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High-frequency dielectric relaxation related to the PE–FE transition in PZT ceramics with low Ti concentration

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Abstract. The dielectric permittivity and the dielectric losses of $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ ($x = 0.03$, $x = 0.04$, $x = 0.05$) ceramics doped with 1% Nb_2O_5 were investigated as functions of frequency and temperature. A large and unambiguous dielectric relaxation is detected at high frequency and is shown to be strongly dependent on the temperature. The minimum of the relaxation time and the maximum of the relaxation strength appear to be clearly connected with the ferroelectric–paraelectric phase transition.

1. Introduction

Solid solutions of lead zirconate titanate $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ (PZT) have been the object of many investigations. The phase diagram is known to strongly depend on the Zr/Ti ratio, as well as on the dopant (Nb, La, ...). The PZT ceramics show antiferroelectric (AFE)–ferroelectric (FE)–paraelectric (PE) phase sequence in the case of $0 < x < 0.06$. The AFE–FE and FE–PE phase transition temperatures and degree of broadening depend both on the Zr/Ti ratio and the concentration of different dopants [1–10].

The ceramics with Zr/Ti ratio 65/35 or close to it, often studied for their electro-optic properties, show a strongly diffuse phase transition [11–13]. A glassy behaviour was recently evidenced in the materials [14, 15].

The Zr-rich ceramics close to the Zr/Ti ratio 95/5 have been intensively studied for a long time because of many still unsolved problems relating, among other things, to two antiferroelectric (of tetragonal and orthorhombic symmetry) and two ferroelectric phases ($F_{R(LT)}$ and $F_{R(HT)}$ both of rhombohedral symmetry). The neighbouring phases coexist in wide temperature intervals which depend strongly on both Ti concentration and dopants like Nb_2O_5 and La_2O_3 [16, 17]. This behaviour was observed even in the Nb-doped lead zirconate [18].

Dielectric measurements constitute a good probe to point out these features. Indeed diffuse phase transitions in materials should be characterized by a noticeable frequency dispersion of the dielectric permittivity ϵ in the vicinity of the Curie temperature T_C which is frequency dependent [19]. On the other hand a normal FE phase transition is related to a sharp peak of ϵ versus temperature, at a T_C which is independent of frequency.

Usually dielectric studies in PZT materials have concerned low-frequency measurements [8, 10, 17, 20, 21]. In particular, a dielectric dispersion was detected for frequencies below

1 kHz [17]. Here, we focus on the measurements in the high-frequency range up to 1 GHz. The high-frequency experiments can provide some information on the polarization fluctuation in ferroelectrics.

A large frequency dispersion was recently reported within this range in BaTiO_2 [22] and KTN [23, 24] in the PE and FE phases and the relaxation process was argued to drive the phase transition mechanism in these compounds. Dielectric properties of zirconium-rich PZT materials are considered in the present paper. No dispersion is observed at low frequencies in any materials. In contrast, a large frequency dispersion step in ϵ occurs at high frequency above 100 MHz even at room temperature.

2. Low-frequency dielectric measurements

The PZT ceramics with low Ti content and niobium doping were prepared using the conventional mixed oxide method with a final sintering at 1250 °C for 3 hours in a double crucible with PbO atmosphere. Structural, optical and electric properties of these samples with a depth of 1 mm is about 30% in the visible light range. The average grain size is found to be about 10 μm [9]. Typical dimensions of the samples used in the dielectric measurements are $1 \times 2 \times 0.5 \text{ mm}^3$. Evaporated gold is employed as electrodes of the ceramics in all low- and high-frequency experiments.

Dielectric permittivity and losses were measured as a function of temperature in PZT ceramics doped with Nb or La. In order to detect a possible dispersion, measurements at fixed frequencies 1 kHz and 1 MHz were considered in a first stage. Several samples with various Ti concentrations ($x = 3, 4, 5\%$) were studied. They are denoted PZT 97/3, PZT 96/4, PZT 95/5.

