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Mechanical and electrical driving field induced high-frequency dielectric anomalies in ferroelectric systems

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Abstract

Polycrystalline or single-crystal ferroelectric materials present dielectric dispersion in the frequency range 100 MHz–1 GHz that has been attributed to a dispersive (relaxation-like) mechanism as well as a resonant mechanism. Particularly in ‘normal’ ferroelectric materials, a dielectric response that is indistinguishable from dispersion or a resonance has been reported. Nevertheless, the reported results are not conclusive enough to distinguish each mechanism clearly. A detailed study of the dielectric dispersion phenomenon has been carried out in PbTiO₃-based ferroelectric ceramics, with the composition Pb_{1-x}La_xTiO₃ ($x = 0.15$), over a wide range of temperatures and frequencies, including microwave frequencies. The dielectric response of La-modified lead titanate ferroelectric ceramics, in ‘virgin’ and poled states, has been investigated in the temperature and frequency ranges 300–450 K and 1 kHz–2 GHz, respectively. The results revealed that the frequency dependence of the dielectric anomalies, depending on the measuring direction with respect to the orientation of the macroscopic polarization, may be described as a general mechanism related to an ‘over-damped’ resonant process. Applying either a uniaxial stress along the measurement field direction or a poling electric field parallel and/or perpendicular to the measuring direction, a resonant response of the real and imaginary components of the dielectric constant is observed, in contrast to the dispersion behavior obtained in the absence of the stress, for the ‘virgin’ samples. Both results, resonance and/or dispersion, can be explained by considering a common mechanism involving a resonant response (damped and/or over-damped) which is strongly affected by a ferroelastic–ferroelectric coupling, contributing to the low-field dielectric constant.

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1. Introduction

Over the last five decades, the investigation of the microwave dielectric properties of ferroelectric materials has been one of the most challenging tasks in the field of ferroelectricity [1]. High stability of the dielectric parameters, such as real and imaginary components of the dielectric constant (κ' , κ'') and low dielectric losses ($\tan \delta$) in a wide frequency range, have led to rising interest in using ferroelectric materials in the high-frequency region [1]. The dielectric dispersion can provide information on the dynamics of the mechanism of phase transitions and shows the frequency region where the ferroelectrics are useful for practical applications [2]. Within the most commonly used ferroelectric materials, the barium titanate and others perovskite-type structure ferroelectrics have been distinguished because they have presented an intrinsic dispersion phenomenon near 1 GHz [3, 4]. This behavior can limit their use specifically to communication systems and electrically controlled devices, such as phase shifters [5]. The physical and dielectric properties, such as the dispersion mechanism, can be investigated by analyzing the complex dielectric constant in a broad frequency range. The study of such mechanisms requires the ability to work over both large frequency and temperature ranges, where coaxial cells and network analyzers are commonly used [6].

In this context, such dielectric dispersions were first observed in the so-called 'normal' ferroelectrics [7, 8], being characterized later in relaxor ferroelectrics (relaxors) [9, 10] and more recently in antiferroelectrics [11] and incipient ferroelectrics [12]. However, it is well known that normal ferroelectrics have micro-sized polar regions (domains) with long-range order [13], while relaxors and doped-incipient ferroelectrics have nanometric polar regions (nanodomains) distributed in a non-polar matrix, in which a short-range order prevails [14]. Therefore, the occurrence of such a common dispersion process in such different kinds of ferroelectric systems has encouraged the development of several mutually excluding models to explain this physical phenomenon [8, 10, 15–17], in terms of either a grain or ferroelectric domain resonance [18, 19], as well as the correlation between the ferroelectric polar structures and their respective dynamical response [20].

Previous investigations of both ceramics and single crystals of BaTiO_3 [7] and other perovskite-type structure ferroelectric materials [21] suggest the presence of a large dielectric dispersion in the gigahertz region, which was reported to be close to dipolar character (that is to say, like a Debye-type relaxation). In spite of still not being clarified, several theoretical attempts have been proposed to explain the origin of this effect. The relation between the high-frequency dielectric dispersion and the microstructure of ceramics was expressed by Hippel [22], who attributed the piezoelectric resonance of the grain as the principal cause of the observed microwave anomalies. Kittel [23] suggested that the motion of the domain walls has an inertial component. He attributed the decrease in the dielectric constant in the microwave region to the resonance of the domain walls in ceramics. Some other models based on the piezoelectric resonance of individual domains [24] or on correlated hopping of off-centered ferroelectric active ions between several potential wells [17] have been proposed in more recent years. In all cases, the structural disorder on the atomic scale, assuming the two-minimum potential relief for some lattice ions, was used as the principal cause for the high-frequency dielectric dispersion. As observed, the dielectric dispersion in ferroelectric materials has been a well-investigated issue, however more recent experimental results [25] showed evidence of resonant dielectric behavior, rather than the previously observed dielectric dispersion. It has been shown that the resonant behavior may coexist, in the same systems that were studied, together with the dispersion behavior, under certain conditions. Therefore, it seems that the high-frequency dielectric response in ferroelectric materials, observed near 1 GHz, is dictated by a universal mechanism involving a resonant response (damped or over-damped), which until now has not been fully clarified.

