were made over 25–600 °C using a Philips PM2525 digital multimeter with a ratio of the temperature rise of 3 °C min^{-1}. It was studied in poled samples at 2 kV mm^{-1} with silver paste electrodes fired on at 600 °C.

3 Results and Discussion

In polycrystalline ceramics sometimes it is not possible to identify each individual component by its own arc in an impedance or modulus spectrum because of the proximity of the times constants. In this case the center of the experimental arcs in the spectrum is frequently displaced below the real axis because of the presence of different elements in the material–electrode system.[1] These are distorted by the others relaxations whose means constants are within two orders of magnitude or less of that for the arc under consideration. Thus, the spectra shows overlapping arcs. Even so, the impedance spectrum in conjunction with a carefully characterization can be used to glean information that is otherwise inaccessible–for example, regarding the conductivities of individual phases.

Two overlapping semicircles were obtained for the studied system. Two RC equivalent circuits were assigned to this response as we can see in Fig. 1(a) where both measured and simulated curves are plotted using the NLLS-fit program[6] for two temperatures.

The resistance values (R) were obtained from the circular arc intercepts on the Z' axis; the capacitance values (C) could be derived from the expression involving the frequency at the peak of the circular arc ($\omega RC = 1$), where $\omega = 2\pi f$ is the frequency (f is the instantaneous frequency at the maximum of the semicircle). The high frequency contribution (R_{FB}, C_{FB}) exhibits C-values in the order of 10^{-10}–10^{-9} F, associated to the ferroelectric bulk or grains response (FB) which

