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Ti-induced and modified dielectric relaxations in PbZr$_{1-x}$Ti$_x$O$_3$ single crystals ($x \leqslant 0.03$) in the frequency range 10 Hz–10 MHz

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Abstract. Three relaxation processes for frequencies from 10 Hz to 10 MHz and for various Ti concentrations in PbZr$_{1-x}$Ti$_x$O$_3$ ($x \leqslant 0.03$) are presented. The lowest relaxation process (below 100 Hz in the paraelectric phase) is attributed to electrochemical processes contributing to the dielectric polarization. The second is strong low-frequency dipolar relaxation (up to 1 kHz in the paraelectric phase) which has a nearly monodispersive character and is related to the disorder in the oxygen sublattice. While for pure PbZrO$_3$ the contribution of the dielectric step $\Delta\varepsilon$, coming from this relaxation, to $\varepsilon'(T)$ was temperature independent, for PbZr$_{1-x}$Ti$_x$O$_3$ it becomes a function of temperature. The third relaxation in the range of a few kilohertz visible in the transient phase and above T_c appears because of Ti introduction and comes from the interface dynamics of the polar regions in the paraelectric phase and motion of the domain walls in the intermediate phase of ferroelectric properties.

1. Introduction

The marked interest recently evidenced in the question of dielectric relaxation in many ferroelectric materials is reflected in the literature. Dielectric dispersion in both ceramics and single crystals has been studied for such model materials as BaTiO$_3$ [1, 2], KNbO$_3$ [3], BaTiO$_3$:Fe [4], BaTiO$_3$:Nb [5], KTaO$_3$:Li [6], KTaO$_3$:Nb [7] and PZT [8]. In general, dielectric dispersion can be expected in several ferroelectric materials in a very wide frequency range from a few hertz up to 1 GHz but the central problem as yet unresolved is that of the origin and physical mechanisms of particular relaxations. Solving this problem could be of considerable importance for the description of the nature of both phase transitions (order–disorder or displacive)† and the mechanisms responsible for the $\varepsilon'(T)$ dependence, especially in the vicinity of the phase transition point. For example the relaxation found near T_c in BaTiO$_3$ in the 10^8 Hz range calls into question the purely displacive mechanism postulated for the phase transition in this material. According to Maglione *et al* [4] the behaviour of the dielectric susceptibility above T_c' in this material originates directly from temperature changes of relaxation step calculated from the Debye-like relaxation observed. On the other hand, for KNbO$_3$ [3], based on Raman and dielectric measurements, a model

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† Ferroelectrics are often categorized as being of either displacive or order–disorder character. In the former case the paraelectric phase is microscopically non-polar and in the latter only non-polar in a macroscopic or thermally averaged sense.

of coupled order–disorder motion of the central ion (Nb) and optical phonon was derived to explain the $\varepsilon'(T)$ response.

Recently many papers dealing with the problem of dielectric relaxations have concentrated mainly on ferroelectric perovskites. Information on relaxation effects in antiferroelectric materials of the same structure is very sparse. In our recent paper [9] we have reported a dipolar relaxation found in pure lead zirconate ($PbZrO_3$) which is the best known perovskite among antiferroelectrics. This relaxation was clearly detected in the paraelectric phase at low frequencies (20 Hz–20 kHz) and thus had a marked influence on the $\varepsilon'(T)$ function measured with an AC field in this range. The contribution of the dielectric strength $\Delta\varepsilon$ to the $\varepsilon'(T)$ function calculated from this relaxation is significant even 100 K above $Tc(= 510\ K)$ and has an unusual form, i.e. $\Delta\varepsilon(T) = $ constant. This disagrees with the results obtained in a similar frequency range by Bidault [10] for several perovskite materials, polar and unpolar, for which $\Delta\varepsilon$ was temperature dependent (673–873 K). This was taken to be related to the occurrence of space charge or a surface layer. On the basis of previously performed x-ray diffraction investigations [11] we suggested that this relaxation could be connected with disorder in the sublattice of oxygen atoms. While this disorder was frozen at room temperature, it might have led to the creation of mobile dipoles in a set of ZrO_6 octahedra relaxing with respect to the Pb sublattice. The large size and mass of these dipoles would explain the low frequency at which this dispersion occurred.

In this paper, we report our dielectric relaxation investigations on $PbZrO_3$ in which Ti ions were introduced to the system, replacing the 'central' Zr ion. The introduction of the substituted component and widening of the frequency range were designed to help to elucidate the nature and origin of the dielectric relaxation observed in $PbZrO_3$.