The objective of the present work is to investigate the nature of the microwave dielectric dispersion in ferroelectric materials, giving a better understanding of the dispersion or resonant behavior verified in ‘normal’ ferroelectric materials at microwave frequencies. The present work proposes the fulfillment of dielectric studies considering both the influence of an external uniaxial stress, acting on the samples in the ‘virgin’ state, and the influence of the measurement electric field (E) directed not only parallel but also perpendicular to the orientation of the polarization (P) in pre-poled and ‘stress free’ PbTiO_3 -based ceramic samples, for a composition whose high-frequency dielectric properties have scarcely been investigated. It is shown that the observed dielectric anomalies in the microwave region really correspond to an over-damped resonance mechanism associated with the polar regions present in the ferroelectric systems. The ‘damping strength’ is described as arising mainly from the ferroelastic dipolar contributions instead of the ferroelectric ones, depending on the relative orientation between the macroscopic polarization and the measurement electric field direction. The dielectric anomalies observed near 1 GHz are discussed considering the influence of a mechanical and electrical driving field on the dielectric response. Thus, we expect to obtain an improved understanding of the physical mechanisms responsible for such dielectric anomalies, which can allow us to elaborate a more general model.

2. Experimental procedure

$\text{Pb}_{1-x}\text{La}_x\text{TiO}_3$ ceramics, with $x = 0.15$ (hereafter labeled PLT-15), were prepared by the conventional oxide mixing process. High reagent grade powders (PbO , La_2O_3 and TiO_2) used as precursor oxides were mixed in a ball mill, dried and calcined at 1123 K for 3.5 h. Disc-shaped samples were uniaxially and isostatically pressed, and then sintered at 1423 K in a saturated PbO atmosphere for 3.5 h. The sintered samples were polished and heat treated at 873 K for 20 min. Structural, microstructural and compositional characterizations of the samples were performed through x-ray diffraction, scanning electron microscopy (SEM) and energy dispersive x-ray (EDX) analysis, respectively. The results revealed a $\text{Pb}_{0.85}\text{La}_{0.15}\text{TiO}_3$ composition with tetragonal symmetry and an average grain size of $2 \mu\text{m}$. Gold electrodes were sputtered onto the samples in the form of discs with a diameter of 2.0 mm and a thickness of 0.5 mm.

The high-frequency dielectric measurements were carried out in the temperature range 300–450 K using a HP-8719C Network Analyzer covering a frequency range of 50 MHz–2 GHz, for the ‘stress free’ and stressed samples in ‘virgin’ state. In order to obtain the dielectric response of materials, the reflectometry technique [6] was employed by using a 50Ω coaxial line. The uniaxial stress was applied using an experimental setup containing a controllable pressure sample holder coupled to the coaxial line, as reported previously [6]. The main function of this sample holder is to provide a controllable and reproducible pressure level on the samples to avoid either undesirable uniaxial compression or contact loss between the sample and the electrodes, originating from thermal expansion or contraction during the heating or cooling process. To determine the frequency dependence of the reflection coefficient (Γ' , Γ''), a careful compensation procedure was carried out to account for spurious reflections that may result from transmission line discontinuities and also to eliminate the effect of the resistances and capacitances of the sample holder. Three different HP standard terminations (open, short and 50Ω), with reflection coefficients of 1, -1 and 0, respectively, were used to calibrate the system in the investigated frequency range. The real and imaginary components of the complex dielectric constant ($\kappa^* = \kappa' - j\kappa''$) were determined from the measured complex reflection coefficient [6]. After that, the dielectric response was established in poled samples ($E_p = 2 \text{ kV mm}^{-1}$) in both parallel and perpendicular directions to the poling direction, at room

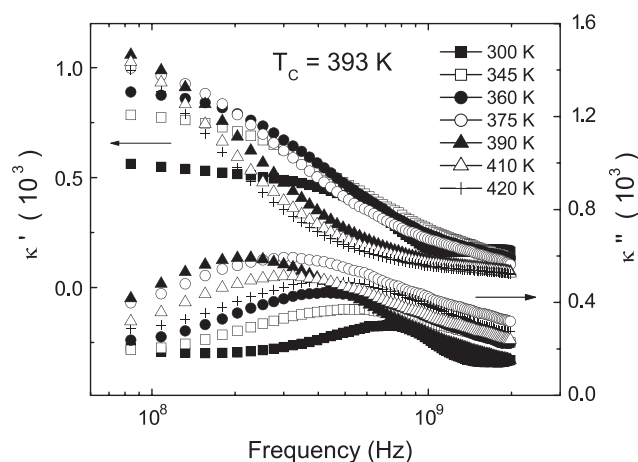


Figure 1. Frequency dependence of the real and imaginary components of the dielectric constant for temperatures below and above the transition temperature, T_C .

temperature and in the same frequency interval, following the same experimental procedure described previously. It is important to point out that the poled samples in the direction perpendicular to the poling direction were obtained from previously poled bar-shaped samples. A careful cutting procedure was carried out in the direction perpendicular to the poling direction in order to obtain the samples in the form of a disc by using a SBT 380 Ultrasonic Machine. A water cooling system was used in order to maintain the poling pattern in the poled samples during the cutting procedure, to avoid thermal variations in the samples. The low-frequency measurements were performed using an HP 4194A Impedance Analyzer in the temperature and frequency ranges 300–450 K and 1 kHz–10 MHz, respectively.