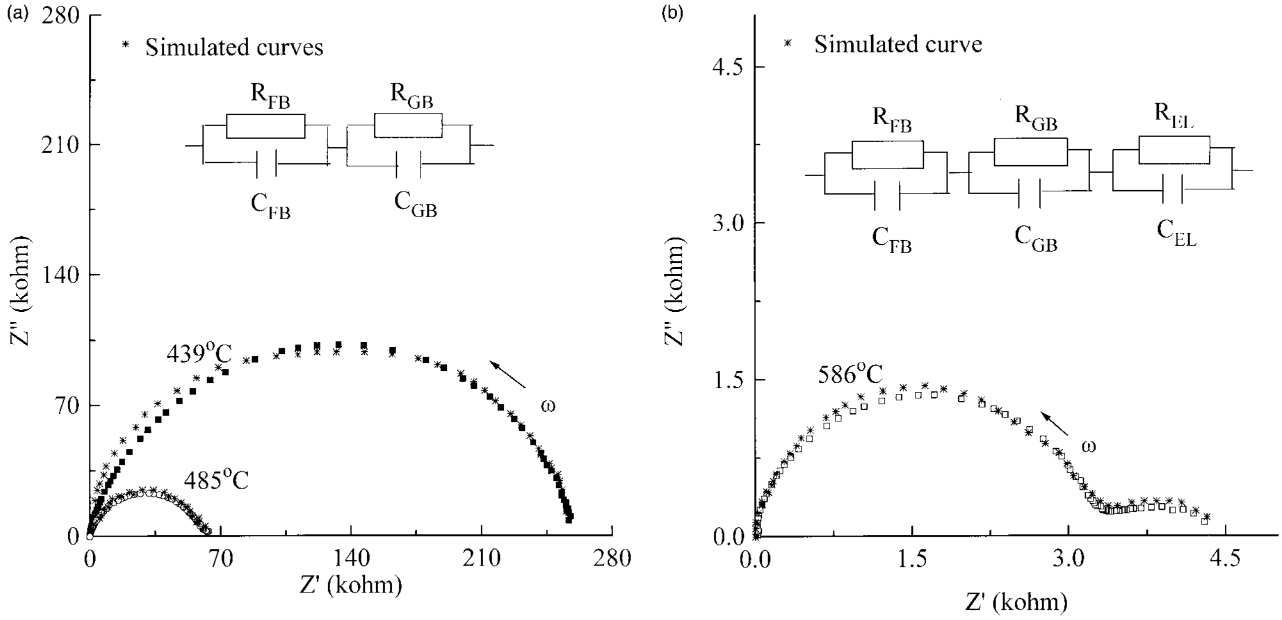

Fig. 1. The complex impedance planes of PZT-53 + 2·5 mol% La_2O_3 measured at (a) 439 and 485 °C and (b) 586 °C. Simulated and measured curves are shown for each temperature. RC parallel circuits in series have been assigned to the ferroelectric bulk or grains (FB), grain boundary (GB) and electrode (EL) response, respectively.

decrease as the temperature rises (Fig. 2). C-values in the order of 10^{-9}–10^{-8} F were obtained from the second semicircle (R_{GB}, C_{GB}) associated to the grain boundary response (GB).

Above 550 °C (823 K) a low frequency arc appears. Approximate calculations give C-values in the order of μF which means that there is the electrode signal. Figure 1(b) shows the complex impedance plots for 586 °C (859 K). These results can be modeled by three RC parallel circuits in series assigned to the ferroelectric bulk (or grains), grain boundary and electrode (EL) responses, respectively, as we can see in Fig. 1 where the measured and simulated curves are shown in the same plot. The response involves non-blocking electrodes where the penetration of the mobile ions can occur. In the opposite phenomenon (blocking electrodes) the capacitance arises from the effect of mobile ions blocked by electrodes at electrode–sample interface and the impedance plane shows a spike at low frequencies.

From the temperature dependence of the ferroelectric bulk (or grains) capacitance values (Fig. 2) it was suspected to show a Curie–Weiss behavior. It was confirmed by plotting reciprocal capacitance ($\frac{1}{C_{FB}}$) against temperature in the inset of Fig. 2. A good linearity covers a wide temperature range in the paraelectric phase (Curie–Weiss behavior); in this case, the lanthanum addition does not affect the first order transition in the ferroelectric bulk.

The ferroelectric bulk and grain boundary phases have conductivities (σ) described by the Arrhenius plots, with distinct activation energies and pre-exponential factors, given by the equation:

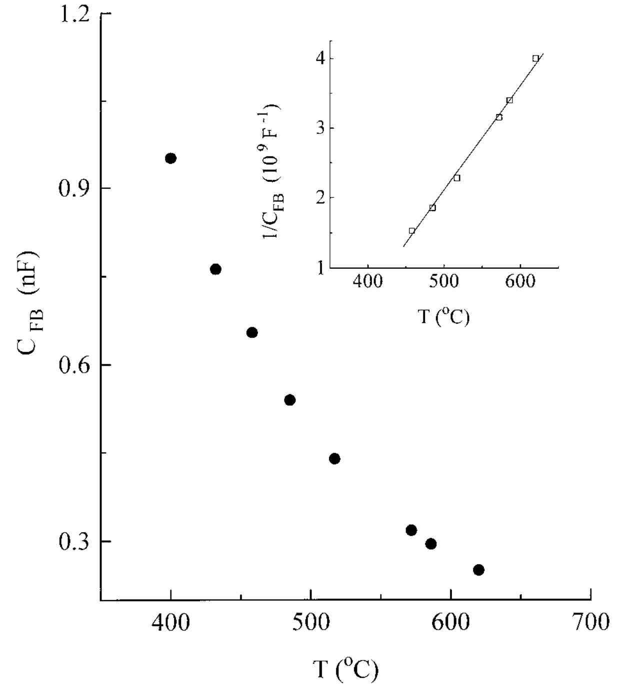

Fig. 2. Temperature dependence of the ferroelectric bulk (or grains) capacitance values for the PZT-53 + 2·5 mol% La_2O_3 ferroelectric ceramic system. C_{FB} decreases rapidly as the temperature increases and it was suspected to show Curie–Weiss behavior, which was confirmed by plotting reciprocal capacitance against temperature in the inset of the figure.