2. The problem of stoichiometry in $PbZr_{1-x}Ti_xO_3$

The properties of solid solutions of the antiferroelectric $PbZrO_3$ with ferroelectric $PbTiO_3$ are described by very complex phase diagrams [12–15]. This refers in particular to $PbZr_{1-x}Ti_xO_3$ (PZT) solid solution with a Ti concentration of a few molar per cent. When Ti ions are added to the system, x-ray investigations show the existence of an intermediate phase below T_c. On the basis of x-ray, dielectric, pyroelectric, piezoelectric and DTA measurements, many workers have tried to relate the width of the transient phase to the concentration of Ti in PZT (the more Ti ions in the system, the broader is the transient phase). This concept was fairly successfully verified in the case of ceramic materials but seemed to fail when single crystals were considered. The problem is in the concentration of point defects in the Pb and/or O sublattices, which is so easily produced in the technological process. For this reason, in the growth process, it is possible to obtain two kinds of $PbZrO_3$ single crystal. The first, exhibiting only one phase transition directly from the cubic (paraelectric) to the orthorhombic (antiferroelectric) phase and the second in which a sufficiently high concentration of point defects can provoke a ferroelectric transient phase appearing below T_c [16, 17]. The temperature range of this transient phase can even be some tens of kelvins [15]. X-ray examination showed that crystals with one phase transition are structurally more perfect than those with two transitions which exhibit structural non-homogeneity, i.e. superposition of two different orthorhombic systems and two different cubic systems (all with nominally differing lattice constants) is present in the antiferroelectric and paraelectric phase, respectively [18]. It is well known that Ti ions introduced into the lead zirconate also radically change the properties of solid solutions obtained from this compound. Ti substitution induces the formation of polar regions even in the paraelectric

phase [19] and also significantly extends the temperature range of the occurrence of the intermediate phase towards lower temperatures [20]. As a consequence, both causes, i.e. the point defects and introduction of Ti ions, can influence the range and nature (ferroelectric or mixture of paraelectric, ferroelectric and antiferroelectric phases) of the intermediate phase in PZT. Thus it may be expected that for a PbZrO$_3$ single crystal with the same Ti concentration the temperature range of the transient phase may vary and could differ considerably from that reported in the literature.

For this reason the Ti concentration in each single crystal under investigation was determined by x-ray microanalysis.

3. Crystal growth and composition determination

Investigations were performed on the crystals produced by the flux method. A mixture of PbZrO$_3$, PbTiO$_3$, PbO and B$_2$O$_3$ was used and the soaking process was carried out in a Pt crucible at a temperature of 1350 K for 4 h. Then the melt was cooled at a rate of 9 K h^{-1} to 1200 K and the solvent was poured off. A constant-temperature gradient of 8 K cm^{-1} was maintained along the crucible axis. Transparent light-grey crystals in the form of thin plates were obtained and used in the investigations. The opposite faces were electroded using cold silver paste and then the dielectric permittivity (ε' and ε'') was measured with a Hewlett–Packard 4192 Impedance analyser. In this layout the sample was considered to be a lossy capacitor with lumped-circuit capacitance C and resistance R. Investigations were performed in the frequency range 10 Hz $< f <$ 13 MHz and temperature range 300 $< T <$ 630 K on PbZr$_{1-x}$Ti$_x$O$_3$ compositions in which $x = 0.0015, 0.018$ and 0.03. To avoid time-dependent effects [21] the capacity was measured after a time (about 20 min) when changes in C had become negligible. The real and imaginary parts of dielectric permittivity were calculated from the relations $\varepsilon' C_0 = C$ and $\varepsilon'' = \varepsilon' \tan \delta$ and where C is the empty-cell capacitance. C and $\tan \delta$ were recorded directly from the analyser.

4. Experimental results

Figure 1 shows the temperature dependence of ε' measured at a frequency of 100 kHz on cooling and heating the PbZr$_{0.97}$Ti$_{0.03}$O$_3$ single crystal. ε_{max} corresponds to the transition from the paraelectric to the intermediate phase and the next anomaly on the $\varepsilon'(T)$ characteristics indicates the transition to the antiferroelectric phase. On heating, changes in ε' are shifted towards higher temperatures owing to the thermal hysteresis effect. The inset in figure 1 shows that the Curie–Weiss-like law above T_c is obeyed satisfactorily.

4.1. Relaxation in the paraelectric phase (10 Hz–20 kHz)

In figure 2(a) and (b) the frequency dependences of the real and imaginary parts, respectively of ε^* for the PbZr$_{0.97}$Ti$_{0.03}$O$_3$ sample were presented for various temperatures from 620 to 510 K i.e. for the paraelectric–intermediate phase transition on a logarithmic scale.

Data obtained for each temperature were systematically fitted to the Cole–Cole expression