3. Results and discussions

3.1. High-frequency dielectric dispersion

The Curie temperature of the samples, $T_C \sim 393$ K, was determined from dielectric measurements of κ' at low frequencies (1 kHz). Figure 1 shows the frequency dependence of the real, κ' , and imaginary, κ'' , components of the dielectric constant for the PLT-15 ceramics that were studied, at different temperatures. A dielectric response indistinguishable from a dispersive behavior was observed in the whole analyzed temperature interval. As can be seen, for a fixed temperature (i.e. at 300 K) and in the frequency range 70–400 MHz, κ' decreases slightly as the frequency increases. Above 400 MHz, κ' decreases quickly, whereas κ'' passes through its maximum value. The frequency corresponding to the maximum imaginary component of the dielectric constant ($f_R = 700$ MHz) is known as the characteristic frequency of the dispersive process, and it is associated with a polarization mechanism responsible for the dissipation. The obtained value for the characteristic frequency is in agreement with those reported for other ferroelectric materials commonly used for microwave applications [18, 26].

The origin of this behavior has been attributed to the ferroelectric domain walls vibrations in the ferroelectric material [27]. In this way, the domain wall motion is well known to contribute to the polarization of ferroelectric materials. The frequency of the domain wall vibration (obtained in the gigahertz region) may be observed by applying an alternating electric field of very high frequency. For frequencies appreciably less than f_R , the ferroelectric domains

contribute their full share to the polarization, so that the real component of the dielectric constant becomes equal to the static dielectric constant and, therefore, the losses (associated with the imaginary component of the dielectric constant) vanish. With the increase in frequency, the domain vibrations increase and consequently the imaginary component of the dielectric constant starts to increase up to its maximum value. On the other hand, for a frequency higher than f_R , the domain wall vibrations are no longer able to follow the field variations and the real component of the dielectric constant approaches its clamping values, κ_∞ . In this frequency range, therefore, κ'' passes through its maximum value and decreases continuously for the highest frequency values.

On the other hand, closer inspection of the data in figure 1 seems to support the picture of a distributed dipolar relaxation mechanism of the dielectric response. Indeed, the value obtained for the characteristic width (λ_D) at a half-height for the imaginary dielectric constant peak (known as the full-width half maximum, FWHM), specifically at room temperature, was found to be around 1.91 decades. This value of the FWHM is higher than the FWHM of a Debye-type peak ($\lambda_D = 1.14$ decades) [28]. Therefore, the result that is obtained reveals that the observed dielectric behavior cannot be associated with a Debye-type relaxation process. Results for the dispersive process obtained in the PLT-15 samples that were studied (in the ‘virgin’ state) clearly show a mechanism with a relaxation time distribution function. The data were fitted by taking into account the most useful distribution functions for the investigation of the relaxation processes, as reported in the literature [29], and the results revealed that the obtained dielectric response was found to be close to a Davidson–Cole (DC) distribution function [30]. The obtained values for the characteristic parameters, such as the mean relaxation time (τ) and the relaxation time distribution parameter (β), which represent the degree of divergence from the ‘ideal’ Debye model, were 1.45×10^{-9} s and 0.75, respectively. Compared to single-exponential Debye behavior corresponding to $\beta = 1$, values of $0 < \beta < 1$ result in broadened imaginary dielectric constant peaks. The smaller the values of β , the greater the deviation with respect to Debye-type relaxation. Such deviations from Debye behavior are commonly ascribed to a distribution of relaxation times arising from disorder [30]. The obtained mean relaxation time is in good agreement with those obtained for similar ferroelectric systems, as reported in previous works [10].

As can be seen in figure 1, the dielectric dispersion occurs not only in the ferroelectric region ($T < T_C$) but also in the paraelectric region ($T > T_C$) close to T_C . This behavior, as pointed out in a recent work [20], suggests the existence of polar regions at temperatures higher than the transition temperature, which could be more evidence of the contribution of an ‘order–disorder’ type paraelectric–ferroelectric phase transition in ABO_3 perovskite structures, as reported in the literature [31, 32]. The existence of an order–disorder component in the paraelectric–ferroelectric phase transition of $PbTiO_3$ explains the persistence, though weak, of the dielectric dispersion above T_C [20]. These results clearly demonstrate that the simple presence of polar regions, independent of their size, volume fraction and correlation length, is a sufficient condition for the existence of such a dielectric dispersion process in ferroelectric systems. It is important to point out that, for higher temperatures, the data also revealed the highest values for the FWHM, showing a distributed dipolar relaxation mechanism for the whole investigated temperature range. At the same time, a decrease in the distribution parameter β , as the temperature increases, confirms that the dielectric spectrum becomes extremely diffuse. Correspondingly, the distribution of relaxation times becomes extremely wide. As can be observed, similarly to the results reported by other authors for $BaTiO_3$ [16, 33], $PbTiO_3$ derived materials [34] or some tetragonal tungsten bronze (TTB) structure systems [35], the obtained dielectric response curves suggest a dispersive mechanism of the complex dielectric constant, without any evidence of a resonant response.