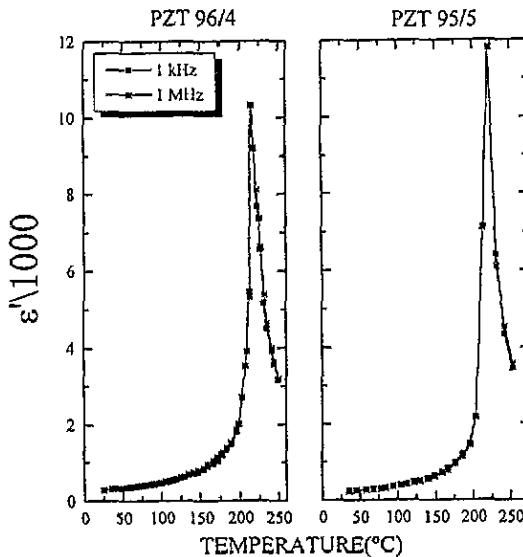


Figure 1. Temperature dependence of dielectric relative permittivity recorded at low frequencies (1 kHz and 1 MHz) in Nb-doped $\text{PbZr}_{0.96}\text{Ti}_{0.04}\text{O}_3$ (PZT 96/4) and $\text{PbZr}_{0.95}\text{Ti}_{0.05}\text{O}_3$ (PZT 95/5).

Figure 1 displays the temperature dependence of the real part of relative permittivity ϵ' recorded at $f = 1 \text{ kHz}$ and 1 MHz in 1% Nb_2O_5 -doped PZT 96/4 and PZT 95/5. In both materials a sharp peak occurs around 220 °C–230 °C, corresponding to the FE–PE phase

transition.

We point out that for each Nb-doped PZT sample, ϵ' has exactly the same value between the frequencies 1 kHz and 1 MHz in the temperature range 20–250°C. From these data, the $\epsilon'(T)$ behaves like that observed for classical ferroelectrics and thus looks very different from relaxor ferroelectrics such as the sample 65/35 or 60/40 [14, 25, 26, 27, 28]. Therefore the FE–PE transition in zirconium-rich PZT ceramics does not appear as diffuse.

The dielectric behaviour connected with the FE–PE transition is similar in all studied materials; only the transition temperature is shifted according to the doping or the Zr/Ti ratio.

We point out the importance of electrodes on the dielectric dispersion. The shift in ϵ' between 1 kHz and 1 MHz which is detected on a sample with painted silver electrodes disappears after annealing the sample at 450°C. The same sample with evaporated gold electrodes does not display any dependence of the dielectric permittivity between 1 kHz and 1 MHz.

Now we describe dielectric measurements at high frequency and for this we focus our attention on the FE–PE transition.

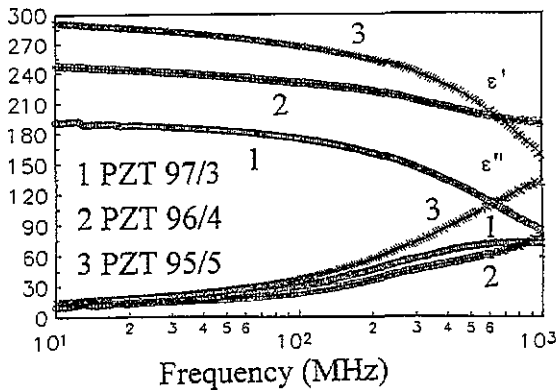


Figure 2. Real and imaginary parts of the dielectric permittivity measured in the high-frequency range at room temperature in PZT 97/3, PZT 96/4 and PZT 95/5 ceramics.

3. High-frequency results

Dielectric properties of the samples at high frequency have been obtained by means of an impedance analyser HP4191 using reflexion techniques. Within these techniques the complex reflection coefficient of the sample placed on the end of a coaxial line is measured [22].