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_s \varepsilon_\infty}{1 + (i\omega\tau)^{1-\alpha}} \tag{1}$$
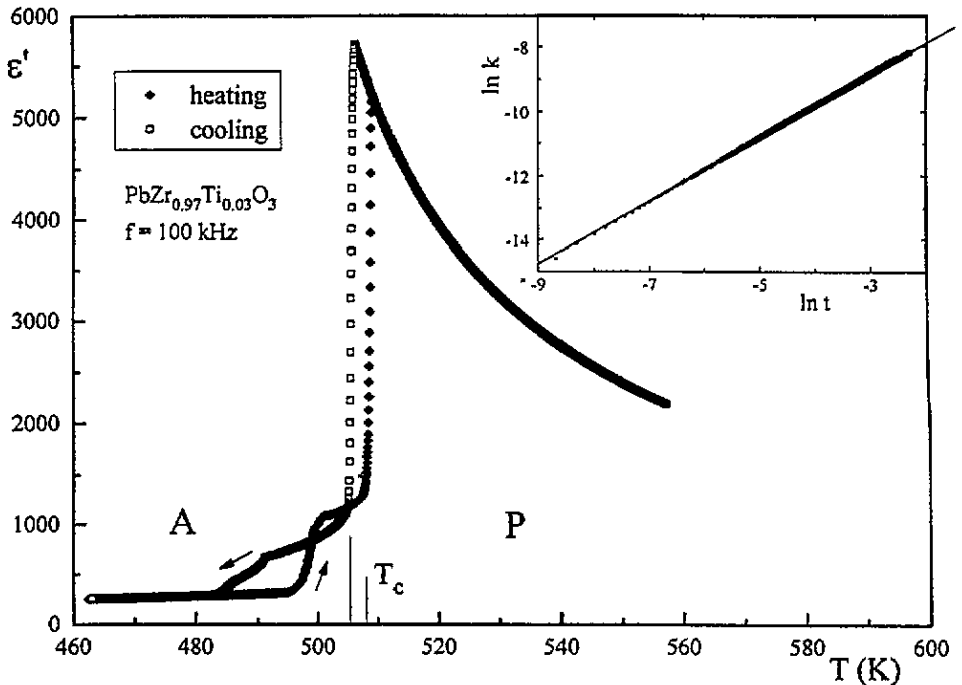
Figure 1. Temperature dependence of the real part of ε' on cooling and on heating for a $PbZr_{1-x}Ti_xO_3$ single crystal measured at a frequency of 100 kHz. The inset shows the Curie–Weiss-like law $\varepsilon = C/(T - T_0)\gamma$ obeyed in the paraelectric phase with $\gamma = 0.98$ ($k = 1/\varepsilon - 1/\varepsilon_{max}$; $t = (T - T_c)/T_c$).

where ε_s and ε_∞ are the static permittivity and permittivity measured above the dispersion region, respectively, τ is the mean relaxation time and ω is the angular frequency. The parameter α determines the distribution of relaxation times and can take values between 0 and 1. When α approaches 0, the customary Debye relaxation is recovered. Thus α is the measure of a departure from pure Debye behaviour, i.e. polydispersion. In all our samples the calculated values of α are less than 0.16.

The large ε'' found at low frequencies (see figure 2(b)) is due to the presence of DC conductivity represented by σ_c and gives a contribution to ε^* in the form

$$\varepsilon^*(\omega) = \varepsilon' - i\left(\varepsilon_p'' + \frac{\sigma_c}{\omega\varepsilon_0}\right) \tag{2}$$

$$\sigma_c = \sigma_0 \exp\left(\frac{-W}{kT}\right). \tag{3}$$

The subscripts p and c refer to the polarization and conductivity contributions, respectively. It may be seen that the imaginary part of dielectric response consist of two components: firstly the frequency-independent conductivity response of free charges; secondly the frequency-dependent polarization loss response of dipoles. With this assumption both parts of ε'' were fitted simultaneously and the relaxation parameters were calculated. A typical example of fit for a chosen temperature is presented in figure 3. The calculated relaxation
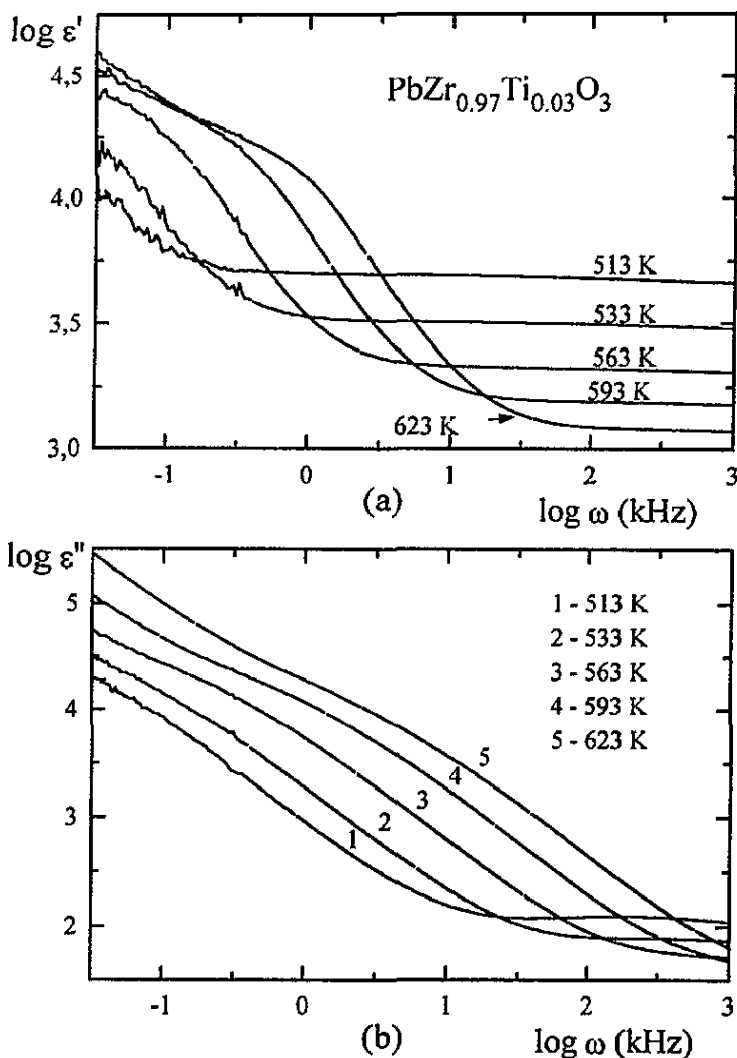
Figure 2. Temperature–frequency functions of (a) ε' and (b) ε'' for the PbZr$_{0.97}$Ti$_{0.03}$O$_3$ sample in the paraelectric phase.

