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Electrical characterizations of PZT ceramics in large frequency and temperature ranges

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Abstract

Electrical properties of $PbZr_{0.75}Ti_{0.25}O_3$ ceramics have been characterized. The measurements have been made in frequency ranging from 20 to 2.10^9 Hz and between 20 and 730 °C for low and medium frequencies. Typically at room temperature, the dielectric constant ε' is higher than 500 at 1 MHz whereas the loss tangent is close to 0.01. From $\varepsilon'(T)$ measurements, the Curie temperature of our sample has been determined at 320 °C. In the paraelectric state, $\varepsilon'(T)$ follows the empirical Curie–Weiss law near the phase transition which is of second order type. The increase of ε' observed at high temperatures and low frequencies in the paraelectric state are explained: this abnormal behavior is due to the migation of oxygen ions towards the electrodes, creating an additional non-ferroelectric interface which generates a Maxwell–Wagner effect.

Keywords: Dielectric properties; Electrical conductivity; Phase transition; PZT

1. Introduction

Ferroelectric materials have been known by chemists for a long time: more than 300 years for the oldest material. However the ferroelectric properties have been discovered more recently.[1] Nowadays they are used in electronics either in the form of ceramics, thick films or thin films. The first applications were based on ceramics for the realization of capacitors more than 40 years ago.[2] After that, the beginning of deposition of ferroelectric films has allowed to envisage applications in microelectronics [3] which at present are a reality with for example FeRAM memories. As ferroelectric materials present also piezoelectric and pyroelectric properties, their potential use is great such as positioners, actuators, filters, radiation detectors, infrared sensors, etc.[4,5] In this view, a ferroelectric material of composition $PbZr_xTi_{1-x}O_3$ (PZT) is of particular interest. Much attention has been made on its piezoelectric properties and on the applications relative to these properties. In this paper we will focus on the non-linear dielectric properties of PZT ceramics. The measurements are made in a large frequency range ($20–2.10^9$ Hz) at room temperature and as a function of temperature up to 730 °C. To our knowledge, there have been few studies on PZT in a so large range of frequency and temperature.

2. Experimental procedure

The sample of ceramic is a disk with a diameter of 12 mm and thickness of 0.8 mm. Its chemical composition has been verified from energy dispersive spectrometry (EDS) measurements using scanning electron microscopy (SEM) with a LEO438 VP apparatus: $x \approx 0.7–0.8$. To perform measurements as a parallel-plate capacitor, each face of the disk is covered by platinum electrode deposited by sputtering. The electrical properties were determined in the frequency range $20–10^6$ Hz with an HP4284A impedance analyzer, and between 10^6 and $1.8\ 10^9$ Hz with an HP4291A impedance analyzer. A home made high power furnace was used to heat the sample from room temperature up to 730 °C (1000 K).

2.1. Dielectric properties at room temperature

Dielectric measurements have been made at room temperature ($RT = 20$ °C) from 20 Hz to 1.8 GHz. We present in Fig. 1 the evolution up to 1 MHz of the real part ε' of the complex permittivity $\varepsilon^* = \varepsilon_0(\varepsilon' - j\varepsilon'')$, ε' is also called dielectric constant ε_r. In a first approximation, ε' is constant with a value of about 570.

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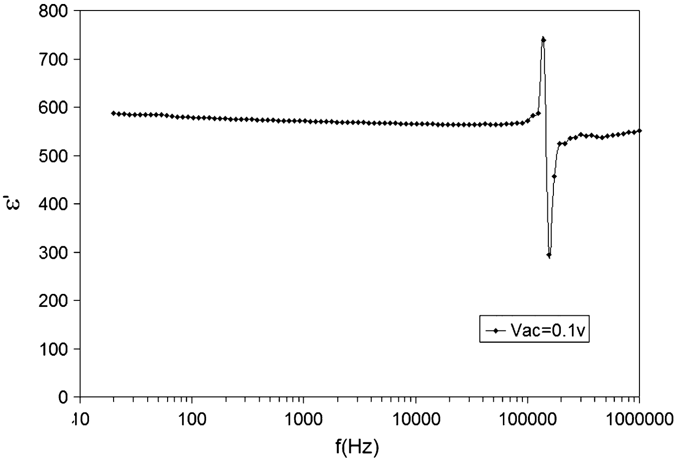

Fig. 1. Evolution at 20 °C of ε' at low frequencies for a PZT ceramic.