$$\sigma = A \exp\left(-\frac{E_a}{kT}\right) \tag{1}$$

where A, E_a, k and T are the pre-exponential factor, the activation energy, the Boltzmann's constant ($k = 8{\cdot}626 \times 10^{-5}$ eV K^{-1}) and the absolute temperature, respectively. Figure 3 shows both Arrhenius dependence which display two regions: a high temperature region ($T > 773$ K) where a strong similarity in both temperature dependences are observed and a low temperature region ($T < 773$ K) where the two activation energies are 1·03 and 1·70 eV for the ferroelectric bulk and grain boundary contribution, respectively. The two slopes cross over above 500 °C showing a change in the conductivity process. The first region ($T > 773$ K) suggests that the conductivity σ_{FB} and σ_{GB} may arise from the same type of physical process, the same conduction mechanism. Both behaviors are parallel and the activation energy value is 1·95 eV. The activation energy value of the ferroelectric bulk in the second region 'suggests' the mobile of oxygen ions by a vacancy mechanism.[7,8]

To examine the dominated contribution to the total conductivity, we have plotted the Arrhenius behavior from the sample response above 773 K in the same Fig. 3. It is clear that at high temperatures the material conductivity is dominated by the ferroelectric bulk conductivity. On the other hand, we found that the temperature dependence of the electrode conductivity which appear above 773 K corresponded to a thermally activated process with a high activation energy, approximately 2·04 eV. The diffusion of oxygen ions may be ruled out; one would expect to find a relatively small activation energy for this process. Thus, the source of the strong temperature dependence of the electrode–sample interface may be an electron transfer reaction at this interface.[8]

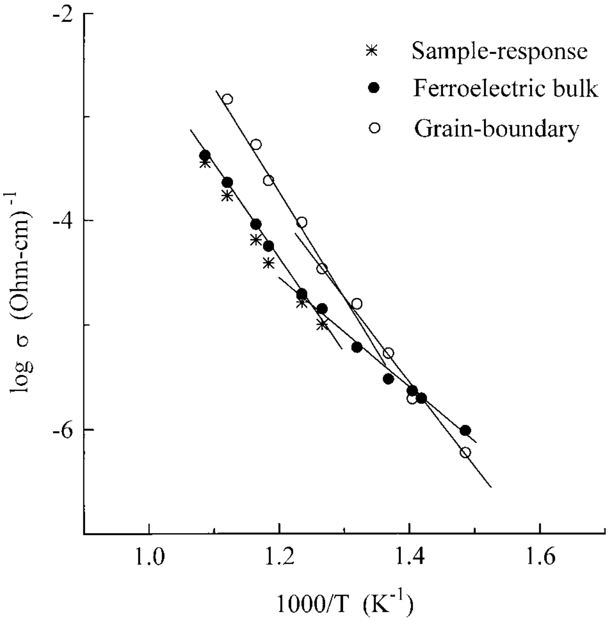

Fig. 3. Arrhenius plot for the ferroelectric bulk or grains (FB) and the grain boundary (GB) conductivities obtained from the impedance data of the polycrystalline PZT-53 + 2·5 mol% La_2O_3 ferroelectric ceramic system. Two linear behaviors with different slopes show a change in the conductivity process. The Arrhenius behavior from the sample response is plotted too. At high temperatures the material conductivity is dominated by the ferroelectric bulk conductivity.