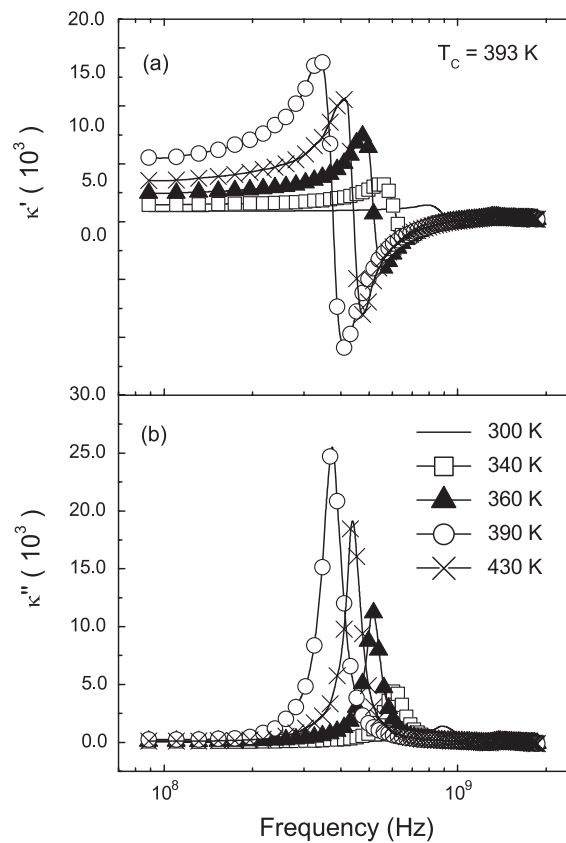


Figure 2. Frequency dependence of the complex dielectric constant for the PLT-15 samples under a uniaxial stress, at different temperatures: (a) real and (b) imaginary components.

3.2. Stress effect analysis

Because the dielectric response in ferroelectric materials is strongly susceptible to the influence of electric and/or mechanical fields, the microwave dielectric properties in the PLT-15 ceramics were investigated under the influence of a mechanical uniaxial stress, applied parallel to the measurement direction. The dielectric properties were obtained over the same frequency and temperature range to that obtained for the ‘stress free’ samples. The results presented in figure 2 clearly show that at room temperature (the solid line), κ' remains essentially flat up to 700 MHz, increases traversing a maximum, and then decreases to its clamped value (figure 2(a)). As can be seen, this anomalous behavior obtained for the stressed samples, and indistinguishable from a resonant response, is observed in the whole analyzed temperature range. On the other hand, the stressed samples also exhibited the highest values of the imaginary component of the dielectric constant, with its κ'' peak apparently shifted to a higher frequency (figure 2(b)), when compared to that obtained for the ‘stress free’ samples. This dielectric response obtained for the stressed ceramics corresponds to a true resonance rather than a dispersion process, with a characteristic frequency of about 900 MHz (at room temperature), higher than that obtained for the ‘stress free’ samples (700 MHz) at the same temperature.

It is interesting to point out, from figure 2(b), that the high values of the maximum imaginary dielectric constant for the stressed samples, when compared to the maximum decrease in the real component ($\kappa_s - \kappa_\infty$), suggest that is not possible to describe the spectrum

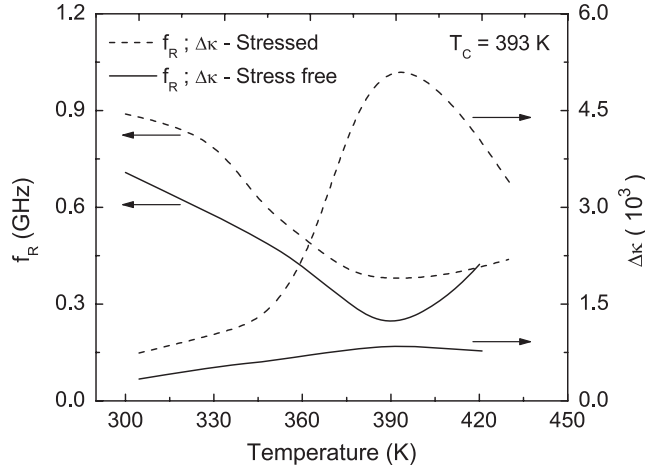


Figure 3. Temperature dependence of the characteristic parameters (f_R , the characteristic frequency, and $\Delta\kappa$, the dielectric strength) for the stressed and 'stress free' PLT-15 samples.

as a classical Debye dielectric dispersion. At the characteristic frequency (900 MHz), the value of κ'' at room temperature is about two times higher than that predicted by Debye's classical model, $[(\kappa_s - \kappa_\infty)/2]$, for the stressed samples. This result has an important physical implication; indeed, it clearly confirms that the high-frequency anomalies do not correspond to a real dispersion process, as predicted by Debye's model (relaxation-like behavior).

As reported in previous works [15, 16], the assumption that the observed dielectric anomaly could be, in this case, related to a piezoelectric resonance of the grains or individual domains suggests that the main influence of the uniaxial stress would be to decrease the losses related to this process, contrary with the results obtained in the present work. Therefore, the true mechanism responsible for the obtained anomalies remains unclear.

In order to obtain additional information on the dielectric spectrum, the obtained results were fitted using equation (1), considering a damped harmonic oscillator model [36], where the frequency dependence of the complex dielectric constant is governed by the expression:

$$\kappa^* = \kappa_\infty + \frac{(\kappa_s - \kappa_\infty)\omega_R^2}{\omega_R^2 - \omega^2 + j\gamma\omega}. \quad (1)$$

The parameter $(\kappa_s - \kappa_\infty)$, defined as dielectric strength ($\Delta\kappa$), is the contribution to the dielectric dispersion of the static dielectric constant, κ_s ; κ_∞ is the contribution to the dielectric constant of the higher-frequency electronic processes; $\omega = 2\pi f$ is the angular frequency; and $f_R = \frac{\omega_R}{2\pi}$ is the characteristic frequency of the process (defined as $\frac{1}{\tau} = 2\pi f_R$, where τ is the mean relaxation time). The dispersion characteristic parameters, such as $\Delta\kappa$, f_R and γ (damping coefficient of the dielectric response), can be obtained directly from the fitting of the obtained dielectric response (frequency dependence of κ' and κ'') using equation (1), which undoubtedly might be an essential feature in order to identify the mechanism involved in the dielectric anomaly.