This value depends on several factors such as the composition (Zr/Ti ratio), the process and the sintering temperature.[6–8] A resonance phenomenon is observed at 180 kHz: it can be ascribed to a piezoelectric effect of the PZT which occurs in the radial mode. The resonance frequency is linked, in particular, to the dimensions of the ceramic disk.

The imaginary part ε'' of ε^* is slightly decreasing down to 100 kHz with a value of 3 at 100 kHz. The corresponding loss tangent tg $\delta = \varepsilon''/\varepsilon'$ has then a minimal value of about 5.10^{-3} at 100 kHz. Above 10 MHz a dielectric relaxation domain is well evidenced both on ε' and ε'' with a critical frequency of about 200 MHz (see Fig. 2).

The origin of this relaxation domain has been attributed in perovskite in general[9,10] to the jump of Ti^{4+} and Zr^{4+} ions between neighbouring sites with different energies, the so-called “double-well potential model”.

2.2. Dielectric properties at high temperatures

Dielectric measurements have been made from room temperature up to 1000 K in the 10 Hz to 1 MHz frequency range. This enables the examination of the transition between the rhomboedric ferroelectric state and the cubic paraelectric state: in fact at a given frequency the evolution of ε' as a function of temperature shows a maximum at a temperature T_c, the Curie temperature. Fig. 3 shows the curves for our PZT sample at different frequencies between 100 Hz and 100 kHz. A maximum is clearly observed at $T_c = 320\,°C$. It is independent of the frequency which is characteristic of a “classical ferroelectric” on the contrary to a “relaxor”. From this value of T_c and the well-established $PbTiO_3$–$PbZrO_3$ phase diagram it is possible to infer that the composition of our PZT sample is $PbZr_{0.75}Ti_{0.25}O_3$, which is in agreement with the EDS measurements.

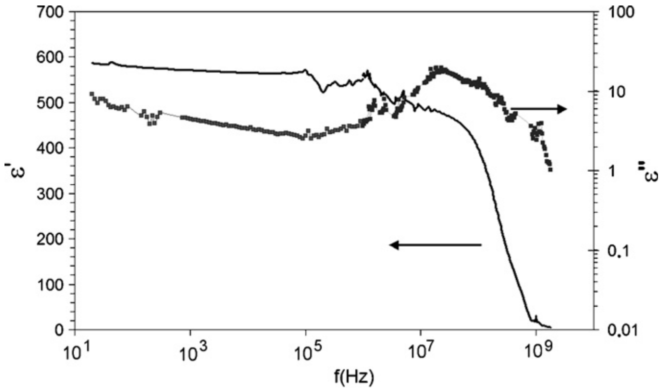

Fig. 2. Evolution at 20 °C of ε' and ε'' from 20 Hz to 2 GHz for a PZT ceramic.

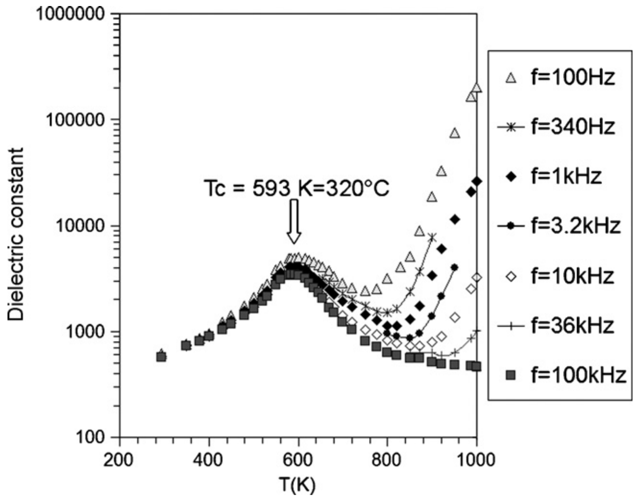

Fig. 3. Evolution of ε' as a function of temperature and frequencies for a PZT ceramic.