3.1 AC behavior

It has been known[2] that all dielectric systems obey the law: $\chi'(\omega) \propto \chi''(\omega) \propto \omega^{n-1}$ with the exponent in the range $0 < n < 1$ and with the consequence that the real and imaginary part of the susceptibility are in the frequency-independent ratio: $\chi''(\omega)/\chi'(\omega) = \cot(n\pi/2)$. This 'non-Debye' behavior is in sharp contrast with the classical Debye law for which this ratio is equal to ωt. Its physical basis is seen in many body interactions between dipoles or charges which are responsible for the dielectric behavior of the solid.[9] This universal law covers the entire range of the exponent n which is mathematically allowed for this type of relation to be valid as a Kramer–Kroning compatible system. The discovery for the two extreme values of n corresponding, respectively, to the strong low-frequency dispersion and to the frequency-independent loss.

As regards fundamental polarization process, it is possible to distinguish between dipolar and charge-carrier-dominated processes. If the dielectric response is clearly dominated by loss peaks, with possibly a DC component at the lowest frequencies but without any strong low-frequency dispersion, then the conclusion must be that the dominant process is a dipolar polarization. Just as a loss peak is the ultimately proof of a dipolar process, so the charge carrier response is finally confirmed by the presence of strong low-frequency dispersion. The presence of strong dispersion tends to suppress the loss peaks from the dipolar interactions. This should be clearly distinguished from the DC conductivity—the latter is independent of the polarizing dipolar species and is always present in all polar materials at sufficiently high temperatures. The former shows that charge carriers of either electronic or ionic nature are hopping in the system and their collective interactions lead to strong low-frequency dispersion.

This is clearly borne out in Fig. 4 by the accompanying plot of the real and imaginary part of the permittivity for two temperatures [$\varepsilon'(\omega) = \chi'(\omega) + 1$ and $\varepsilon''(\omega) = \chi''(\omega)$ in ferroelectric systems]. Both parameters were calculated from the real (Z') and imaginary (Z'') impedance values by using the expressions:

$$\varepsilon'(\omega) = \left(\frac{g.f.}{\varepsilon_o}\right)\left(\frac{1}{\omega Z''\left(1 + \left(\frac{Z'}{Z''}\right)^2\right)}\right) \tag{2}$$

$$\varepsilon''(\omega) = \frac{\sigma(\omega)}{\varepsilon_o \omega} \tag{3}$$

where $g.f.$ is the geometrical factor, ε_o ($8{\cdot}85 \times 10^{-12}\,\mathrm{F\,cm^{-1}}$) is the vacuum dielectric constant and the conductivity values [$\sigma(\omega)$] were obtained from expression:

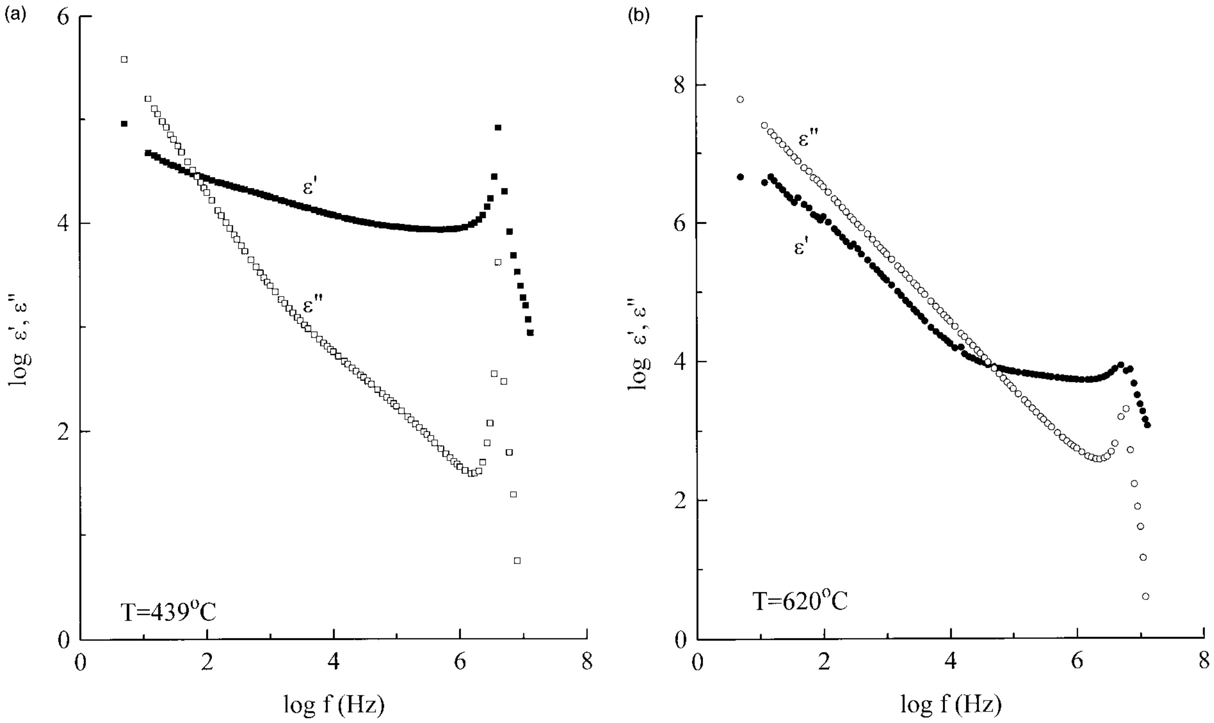

Fig. 4. The dielectric response of the polycrystalline PZT-53 + 2·5 mol% La_2O_3 ferroelectric ceramic system represented as the real and imaginary components of the dielectric permittivity against frequency in a log-log plane for (a) 439 °C and (b) 620 °C. Three regions are observed: the strongly dispersive region at low frequencies (LFD) where both behaviors show a parallel linear dependence, the almost flat universal law with n close to unity for $\varepsilon'(\omega)$ behavior while $\varepsilon''(\omega)$ decrease as a linear dependence and the high frequency dispersion.

$$\sigma(\omega) = g.f. \left(\frac{Z'}{(Z')^2 + (Z'')^2} \right) \tag{4}$$

A family of characteristics of $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ is shown which clearly consist of three regions of frequency dependence:

(a) The strongly dispersive region at low frequencies (LFD) where both behaviors show a parallel linear dependence.
(b) The almost flat universal law with n close to unity for $\varepsilon'(\omega)$ behavior while $\varepsilon''(\omega)$ decrease as a linear dependence.
(c) The high frequency dispersion.

The strong low-frequency dispersion 'may arise' from the same type of mechanism as that responsible for the more usual 'universal response' but with a peculiarity low value of the exponent n. The 'dispersive law' ω^{n-1} is indicated with $n \ll 1$ (0·04 and 0·03 in our system for 439 and 620 °C, respectively) and the material is very lossy with $\tan\delta \gg 1$. The LFD occurs involving the translation of charge carriers, a conductive response. Jonscher has suggested[10] that the dispersion may be caused by the presence of impurities and the crystalline imperfections that affect the progress of charge carriers through a lattice. The conducting species moving by discontinuous jumps interact with another in a manner demanded by the 'screened hopping' mechanism of the 'non-Debye' analysis (a 'cooperative hopping').

LFD depends upon transport of charges in the system and on the presence of blocking or non-blocking electrodes. The natural limit of this process is the formation of a fully developed space charge barrier of the Schottky type. It is not to be confused with the familiar polarization effects found at low frequencies, caused by the use of blocking electrodes; at low frequencies the charge carries respond by moving bodily, by a sequence of activated hops, towards the appropriate electrode. This transition of charge within the bulk therefore produces an increase in the dielectric permittivity.

LFD also represents a form of transport and its outstanding feature is the accompanying storage of charge, in complete contrast to the conventional direct current (DC) transport where there can be no storage. This manifest itself in the existence of discharge currents which persists for long times.