Figure 2 shows the frequency dependence of $\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega)$ for various niobium-doped $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ ceramics (PZT 97/3, PZT 96/4, PZT 95/5) recorded at room temperature. This result is perfectly reproducible for samples of different sizes and different sample holders. It is clearly seen that for three samples, $\epsilon'(\omega)$ exhibits a decrease around 200 MHz whereas $\epsilon''(\omega)$ correspondingly increases. It is obvious that the dispersion step in ϵ' and the maximum in ϵ'' occur at frequencies much above the available maximum frequency (1 GHz) of our impedance analyser. This means that the value of the relaxation frequency lies above 1 GHz at room temperature. Our results are consistent with those recently reported, at room temperature only, in a bulk PZT by Li *et al* [29] as well as

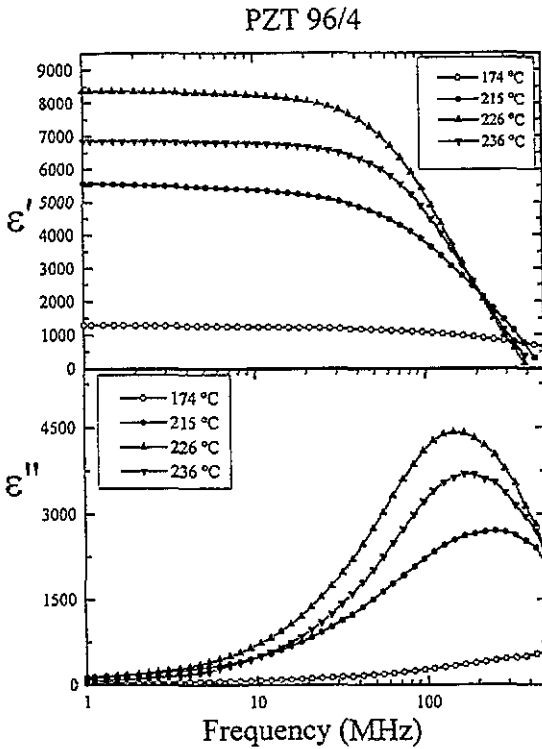


Figure 3. Dispersion of ϵ' and ϵ'' in PZT 96/4 recorded at various temperatures. The solid lines are guides for the eyes. Note the decrease of the position of the ϵ'' maximum between 174 °C and 226 °C and then its increase between 226 and 236 °C.

in pure PbZrO_3 ceramics by Lanagan *et al* [30]. They are also in agreement with results obtained by Kersten and Schmidt [31] in PZT with large x content. This last result was analysed in detail by Sayer *et al* [32]. These authors attributed the frequency dispersion to the equivalent electrical circuit components associated to the material with its electrodes. Our results show, on the contrary, that the frequency dependence of ϵ^* is intrinsic to the PZT material since it is detected in bulk as well as thin films [32]. The resistance and capacitance values of the equivalent circuit are expected to be largely different for bulk and thin-film materials. The possibility of an extrinsic origin of the dielectric dispersion observed in the present work is definitively discarded by the temperature dependence of the relaxation, as shown below.

Figure 3 illustrates the frequency and temperature dependences of both ϵ' and ϵ'' for PZT 96/4. The dispersion step in ϵ' considerably increases for temperatures above 150 °C, then still more on approaching 200 °C and finally decreases rapidly in the cubic phase. The maximum in ϵ'' is detected in the available frequency range for temperatures above 200 °C so that the dielectric dispersion parameters can be properly determined above this temperature only. The relationship between the dielectric data and the FE–PE phase transition can be thus studied. The Cole–Cole relaxation model,

$$\epsilon^* = \Delta\epsilon/[1 + i(\omega\tau)^{1-\alpha}] + \epsilon(\infty)$$

was used to fit the experimental dielectric data, where $\Delta\epsilon$ is the relaxation strength, τ the relaxation time and α the parameter describing the distribution around a mean relaxation value.