It is interesting to present $1/\varepsilon'$ as a function of temperature: this is given in Fig. 4. From the curves it is possible to infer two informations:

(i) In the paraelectric state ($T > T_c$), the evolution is linear which is in agreement with the empirical Curie–Weiss law: $1/\varepsilon' = K(T - T_0)$ where K is constant and T_0 is the Curie–Weiss temperature.
(ii) There is no discontinuity in the vicinity of the minimum of the curves and all the straight lines plotted in the paraelectric region indicate the same Curie–Weiss temperature $T_0 = T_c$. All these features are characteristic of a phase transition of a second order type in the Landau theory of phase transition.

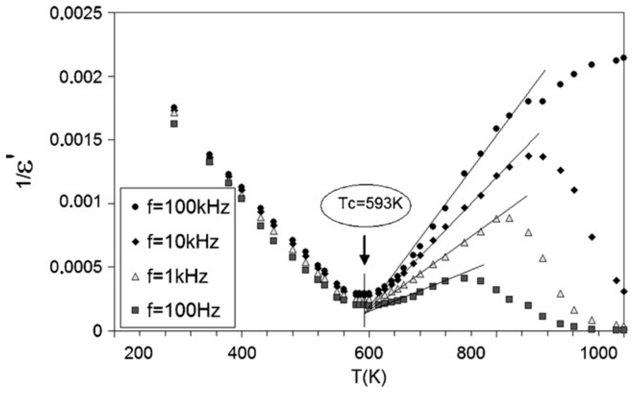

Fig. 4. Evolution of $1/\varepsilon'$ as a function of temperature and frequencies for PZT ceramic.

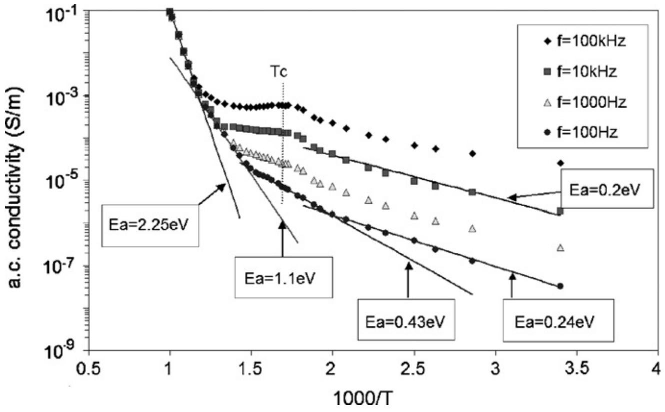

Fig. 5. Evolution of σ_{ac} as a function of frequencies and inverse of temperature for a PZT ceramic.

2.3. dc and ac conductivity

The ac complex conductivity σ^* is linked to ε^* by the formula:

$\sigma^* = j\omega\varepsilon_0\varepsilon^* = \omega\varepsilon_0\varepsilon'' + j\omega\ \varepsilon_0\varepsilon'$. Usually, in the literature, the ac conductivity is the real part of σ^* so $\sigma_{ac} = \omega\varepsilon_0\varepsilon''$. We have computed σ_{ac} as a function of frequency and temperature from room temperature up to 1000 K. Fig. 5 we present the evolution of σ_{ac} as a function of $1/T$ at four frequencies. Three main regions can be distinguished with different activation energies E_A which increase with temperature. Thus, each region can be described by an Arrhenius formula $\sigma_{ac} = \sigma_0 \exp(-E_A/kT)$. It is possible to link each region to movements of electrical charges which are thermally activated. In Table 1 we summarize these attributions.