To examine the dc behavior, we reconstructed the Arrhenius plot of the total conductivity (σ), obtained from expression (4) for several frequencies (Fig. 5). The conductivity rises as a thermally activated process. At higher temperatures a linear behavior is identified as the σ_{dc} component whose activation energy is 1·92 eV.

The σ_{dc} fit particularly nice with the ferroelectric bulk conductivity σ_{FB} (it is not shown). The ferroelectric bulk dominates in the conductivity of the sample (as we could see in Fig. 3) and gives up the DC component. The energy activation values are almost identical.

3.2 Conductive mechanisms

The presence of defect points, whether randomly distributed or not, teals in turn to a level of disorder that arising in the neighborhood of each defect as the result of the local strain introduced by the defect. This strain affects significant numbers of nearest neighbors, changing their energetic and spatial characteristics.

The lanthanum-doped lead zirconate titanates are donor doped ceramics which show a conduction mechanism due to the very low concentration of oxygen vacancies. These are highly insulating at room temperature due to the cation vacancy compensation, as we pointed out in the introduction. Once a vacancy has been created, further motion of atoms is relatively easy by a neighboring atom hopping into the vacancy, which is therefore translated to another site, and so on; but there is virtually no ionic transport in the lattice due to the low mobility of the cation vacancies. Thus, oxygen ions are known to show a certain motion in perovskite ceramics.

Donor-doped ceramics represent a mixed ionic-electronic conductive behavior. Ionic transport is in many respects similar to electronic hopping in that charge carriers displace themselves in a random manner between preferred sites, which in the case of ions are either interstitial positions in a more or less perfect lattice, or may be lattice vacancies created. The ions cannot tunnel across relatively large inter-site space because of their large mass—typically 10^4–10^5 times the electron mass, so that the ionic transport occurs by nearest neighbor hopping. In the electronic hopping much larger distances may be traversed, specially in shallow donor or acceptor sites. A fundamental parameter in any electronic or ionic hopping process is the energy required to execute the hop, i.e. the activation energy.

To discuss the conductive mechanism in the studied system we have added the thermally stimulated current results[5] to the impedance spectroscopy analysis. Below Curie temperature ($T_c = 265$ °C), the pyroelectric effect was observed which dessapeared at T_c. Above that point negative values for the current were obtained until approximately 520 °C and then, the current rises even to higher values than those of below T_c. Figure 6 shows these regions. Region II is in the same temperature range of the low-temperature Arrhenius plot for the ferroelectric bulk contribution (Fig. 3). Both results induce that the majority mobile ionic species are oxygen ions which move by a vacancy mechanism.[11] The mobility of the oxygen vacancies is thermally activated with an activation energy of 1·03 eV, as we could obtain from the Arrhenius plot of the ferroelectric bulk (or grains).

Region III suggests another conductive mechanism which agrees with the slope change from Fig. 3.

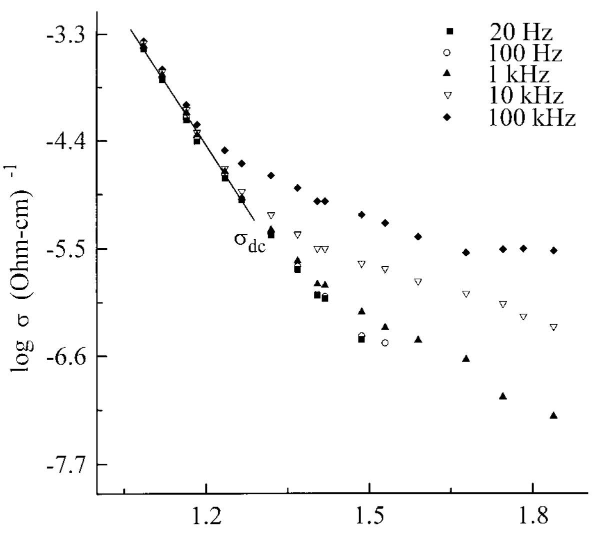

Fig. 5. Arrhenius plot of the total conductivity for the PZT-53 + 2·5 mol% La_2O_3 ferroelectric ceramic system at several frequencies. The conductivity rises as a thermally activated process and at higher temperatures a linear behavior is identified as the σ_{DC}.