Figure 3 displays the variation of f_R and $\Delta\kappa$ versus temperature for the PLT-15 ferroelectric ceramics. In order to compare the temperature evolution of the characteristic parameters, the results for the stressed and 'stress free' samples are presented in the same figure 3. As can be observed, the temperature dependences of f_R and $\Delta\kappa$ are quite similar for the stressed and the 'stress free' samples. Hence, with the application of uniaxial mechanic stress, although the dielectric response evidences resonance characteristics, this behavior

remains modulated by the paraelectric–ferroelectric phase transition. As a result, the thermal evolution indicates that, in both cases, the characteristic frequency goes through a minimum while the dielectric strength passes through a maximum around 393 K, which coincides with the paraelectric–ferroelectric phase transition temperature (T_C), as observed in the low-frequency dielectric measurements [20]. This result indicates that the maximum dielectric dispersion appears near the transition temperature, independently of the applied external mechanical driving field.

The behavior of f_R from the paraelectric-to-ferroelectric phase transition can be explained satisfactorily by the previously proposed relation for f_R [20]. As reported recently [20], in analogy with the oscillating membrane theory and in accordance with the sideways motion of the boundaries of the polar regions, it was suggested that f_R is generically governed by the ratio between the effective force constant (K_{eff}) and the effective mass (M_{eff}) of the polar region's boundaries, $f_R = \sqrt{K_{\text{eff}}/M_{\text{eff}}}$. This relation has been proposed taking into account that dielectric dispersion processes, observed in the microwave frequency range for ferroelectric and relaxor materials, can be associated to the field-induced vibration of the polar region boundaries (domain walls) and nano-domains (interphase boundaries between the polar region and the nonpolar matrix), respectively. The effective mass is the mass of the domain walls and interphase boundaries for normal ferroelectrics and relaxors, respectively, while the force constant may be associated to the interaction between the polar regions and is dictated by elastic properties of the respective polar region boundaries. For temperatures higher than T_C , the high thermal energy reduces the dipolar interactions, contributing to a low K_{eff} and, consequently, a relatively low value for f_R . With a decrease in temperature, the thermal energy decreases in favor of the formation of the polar regions, promoting the increase in M_{eff} , and consequently f_R slightly decreases. For temperatures near T_C , a sudden increase in the interaction energy, and consequently in the K_{eff} , takes place, resulting in an increase in f_R . Indeed, in the case of the studied composition (PLT-15), the paraelectric–ferroelectric phase transition is predominantly a displacive-type transition [37]. Therefore, an abrupt crossover between the two structural phases (ferroelectric–paraelectric) is expected, which means an accelerated disappearance of the polar regions (domains and domain walls). This fact results in a sudden change in both the order parameter and elastic properties, which is thus reflected in the force constant.

On the other hand, it is important to point out that the damping coefficient values (γ), obtained from the fitting of the experimental data by using equation (1) at room temperature, were lower for the stressed samples ($0.45 \times 10^9 \text{ s}^{-1}$) than those obtained for the 'stress free' samples ($8.80 \times 10^9 \text{ s}^{-1}$). This result suggests that the high-frequency dielectric anomalies, dispersion or resonance, can be described as either over-damped or damped resonant responses, respectively, where the main contribution to the dielectric response can be associated to the ferroelastic and/or ferroelectric components of the ferroelectric materials, which directly influence the damping of the system.

Referring to the obtained results, the essential aspect to be discussed can be summarized as the feature that, with the application of an external mechanic driving field, the dielectric response of the system clearly passes from a dispersive to a resonant dielectric behavior. In this way, considering an 'over-damped' resonant response, the variations in the strength of the damping coefficient of the system originate mainly due to the contributions of either ferroelastic or ferroelectric dipolar components. For lower damping systems, such as the case of the obtained resonant behavior for the stressed samples, the main contribution to the dielectric response is governed by the ferroelectric dipolar component. In contrast, for higher damping coefficient systems, the major contribution to the dispersive behavior (as observed in the 'stress free' samples) is due to the ferroelastic dipolar component, which prevails over the ferroelectric dipolar component.

On the other hand, it is well known that ordinary ferroelectric materials are classic hybrids ferroics, that is to say, they present a strong coupling between the ferroelectric–ferroelastic dipolar components [38, 39]. When applying a uniaxial mechanic stress, a reorientation of the electric and elastic dipoles takes place. In the same way, a mechanic strain in the material can be observed on applying an driving electric field. Then, as in the case of the stressed samples, applying a uniaxial stress parallel to the measurement direction promotes the dipolar reorientation in the perpendicular direction of the applied uniaxial stress, that is to say, an induced polarization may appear in the direction perpendicular to the applied uniaxial stress direction. Therefore, applying a uniaxial stress parallel to the measurement direction is equivalent to apply a poling electric field in the direction perpendicular to the measurement direction.

Thus, in order to obtain a better understanding of the current analysis, the observed anomalies around 1 GHz for the studied PLT-15 ceramics will be investigated, taking into account the influence of the relative orientation of the macroscopic polarization on the dielectric dispersion in the poled samples.