times τ obey an Arrhenius-type function:

$$\tau = \tau_0 \exp\left(\frac{E_a}{kT}\right) \tag{4}$$

as shown in figure 4 for different samples. The values of the activation energy are given in the figure for each Ti concentration and compared with that for pure PbZrO$_3$.

By fitting the lowest-frequency data of ε'', values of thermally stimulated conductivity σ_c were obtained and presented in figure 5 in the form $\ln \sigma_c$ versus $1/T$. Using a simple linear regression method the values of activation energy W were calculated and added to the figure. The value of σ_c in pure PbZrO$_3$ varies between about 10^{-6} and 10^{-5} Ω^{-1} m^{-1}. The contribution of Ti to PZT is shown as an increase in the value of the DC electrical conductivity up to about 10^{-4} Ω^{-1} m^{-1}.
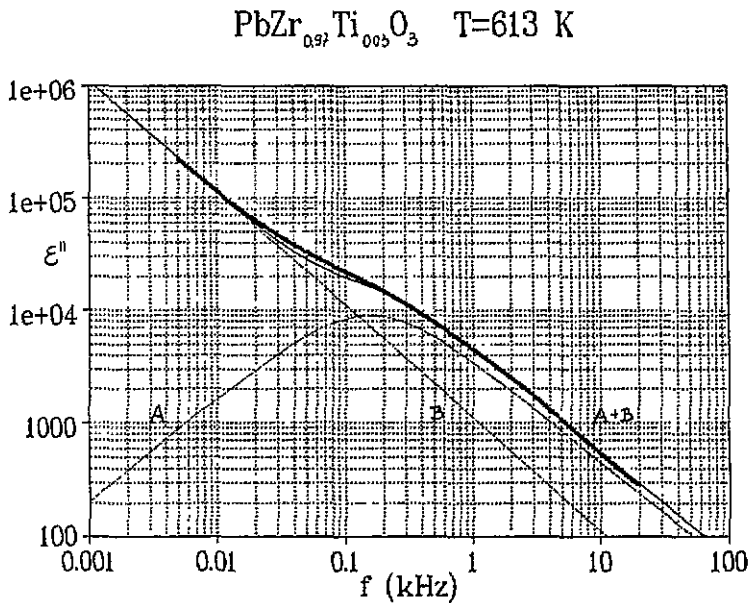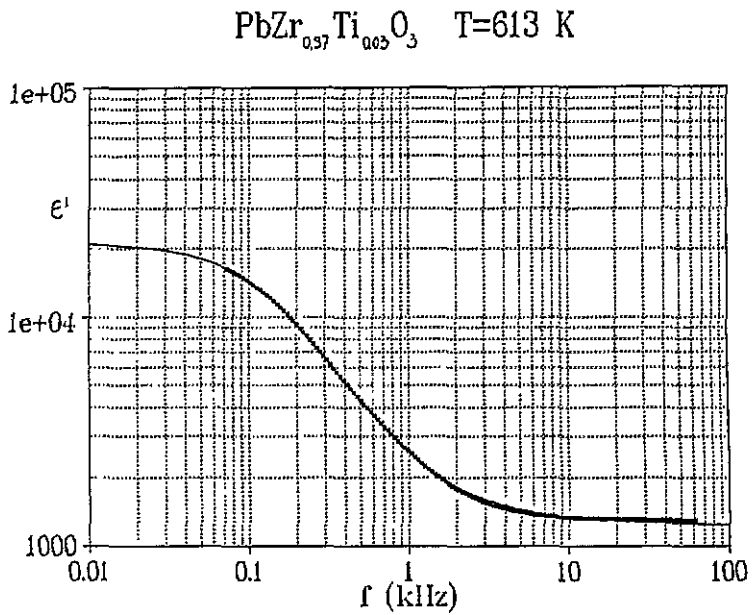
$$\mathrm{PbZr}_{0.97}\mathrm{Ti}_{0.03}\mathrm{O}_3 \quad \mathrm{T=613\ K}$$

$$\mathrm{PbZr}_{0.97}\mathrm{Ti}_{0.03}\mathrm{O}_3 \quad \mathrm{T=613\ K}$$

Figure 3. (a) An example of the fitting procedure using the Cole–Cole formula for $\varepsilon'(\omega)$ ($\alpha = 0.11$) at 613 K. (b) $\varepsilon''(\omega)$ at 613 K separated into 'pure' $\varepsilon''(\omega)$ (curve A) and that from the DC conductivity (σ_c) contribution (see text) (curve B).