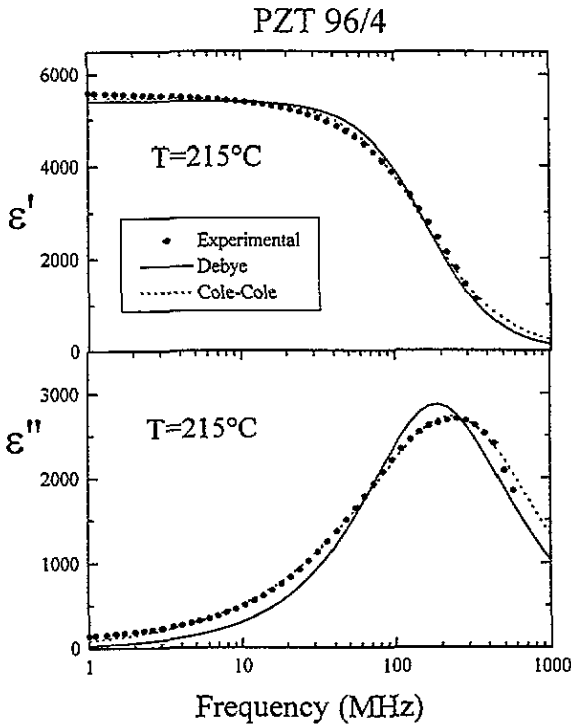


Figure 4. Experimental and calculated dielectric dispersion at 215°C in PZT 96/4. Note the agreement which is achieved for both ϵ' and ϵ'' between experimental data and the values calculated with the Cole-Cole form, except in ϵ'' for frequencies above 600 MHz.

It is shown in figure 4 that a simple Debye model

$$\epsilon^* = \Delta\epsilon/[1 + i\omega\tau] + \epsilon(\infty)$$

fails to fit the results for ϵ' and ϵ'' at 215°C exactly and that the Cole-Cole equation is required to achieve a better agreement with the experimental data. A small discrepancy above 600 MHz is noted between the experimental data and the values calculated with the Cole-Cole form. This may originate from the inductance and resistance of the contact in this frequency range. As suggested by Li *et al* [29], the field inhomogeneity within the sample can be also invoked for frequencies higher than 600 MHz.

The same behaviour as in PZT 96/4 is observed in PZT 97/3. The temperature dependence of the parameters $\Delta\epsilon$, $\tau^{-1} = f_r$ and α deduced from fitting of dielectric data in PZT 96/4 is analysed below.

We now discuss the origin of this large dielectric dispersion detected in PZT ceramics in the radiofrequency range.

We first clarify the intrinsic nature of the observed relaxation. This relaxation cannot be attributed to the electrical circuit RC formed by the electroded sample at the end of the electrical line of the analyser. In this case the product of the capacity C by the relaxation frequency f_r is expected to be equal to the contact resistance R and therefore to be temperature independent since this metallic resistance must have a monotonic and small variation versus temperature. Our data reported in figure 5 show that this possibility has to be discarded, since $f_r C$ is very temperature dependent.

The parameter α describing the distribution of relaxation times is also given in figure 5

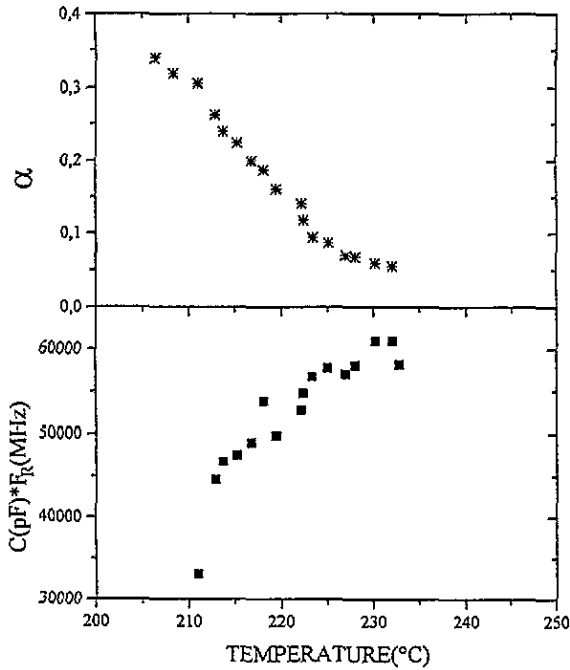


Figure 5. Variation of the product capacitance \times relaxation frequency and the parameter α versus the temperature as obtained for PZT 96/4.

as a function of temperature. It is interesting to note that the dispersion is almost monodispersive in the FE phase in the close vicinity of the phase transition and in the PE phase.