3.3. Poling field effect analysis

The samples were poled according to the procedure described in section 2. The temperature dependence of the dielectric constant (real and imaginary components) was examined parallel (κ'_{\parallel}) and perpendicular (κ'_{\perp}) to the polarization direction. The results are shown in figure 4.

The results reveal that the dielectric response, observed in the sample measured parallel to the poling direction, presents an ‘apparent’ dielectric dispersion process, which in turn is similar to that observed for the unpoled sample (see figure 1). However, it is observed that the maximum of the imaginary component of the dielectric constant (κ''_{\parallel}), for the sample measured parallel to the poling direction, is around four times higher than $(\kappa_{s\parallel} - \kappa_{\infty\parallel})/2$. Furthermore, a detailed inspection for the FWHM of the imaginary dielectric constant peak for the sample measured parallel to the poling direction revealed that the observed dielectric dispersion does not have a relaxation-like character, since the FWHM of the peak was found to be about 0.85 decades. This value is lower than the characteristic width of a Debye-like process ($\lambda_D = 1.14$ decades, the low limit value for FWHM). Indeed, this implies that it is not possible to describe the observed dielectric spectrum as a classic Debye dielectric relaxation, as discussed in the section 3.2. Therefore, it is possible to affirm that the observed dielectric anomaly really corresponds to a resonant-like dispersion rather than a simple relaxation-like dielectric behavior.

Figure 4 also displays the dielectric response in the sample measured perpendicularly to the poling direction. The results show that κ'_{\perp} slightly increases up to 500 MHz. However, after that, it abruptly increases and subsequently decreases for higher frequencies to its clamped values. The maximum of the imaginary component of the dielectric constant (κ''_{\perp}) also presents a remarkably high value, now observed around 1.03 GHz. The imaginary component of the dielectric constant for the sample characterized perpendicularly to the poling direction is about seven times higher than the values predicted by the theoretical Debye model. These results show that the dielectric response obtained for the samples measured perpendicularly to the poling field is characterized by a resonant mechanism, which may be associated with a damped resonance process rather than with a simple Debye dielectric relaxation.

The above described experimental results clearly show that in the same sample, depending on the relative orientation between the measuring direction and the macroscopic polarization direction, the dielectric dispersion in the gigahertz region seems to behave as either a dispersive (relaxation-like) mechanism or a resonant mechanism. This change in the dielectric response

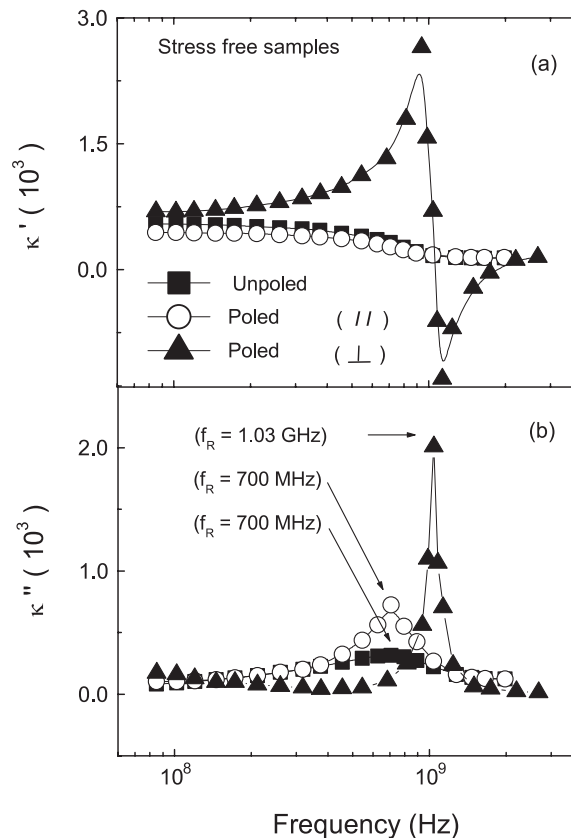


Figure 4. Frequency dependence of the complex dielectric constant, at room temperature, for the PLT-15 unpoled ‘stress free’ samples, and the poled samples measured in the parallel and perpendicular directions of the poling direction: (a) real and (b) imaginary components.

can be well described considering a general resonant behavior, which can be associated with an ‘over-damped’ resonance process. Therefore, it can be affirmed that the microwave dielectric spectra observed in ferroelectric materials may be described in terms of an ‘over-damped’ resonance involving either dispersive or resonant behavior, rather than a simple dispersion process, which is intimately related to the variation in the damping strength of the system. At the same time, the damping strength is affected by the coupling between the ferroelectric and ferroelastic dipolar components. The values of γ were now obtained for the poled samples by fitting the experimental data, and are shown in table 1, together with those obtained for the ‘stress free’ and stressed samples. As observed, the damping coefficient also shows a decrease when the dielectric behavior passes from a dispersive (relaxation-like) behavior to a pure resonant response. As can be seen, the γ value for the poled samples measured in the direction parallel to the poling direction was about 8.97×10^9 s $^{-1}$, which is similar to that obtained for the ‘stress free’ samples and, at the same time, higher than those obtained for the poled samples measured in the direction perpendicular to the poling direction.