While the value of the energy W has been calculated from equation (3), which is characteristic for a system with hopping charge carriers, E_a refers to a relaxational motion with evident loss peak. Values of W and E_a are of the same order, 1 eV and are typical for single-particle excitation. This coincidence does not seem to be accidental since in
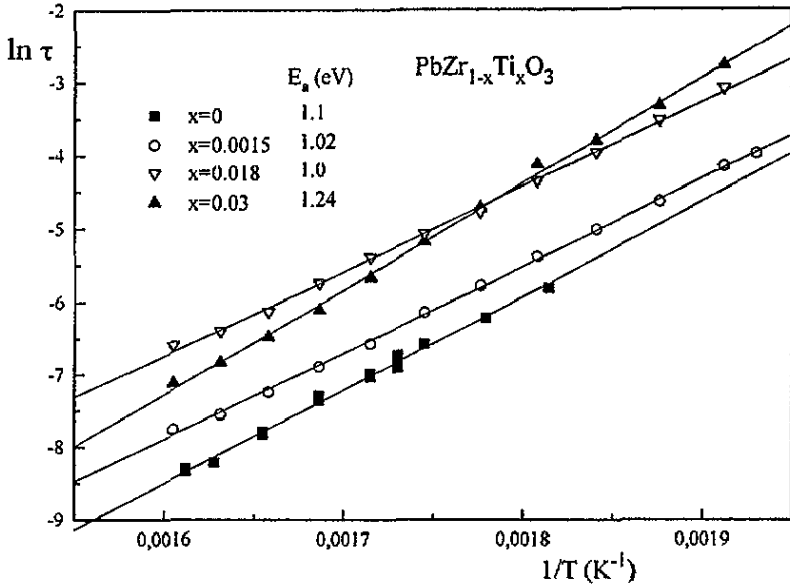
Figure 4. Arrhenius plots of the relaxation times for various Ti concentrations. E_a-values were calculated with an error of ± 0.02 eV.
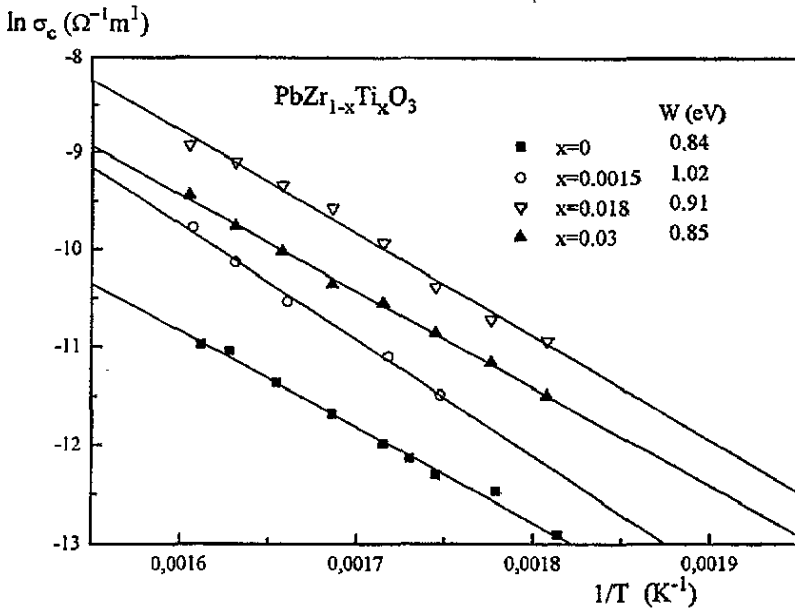

Figure 5. Plots of the thermally stimulated conductivity σ_c versus reciprocal of temperature. W-values were calculated with an error of ± 0.02 eV.

a disordered system even single-particle moment may produce a large change in dipole moment and thus lead to the low-frequency relaxation observed. However, the relaxation

time $\tau_0 = 10^{-12}$ s in (4) is lower than that corresponding to the usual ionic frequencies of 10^{13} Hz ($\tau \simeq 10^{-15}$ s) and thus indicates that this is more cooperative rather than a single-ion process.