The parameter α deviates from the ideal Debye model by an amount at the maximum equal to 0.35 only for temperatures far away from the phase transition. In fact for these temperatures the frequency corresponding to the maximum of ϵ'' and to the decrease of ϵ' (see figure 3) is close to the frequency of the limitation of accuracy. Therefore the deviation α from the monodispersive behaviour could be not intrinsic but could arise from a limited accuracy of data in the very-high-frequency range. It may be concluded that the dielectric response is consequently mainly monodispersive in PZT ceramics with low Ti concentration, following the ideal Debye law quite closely.

Among the different physical origins of the intrinsic relaxation detected in PZT 97/3 and PZT 96/4, the grain influence as well as the domain motion can be ruled out for the following reasons.

First, the expected frequency of a shear resonance in a PZT grain of $10 \mu\text{m}$ has been calculated as approximately 240 MHz [33] at room temperature, which is much lower than the relaxation frequency detected in our measurements. Second, our data show that the relaxation has probably the same origin in the FE and PE phases, which thus excludes the influence of the macro ferroelectric domains but is not contradictory with the presence of clusters with micro or nanosize. The switching process of ferroelectric microdomains can be therefore invoked to explain the high-frequency dispersion.

The temperature dependence of the parameters $\Delta\epsilon$ and $f_r = \tau^{-1}$ are reported in figure 6 for PZT 96/4. The maximum of $\Delta\epsilon$ and the minimum of f_r occur at the same temperature, which is the PE-FE transition temperature 226°C . The relaxation process therefore exhibits

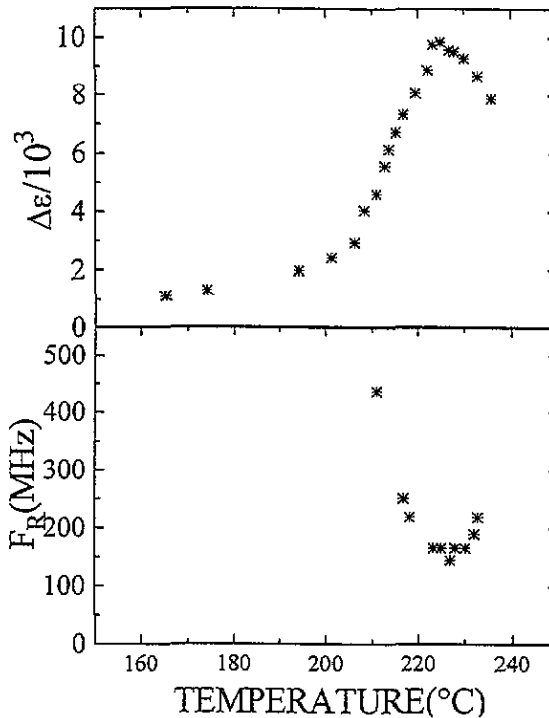


Figure 6. Temperature dependence of the relaxation frequency and the relaxation strength in PZT 96/4 as deduced from the fit of dielectric data with the Cole-Cole equation.

a critical slowing down. The critical temperature is given by the value where f_r can be extrapolated to zero. We find $T_C = 227^\circ\text{C}$, which can be compared with the value deduced from the Curie-Weiss law shown by the dielectric permittivity inverse as measured at 1 MHz, $T_0 = 198^\circ\text{C}$. The paraelectric-ferroelectric phase transition in PZT ceramics with low Ti concentration is clearly related to a relaxation critical slowing down, as in order-disorder systems.

Consequently the dielectric behaviour in PZT ceramics rich in zirconium is considerably different from that in PZT ceramics close to the 50/50 concentration, for which the very diffuse phase transition has been attributed to a dipolar glass mechanism [15].

The relaxation process is similar to that observed in BaTiO_3 -derived ceramics [34]. In this compound, the relaxation was ascribed to the coherent motion of off-centred titanium ions, in agreement with structural data. The same chain model may hold for PZT ceramics.

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