Thus, from the obtained results, it is possible to affirm that the dispersive behavior observed for the ‘stress free’ samples may be a consequence of an increase in the damping strength, giving rise to an over-damped resonance (reflected by the dispersive behavior). On the other hand, the resonant behavior observed for the poled samples measured in the direction

Table 1. Dispersion characteristic parameters obtained for the PLT-15 samples, at room temperature.

Sample	k_∞	Δk	f_R (GHz)	γ (10^9 s^{-1})
Stress free	113	453	0.70	8.80
Stressed	266	691	1.44	0.45
Poled \parallel	145	300	0.70	8.97
Poled \perp	149	541	1.04	1.15

perpendicular to the poling direction, as well as in the stressed samples, may be a consequence of a decrease in the damping strength, giving rise to a damped resonance (reflected by the resonant behavior). It is important to point out that, although the dielectric behavior observed for the samples measured in the direction parallel to the poling direction has a true resonant-like character, from the previously described analyses an ‘apparent’ dispersion behavior (relaxation-like) was observed because of the high component of the damping coefficient.

Therefore, in normal ferroelectrics the gigahertz dielectric anomalies must be interpreted as a resonance mechanism instead of a dispersion mechanism. The question as to whether these high-frequency anomalies behave as a dispersive (relaxation-like) process or a resonant process, described in general by an ‘over-damped’ mechanism, may be a consequence of the coupling between the ferroelectric and the ferroelastic dipolar components, whose contribution determines the character of the high-frequency dielectric dispersion. This aspect will be discussed in detail in the next section.

3.4. Discussion

The ferroelectric phenomenon, in most cases, may be followed by a ferroelastic behavior, that is to say, an ‘unintentional’ stress can be present when an electric field \mathbf{E} is applied. As in ferroelectric materials, a ferroelastic crystal contains two or several stable states of orientation when there is no mechanical stress. It is possible to change it reversibly from one state to another by applying a stress σ in defined directions. Thus, there exists a strain–stress elastic hysteresis with spontaneous strain ε_s and a coercive stress. In this way, a transition from a ferroelastic phase to a higher-temperature phase, termed paraelastic, occurs by an increase in symmetry and a change in the crystalline system [40]. The additional ‘unintentional’ stress originating when applying an electric field may be sufficient for ferroelastic switching to occur [41]. The basic assumption of the polarization switching model is that a single ferroelectric crystallite in a polycrystalline ceramic, which is subjected to an electric field [42] or to a mechanical stress [43, 44] or both, undergoes a change in polarization and a corresponding change in strain. Nevertheless, either partial or complete coupling may exist between the ferroelectric and ferroelastic properties. When such coupling occurs, ε_s may be modified by applying an electric field and P_s may be modified by applying a mechanical stress. Depending on the crystal structure and the order parameter, the ferroelectricity and the ferroelasticity in a crystal could be fully or partially coupled.

Concerning the obtained results for the PLT-15 ceramics, it can be noted that two polarization mechanisms are always present under certain conditions. For all the samples where an external driving field was applied (a uniaxial stress and/or a poling field applied in the directions perpendicular and parallel to the measurement direction) a resonant-like dispersion has been observed. In particular, either uniaxial stress or a poling field applied in the direction perpendicular to the measurement direction promotes a redistribution in the orientation of the dipolar configuration over the direction perpendicular to the measurement direction. Therefore,

the observed resonant behavior, for these conditions, could be associated with a slightly partial coupling between the ferroelastic and ferroelectric dipolar components, with the ferroelectric dipolar component being the main factor responsible for the resonant dielectric response.

On the other hand, for the unpoled and ‘stress free’ samples the observed behavior may be caused by the coupling between the ferroelectric and the ferroelastic dipolar components. Under these conditions, the dipoles are unable to be reoriented ‘freely’ with the ac electric fields of the measurements. Therefore, the dielectric response is governed mainly by the contribution of the ferroelastic dipolar components, originating the dispersive dielectric behavior.

In order to describe these results, the ferroelastic contributions to the piezoelectric response are taken into account [45]. In this case, the theoretical approach will be considered in order to investigate the influence of the external poling electric field on the dielectric response. Thus, the analyses of the data are considered when an oscillating external electric field parallel or perpendicular to the poling direction is applied to the sample. The piezoelectric effect can be represented by equation (2), where c and e are the converse of the piezoelectric compliance [c^E] = [s^E]⁻¹ (or elastic stiffness) and the piezoelectric tensor defined as [e] = [d][c^E], respectively [41]. The symbols ν , μ and m correspond to the condensed index of the tensor notation ($\nu, \mu = 1, 2, \dots, 6$ and $m = 1, 2, 3$):

$$\sigma_\nu = c_{\nu\mu}^E \varepsilon_\mu + e_{m\nu} E_m. \quad (2)$$

Taking into account the symmetry for a poled ceramic material (∞ mm) and the applied electric field, for the two investigated situations equation (2) can be expanded as follows:

(1) applying only an E_3 electric field (parallel direction),

$$\sigma_1 = c_{11}\varepsilon_1 + c_{12}\varepsilon_2 + c_{13}\varepsilon_3 + e_{31}E_3 \quad (3)$$

$$\sigma_2 = c_{12}\varepsilon_1 + c_{11}\varepsilon_2 + c_{13}\varepsilon_3 + e_{31}E_3 \quad (4)$$

$$\sigma_3 = c_{13}\varepsilon_1 + c_{13}\varepsilon_2 + c_{33}\varepsilon_3 + e_{33}E_3 \quad (5)$$

$$\sigma_4 = c_{44}\varepsilon_4 \quad (6)$$

$$\sigma_5 = c_{55}\varepsilon_5 \quad (7)$$

$$\sigma_6 = c_{66}\varepsilon_6 \quad (8)$$

(2) applying only an E_1 electric field (perpendicular direction),

$$\sigma_1 = c_{11}\varepsilon_1 + c_{21}\varepsilon_2 + c_{31}\varepsilon_3 \quad (9)$$

$$\sigma_2 = c_{12}\varepsilon_1 + c_{22}\varepsilon_2 + c_{32}\varepsilon_3 \quad (10)$$

$$\sigma_3 = c_{13}\varepsilon_1 + c_{23}\varepsilon_2 + c_{33}\varepsilon_3 \quad (11)$$

$$\sigma_4 = c_{44}\varepsilon_4 \quad (12)$$

$$\sigma_5 = c_{55}\varepsilon_5 + e_{15}E_1 \quad (13)$$

$$\sigma_6 = c_{66}\varepsilon_6. \quad (14)$$

Applying an electric field in two mutually perpendicular directions in equation (2), the piezoelectric expansion leads to six components of the total stress for the parallel and perpendicular directions, expressed by equations (3)–(8) and equations (9)–(14), respectively.

It is noticeable from equations (3)–(8) that, due to the piezoelectric effect, the electric field acting in the parallel direction (E_3) generates only compressive or extensional stress, contributing just for the three principal components of the stress (σ_1 , σ_2 and σ_3), without any contribution for the shears components. Otherwise, the electric field applied in the perpendicular direction (E_1) (see equations (9)–(14)) causes only a shear stress σ_5 (equation (13)), without any contribution for the principal components of the stress (σ_1 , σ_2

and σ_3). It is important to point out that, in equation (13), the elastic stiffness c_{55} is identical to c_{44} , after considering the respective symmetry operations. Therefore, the fundamental difference between both cases is that stress generated by electric fields parallel to the poling direction causes compressive or extensional variations in the sample [45]. In terms of elasticity theory, the dispersion or resonant behavior might be associated with the influence of the electric field on the elastic dipole. In this way, in order to clarify this issue it is necessary to use some basic elasticity concepts. The behavior of an elastic dipole in the presence of stress can be characterized by the relation $\sigma_v = c_{v\mu} \lambda_\mu$, where λ is the strain tensor, which determines the interaction of the elastic dipole with the stress field [46]. Formally, σ is defined as the negative stress needed to maintain constant strain per unit concentration of elastic dipoles. Since the λ tensor represents a strain tensor, it must be symmetric and, therefore, can be characterized by a strain ellipsoid with three mutually perpendicular principal axes. When expressed in the coordinate system of the principal axes, the λ tensor becomes diagonal, with the three components λ_1 , λ_2 and λ_3 as the principal values. By expanding the relation for the elastic dipole definition, it is not difficult to notice that results do not depend of the shear components of stress field. This suggests that the resonant behavior obtained for the perpendicular direction is governed just for the electrical component of the equation (2), where only the shear components of the piezoelectric coefficients play a principal role, without any contribution from the components along the principal axes (σ_1 , σ_2 and σ_3).

Considering that elastic dipoles in displacive ferroelectrics lie parallel to the electric ones, and that they interact only with the compressive or extensional stresses [46], they are excited only by the application of a poling electric field parallel to the measurements direction. This suggests that the resonant response obtained for the perpendicular direction is governed only by ferroelectric components, because only the shear stress components are generated by a piezoelectric contribution, without any ferroelastic contribution. Otherwise, the dielectric behavior (associated with an over-damped resonance) observed in the parallel direction results from a coupling between the ferroelastic and ferroelectric contributions. In this case, the ferroelastic contribution becomes the main factor responsible for the increase in the damping coefficient, contributing to the decrease in the characteristic frequency.

It is important to point out that, applying a uniaxial stress parallel to the measurement direction, the resonant response that is observed can be explained by considering that the ferroelectric and ferroelastic domains tend to be oriented perpendicular to the mechanical stress and, consequently, perpendicular to the measuring electric field direction. As observed, this condition is analogous to the case of applying a poling electric field perpendicular to the measurement direction. Thus, either a dispersion or a resonance mechanism are always presented, without the presence of an intermediate case. This result confirms that the ferroelectric and ferroelastic contributions to the high-frequency dielectric anomalies are always coupled to each other.

4. Conclusions

The microwave dielectric response of PLT ferroelectric ceramics was investigated in detail considering the influence of external (electric and mechanic) driving fields. Two high-frequency dielectric anomalies were found in the same material that was studied, which were discussed in the light of an over-damped resonant process. The present work has successfully approached this question by conducting dielectric studies on samples that were stressed (in the virgin state) and 'stress free' (in the poled state). It was confirmed that the obtained anomalies are strongly influenced by the contribution of the ferroelectric and/or ferroelastic dipolar components, which are characteristics of ferroelectric materials. In particular, for all

the samples where an external driving field was applied (a uniaxial stress and/or a poling field applied in the perpendicular and parallel directions to the measurement direction) a resonant-like dispersion was observed. In contrast, a dispersive (relaxation-like) behavior related to an over-damped resonance was obtained for the unpoled (and ‘stress free’) samples. The results can be explained well by considering the influence of the ferroelastic–ferroelectric contributions coupling to the high-frequency dielectric response.

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