Unlike pure PbZrO$_3$, in the paraelectric phase the dispersion step ($\varepsilon_s - \varepsilon_\infty$) becomes temperature dependent (figure 6).
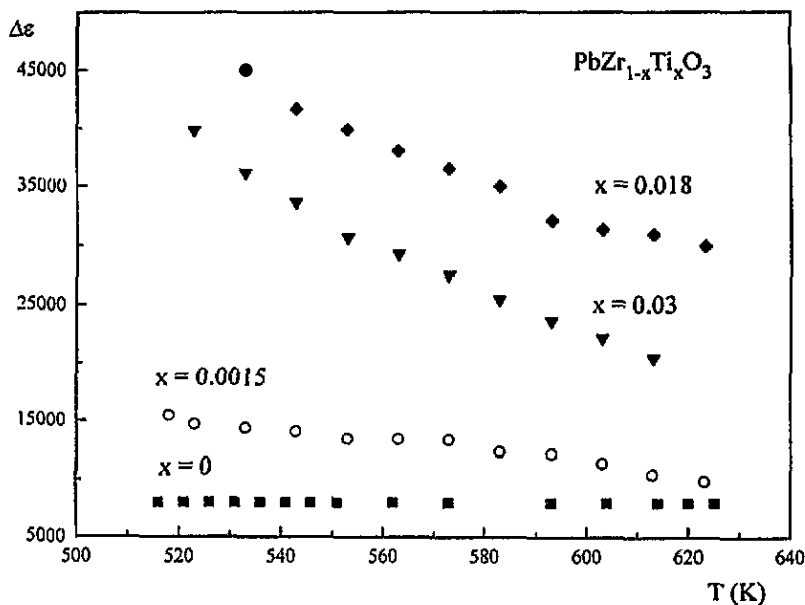

Figure 6. Dispersion step $\Delta\varepsilon = (\varepsilon_s - \varepsilon_\infty)$ versus temperature in the paraelectric phase for various Ti concentrations in PZT and compared with pure PbZrO$_3$.

4.2. Relaxations in the transient phase (1 kHz–1 MHz)

As mentioned above, when Ti ions are substituted for the central Zr ions, a new phase called the intermediate phase is created below T_c. In this phase and up to a little above $T_c(T_c + 30$ K) we observed a new independent relaxation process in the frequency range 1 kHz–1 MHz. While the low-frequency relaxation process was nearly monodispersive ($\alpha \simeq 0.11$–0.16), the second process at higher frequencies is strongly polydispersive ($\alpha \simeq 0.4$ for $x_{Ti} = 0.03$). The real and imaginary parts of this relaxation process for PbZr$_{0.97}$Ti$_{0.03}$O$_3$ in the intermediate and paraelectric phases up to 533 K are presented in figures 7 and 8.

On the assumption that the left side of the observed 'new' relaxation corresponds to the right side of the low-frequency part of relaxation, the overall dielectric response has been fitted to a superposition of two Cole–Cole equations (equation (1)). The sample fits are presented in figures 9(a) and (b) for the real and imaginary parts, respectively. The parameters τ and $\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty$ of the second relaxation calculated from the fits are given in figure 10.

In the paraelectric phase the mean relaxation time τ of the second process is temperature dependent. Near T_c, τ reaches a value of 3.4×10^{-6} s and below T_c becomes virtually constant. $\Delta\varepsilon$ coming from this relaxation also exibits a distinct anomaly at T_c and follows
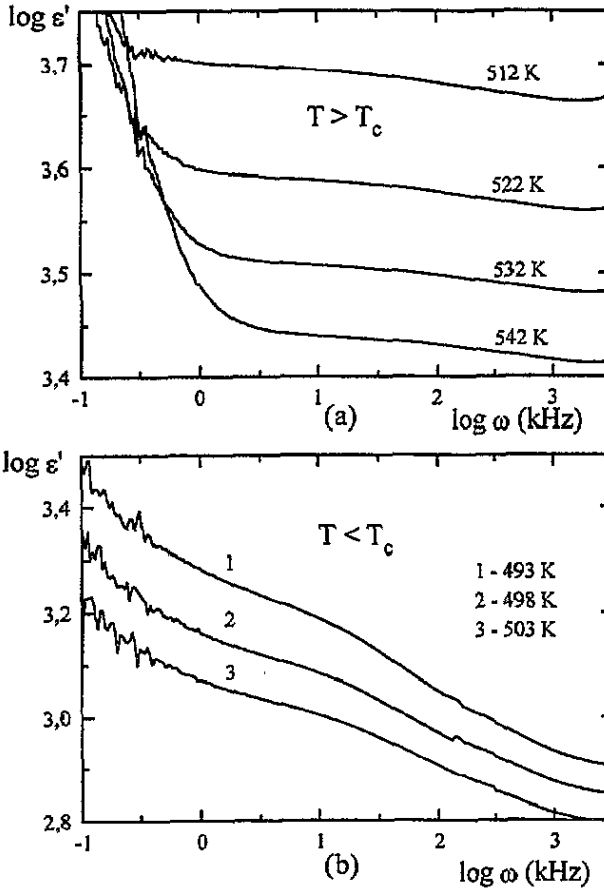
Figure 7. The real parts of the higher-frequency relaxation process for $PbZr_{0.97}Ti_{0.03}O_3$ in (a) the paraelectric and (b) the intermediate phases.

the shape of $\varepsilon'(T)$ presented in figure 1, showing clearly that this relaxation is closely related to the phase transition.

5. Conclusions

The overall dielectric response investigated for $PbZr_{1-x}Ti_xO_3$ single crystals at frequencies up to 10 MHz can be divided into three parts.

(1) A strong very-low-frequency response below 100 Hz at 623 K (figure 3; note the logarithmic scale) in the paraelectric phase visible in the imaginary and real part of the dielectric permittivity is related, in our opinion, to electrochemical processes contributing to the dielectric polarization whether it be a volume or a surface.