At temperatures under 400 °C, the activation energies of the first region are low: 0.2–0.43 eV. It is attributed to electron jumps, in agreement with published results on titanates in general.[11–13] The existence of conduction electrons is due on the one hand to the deficiency in oxygen of PZT and on the other hand to Ti^{4+} ions which trap electrons to give Ti^{3+} centers and then released these electrons. From 400 to 580 °C the activation energy of the second region is 1.1 eV: this value, about three times the previous one, is attributed to “bigger” charges than electrons: it is due to oxygen vacancies movements. Indeed in the literature oxygen vacancies in titanates have activation energies for jumps between 1 and 1.2 eV.[11–13] Above 580 °C the activation energy of the third region is 2.25 eV which is two times the one of the second region. In this temperature range very few studies have been made whereas it corresponds to the annealing temperature range of ceramics. Nevertheless we attribute this phenomenon to the migration of oxygen ions towards the electrodes. This assumption is based on a remark of Waser and Smyth [14]: for oxygen pressures below the one of the stoichiometric composition, and for temperatures where a balance can occur in a reasonable time, typically above 873 K, the oxide loses oxygen to stay in thermodynamic equilibrium with the atmosphere. It can be noted but not given here [15] that the dc conductivity presents high temperature regions with activation energies of 1.1 and 2.25 eV in excellent accordance with the ac conductivity ones.

Table 1
Mechanisms of ac conductivity in a PZT ceramic

Temperature	Activation energy (eV)	Origin
20–400 °C	0.2–0.43	Electrons
400–580 °C	1.1	Oxygen vacancies
$T > 580$ °C	2.25	Oxygen ions

This phenomenon may be related to the sharp increase in the conductivity noted Fig. 5 above 850 K because the migration of oxygen ions leads to the creation of additional vacancies, favoring an increase of conduction. As the oxygen ions cannot go through the metallic electrodes, the electrodes act as blocking electrodes. That is the reason why we can deduce from the impedance diagrams study that an ionic accumulation process starts for temperatures above 850 K. Fig. 6 shows these impedance diagrams. The arc associated with the conduction in the bulk material decreases with the temperature increase. So when the temperature increases and reaches high values, the intrinsic part of the impedance diagram decreases while the extrinsic part due to the ionic accumulation increases. Fig. 6, from the very small arcs associated to the electrode effect, values of capacitances ranging from 2.5 to 5 μF were deduced.

For us, this electrode effect is due to the migration of oxygen ions because it may not be a movement of cations vacancies that are considered as frozen at temperatures below approximately 1400 K.[14] The literature provides few references for the study of the conductivity of titanates at high temperatures, especially above 800 K. A similar mechanism of blocking electrodes with an activation energy of 2.04 V was proposed by Pelaiz Barranco et al. for a PZT ceramic doped with lanthanum.[16]

As observed Fig. 3 in the paraelectric region and at frequencies lower than 100 kHz, the increases of ε' at high temperatures are so due to the migration of oxygen ions. This behavior is confirmed on curves of ε' as function of the frequency for temperatures between 293 and 1000 K plotted in Fig. 7. These curves also reflect the electrodes effect highlighted by the variation of ε' at 1000 K on about two decades between 100 Hz and 100 kHz. The variation of ε' above 800 K reflects the creation of a non-ferroelectric interface at the electrodes which induce a Maxwell–Wagner effect. At high temperatures, the equivalent electric scheme of the sample is then composed of two resistance–capacitance (RC) circuits in series: the first is representative of the bulk material and the second is due to the space charge created by the accumulation of oxygen ions.[17]

When the frequency increases, the electrode effect progressively disappears and at 100 kHz all the curves merge. It is

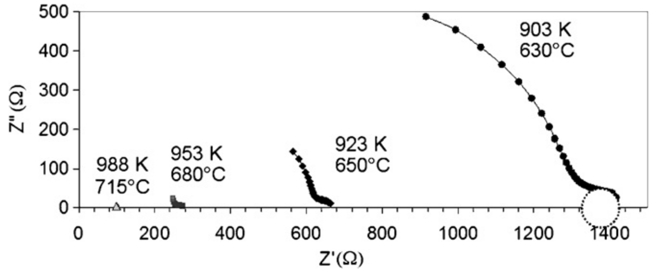

Fig. 6. Impedance diagrams of the PZT ceramic for temperatures above 850 K.