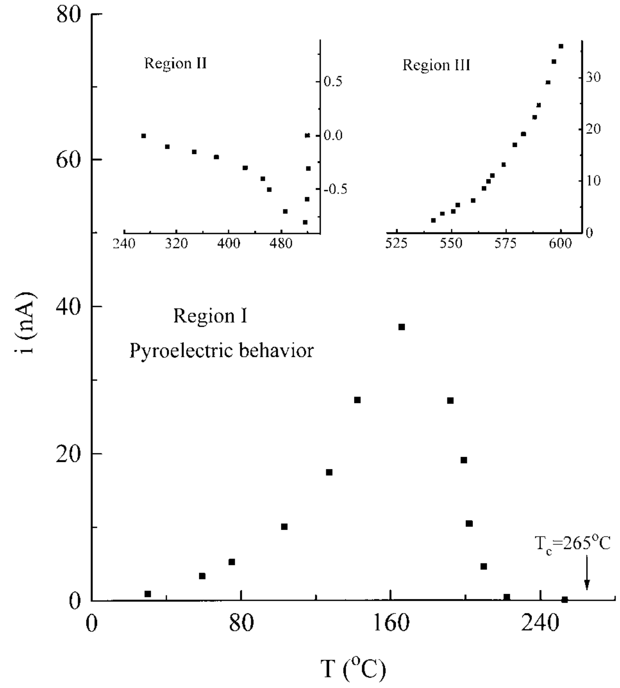

Fig. 6. Thermally stimulated current results for the polycrystalline PZT-53 + 2·5 mol% La_2O_3 ferroelectric ceramic system. Below Curie temperature ($T_c = 265$ °C), the pyroelectric effect is observed which dessapeared at T_c. Above that point negative values for the current are shown until approximately 520 °C and then, the current rises even to higher values than those of below T_c.

As we pointed out, at this high temperature zone, the ferroelectric bulk dominates in the conductivity of the sample and gives up the DC component. On the other hand, the presence of the electrode contribution plays an important role in the conductive mechanism; a strong low frequency dispersion support the translation of charge carriers at a wide frequency range. Also, this provokes that the center of the experimental ferroelectric bulk arc in the impedance spectrum is more displaced than that of in the other temperature range. From the energy activation values and ac behavior at low frequencies we conclude that there is an electronic conductivity even the mobile oxygen ions could be present too.

4 Conclusions

- The ferroelectric bulk (or grains), grain boundary and a non-blocking electrode contributions were studied in a lanthanum-doped lead zirconate titanate ferroelectric ceramic, by using an impedance spectrum in a wide temperature range above the Curie temperature. RC equivalent circuits were assigned to each contribution and the simulated curves showed a nice fitting with the experimental results.
- Arrhenius plots suggested the mobile of oxygen ions by a vacancy mechanism below 773 K. The thermally activated process at the electrode-sample interface above 773 K showed a high activation energy that induced an electron transfer reaction at this interface.
- AC and DC conductivity components were found; a Jonscher power-law behavior was obtained and a strong low frequency dispersion was observed in a wide frequency range which supports that the carriers of either electronic or ionic nature are hopping in the system and their collective interactions lead to this phenomenon. The ferroelectric bulk (or grains) conductivity gives up the main contribution to DC component.
- A mixture of ionic–electronic conductive behavior was analyzed from the experimental results of impedance spectroscopy and thermally stimulated current.

Acknowledgements

The authors wish to thank Dr Alfonso Huanosta Tera from the Institute of Material Researches, UNAM, México for comments and installation support. Special thanks to The Third World Academy of Science (TWAS) for partial financial support.

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