(2) A strong low-frequency dipolar relaxation up to 1 kHz in the paraelectric phase giving a marked contribution to the $\varepsilon'(T)$ dependence, which is contrary to the behaviour of pure $PbZrO_3$. For pure $PbZrO_3$ a strong low-frequency relaxation for which $\Delta\varepsilon$ was

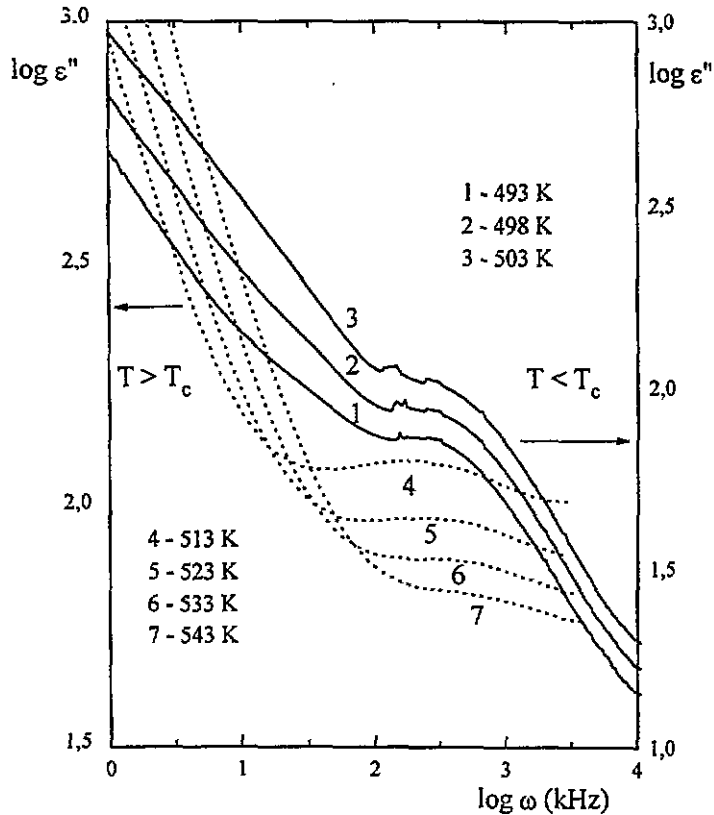**Figure 8.** The imaginary part of the higher-frequency relaxation process for $PbZr_{0.97}Ti_{0.03}O_3$ in the paraelectric and intermediate phases.

invariant with temperature is found, similar to that for polarization limited by non-thermal forces, e.g. by elastic constraints [22]. The introduction of Ti ions does not significantly change the frequency range of occurrence of this relaxation in comparison with pure $PbZrO_3$ but clearly changes the relaxation strength $\Delta\varepsilon$ which at the same time becomes temperature dependent. We suggest that in a $PbZrO_3$ single crystal with Ti ions replacing Zr there is a specific coupling between local polarization induced by Ti, polarization limited by non-thermal forces and the electronic conductivity (see, e.g., [5]).

(3) Much weaker relaxation in the range of few kilohertz is clearly visible in the transient phase and above T_c. This relaxation appears owing to Ti introduction and generally comes from the interface dynamics in both the paraelectric and the intermediate phases. In the paraelectric phase the local polar regions are formed and their size increases with respect to the paraelectric matrix on approaching T_c from the high-temperature side. In an AC electric field the behaviour of phase boundaries between the polar region and paraelectric matrix would thus be responsible for the relaxation observed. In the intermediate phase of ferroelectric properties, dielectric relaxation may be related to motion of the walls in a complex domain structure observed under a polarizing microscope. The polydispersive behaviour found in this phase would also favour the explanation proposed. The ε time variation observed by Roleder *et al* [21] in the intermediate phase provides additional evidence for the existence of domain-wall relaxation in this phase. On the other hand