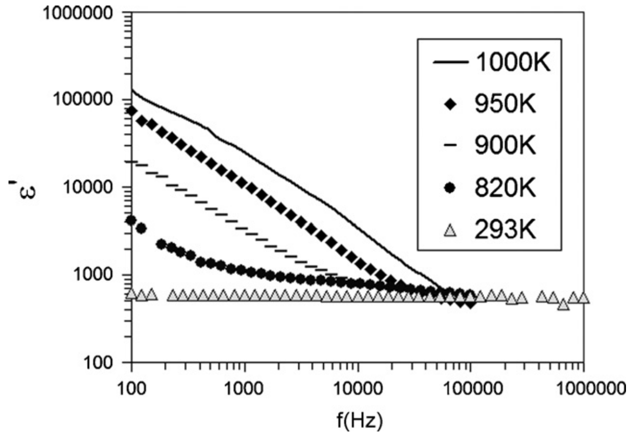

Fig. 7. ε' in function of the frequency for temperatures between 293 and 1000 K.

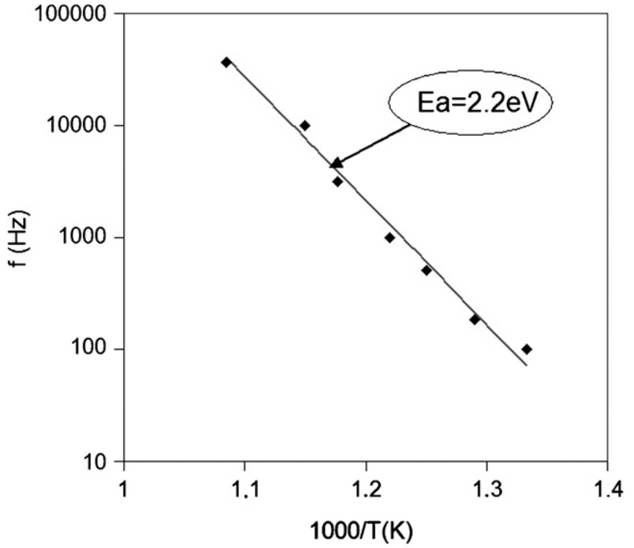

Fig. 8. Frequency of the ε' minimas observed in the paraelectric region in function of the reciprocal temperature.

probably because the jumps of the "big" carriers as oxygen vacancies and ions cannot "follow" the variations of the ac electrical field at high frequency.

It is noticeable that the ε' minimas observed in the paraelectric region (above T_c), and for each frequency, is not defined at the same temperature. This shows that the phenomenon of ionic migration is thermally activated. Fig. 8 gives the value of the activation energy: $E = 2.2$ eV. We can see that this one is very similar to that found for the conductivity above 850 K, namely $E = 2.25$ eV. So the increase of ε' observed in the paraelectric region is due to a thermally activated process, i.e. the migration of the oxygen ions at very high temperatures.

3. Conclusion

We have presented a study of the electrical properties of a PZT ceramic. Different parameters have been varied: the frequency in the range 20 Hz to 2 GHz, the temperature from 20 to 730 °C. At room temperature and for frequencies up to 1 MHz, the dielectrical study of the ceramic gives a dielectric constant $\varepsilon' \cong 600$ and a loss tangent tg $\delta \cong 0.01$. Above 1 MHz the ceramic shows a dielectric relaxation domain with a critical frequency $F_C \cong 200$ MHz. Measurements at high temperatures permit to determine, from the maximum of $\varepsilon'(T)$, the Curie temperature $T_c = 320$ °C of the ferroelectric–paraelectric phase transition of our PZT ceramic. The study of the electrical properties at high temperatures let us to highlight the displacements of thermally activated charges. In particular, we have explained the increase of ε' at high temperatures observed at low frequencies in the paraelectric state: this abnormal behavior is due to the migation of oxygen ions towards the electrodes, creating an additional non-ferroelectric interface which generates a Maxwell–Wagner effect.

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