$$\mathrm{PbZr_{0.97}Ti_{0.05}O_3} \quad T{=}503 \ K$$

$$\mathrm{PbZr_{0.97}Ti_{0.03}O_3} \quad T{=}503 \ K$$
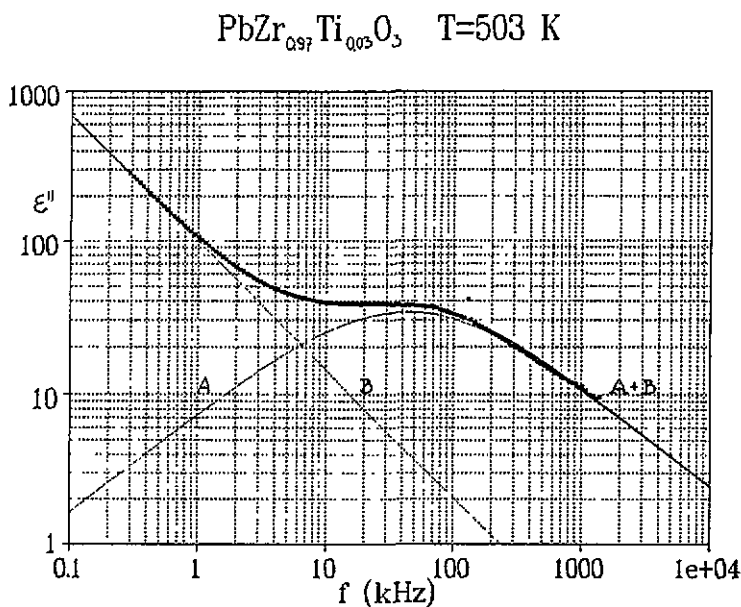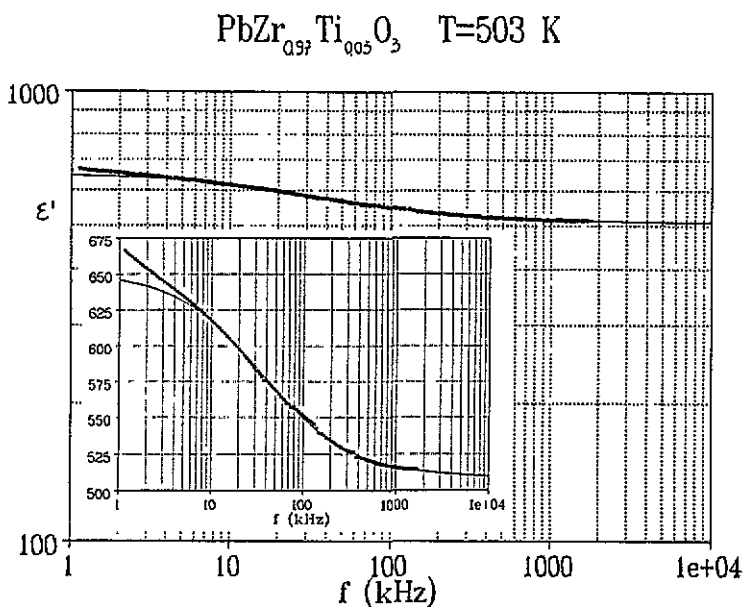
Figure 9. (a) $\varepsilon'(\omega)$ on a log–log and linear-log scale (see inset) at 503 K: an example of the fitting procedure using the Cole–Cole formula ($\alpha = 0.4$). (b) $\varepsilon''(\omega)$ at 503 K separated into the higher-frequency $\varepsilon''(\omega)$ (curve A) and the high-frequency response of the low-frequency relaxation (curve B).

the action of a sufficiently strong DC electric field, which eliminates or pins the domain structure, removes the relaxation process. This can also be seen as further proof that this relaxation is due to interface dynamics.
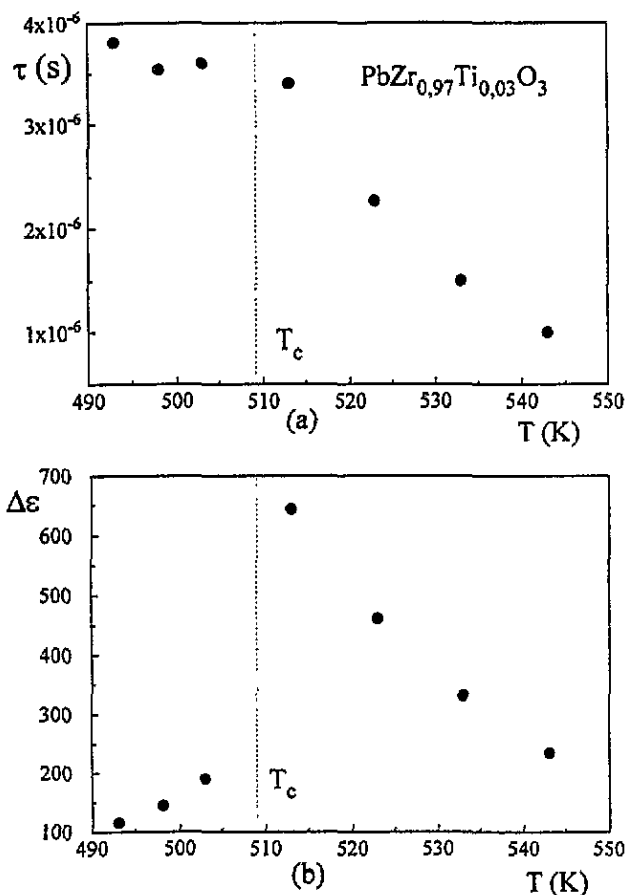
Figure 10. Calculated parameters (a) τ and (b) $\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty$ of the higher-frequency relaxation process presented as functions of temperature slightly above and below the phase transition.

In the case of pure $PbZrO_3$ which exhibits a defect-induced transient phase, one could expect the appearance of a similar kind of relaxation. Indeed this kind of behaviour was perceived in the paraelectric phase of single $PbZrO_3$ crystals with a narrow transient phase (2–3 K). However, the strength of dielectric dispersion observed was much weaker than found in PZT samples and at the same time difficult to describe quantitatively. The weakness of this process indicates that in fact for the relaxation detected in the range of a few kilohertz in PZT crystals we cannot exclude a contribution from the dipole-like motion of polar regions induced by structural imperfections (point defects).

Acknowledgments

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