Materials Research, Vol. 7, No. 2, 325-328, 2004.

High Frequency Dielectric Relaxation in Lanthanum Modified $PbTiO_3$ Ferroelectric Ceramics

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Received: February 5, 2003; Revised: September 30, 2003

Dielectric measurements of lanthanum modified lead titanate ceramics were carried out in a frequency and temperature range of 70×10^6 Hz – 2×10^9 Hz and 300 K - 420 K, respectively. Dielectric relaxation appears around 7×10^8 Hz at room temperature, and the maximum of the dielectric relaxation was around 393 K, the transition temperature (T_c). The relaxation frequency passes through a minimum at T_c and the dielectric relaxation exists in both paraelectric and ferroelectric phases. A fitting of the experimental data with the Debye relations gives some keys for understanding the dielectric behavior of such materials.

Keywords: *dielectric relaxation, ferroelectric ceramics, microwave dispersion*

1. Introduction

Dielectric resonators and greater speed data transmission devices have led to a rising interest in the gigahertz region and have prompted research on ferroelectric materials at microwave frequencies[1-3]. Within them, the barium titanate and other perovskite-type systems have been distinguished because they present intrinsic relaxation near 1×10^9 Hz, specifically at room temperature. The nature of the high frequency dielectric dispersion of ferroelectric ceramics in the range of 10^6 - 10^9 Hz has been studied since 1940[4], however in the last 15 years a special attention has been paid on the properties of those ferroelectrics with a relaxor-type response[5]. In this way, the peculiarities in the dielectric properties, such as relaxational character of polarization, may be investigated by the frequency dependence of the real, ε' and imaginary part, ε'' of dielectric permittivity[6,7]. Table 1 shows, for some selected dielectric materials, the dielectric permittivities for high (ε_∞) and low (ε_0) frequency values obtained from refraction index and static field, respectively[8]. The observed difference between the high and low frequency dielectric permittivities is the main characteristic of the relaxational character of polarization.

In order to clarify the dielectric dispersion at high frequency, some models using resonant cavity method, have been proposed in many works[4,9,10]. Specially, in the microwave range, because of the high dielectric permittivity and dielectric loss values of some ferroelectric materials, this type of characterization becomes more difficult. Therefore the quality of the results largely depends on the initial calibration of the system. That is the reason why few works focusing continuous frequency method can be found actually in the literature. Dielectric studies have been recently performed in a wide temperature range (300 - 900 K) mainly by coaxial technique using the reflectometric method[11] where the complex dielectric permittivity is obtained from the frequency dependence of the complex reflection coefficients.

The aim of the present work is to investigate the dielectric behavior of modified lead titanate ($PbTiO_3$) ferroelectric ceramics in the microwave frequency region, over a wide frequency range (10^6 - 10^9 Hz). The dielectric response was obtained in the temperature range of 300 – 420 K, and the results are discussed in terms of the ferroelectric domain walls motion.

2. Experimental

Dielectric measurements were carried out in La modified $PbTiO_3$ ceramic samples as a function of frequency and temperature. PLT ceramics were prepared by the conven-

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Articles presented at the XV CBECIMAT, Natal - RN, November de 2002.

tional oxide mixture method using a nominal composition of $Pb_{1-x}La_xTiO_3$, where x = 0.15. High reagent grade powders PbO, La_2O_3 and TiO_2 were used as raw materials, and the ceramic samples were sintered for 3.5 h at 1150 °C in a PbO atmosphere. Structural, microstructural and compositional characterizations of samples were made through X-ray diffraction, SEM and EDS analysis, respectively. The results revealed a PLT composition with a tetragonal symmetry and an average grain size of 2 µm. Gold electrodes were applied by sputtering to the opposite faces of the samples, in form of discs with 2.0 mm in diameter and 0.5 mm in thickness, to insure good electric contacts.

Dielectric characterization was carried out from room temperature up to 420 K using a Network Analyzer HP-8719C in the frequency range of 70×10^6 to 2×10^9 Hz. In order to obtain the dielectric response of the materials, the reflectometry technique was applied by using a 50 Ω coaxial line. For an accurate determination of the frequency dependence of the reflection coefficients (Γ´,Γ´´), careful compensation procedure was carried out (1) to take into account spurious reflections that may result from transmission line discontinuities, and also (2) to eliminate the effect of the resistances and capacitances of the sample holder. Three different HP standard terminations (open, short and 50 Ω), with reflection coefficients of 1, -1 and 0, respectively, were used to calibrate the system in the investigated frequency range. The real and imaginary parts of the complex dielectric permittivity were determined from the measured complex reflection coefficients[11].

3. Results

Low frequency measurements were also carried out using an Impedance Analyzer HP-4194A, in order to obtain the ferroelectric-paraelectric phase transition temperature (T_c = 393K) from the temperature dependence of dielectric permittivity at 1 kHz. This T_c value is indeed slightly lower than expected for this samples' composition due to some impurities. Figure 1 shows the frequency dependence of the real and imaginary components of dielectric permittivity at room temperature. In the frequency range of 7×10^7 - 4×10^8 Hz, ε´ decreases only slightly as the frequency increases. Above 4×10^8 Hz, ε´ decreases quickly, whereas ε´´ passes through its maximum value. The frequency corresponding to the maximum of imaginary component of dielectric permittivity ($f_r = 7 \times 10^8$ Hz) is known as relaxation frequency, and it is associated to a polarization mechanism responsible for the dissipation. The value obtained for the relaxation frequency is in agreement with the range of values reported for other ferroelectric materials commonly used for microwave applications[10-12].

Table 1. Relaxational character of polarization represented by the high (ε_∞) and low (ε_o) frequency dielectric permittivities for some dielectric materials.

Materials	ε_o	ε_∞
LiCl	11.05	2.75
AgBr	13.10	4.62
MgO	9.80	2.95

The origin of the above dielectric relaxation phenomenon may be attributed to the ferroelectric domain walls vibrations in such a king of material. The domain wall motion is well known to contribute to the polarization of ferroelectric materials. The frequency of the domain walls vibration (obtained at 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 permittivity becomes equal to the static dielectric permittivity and therefore the losses (associated to the imaginary component of dielectric permittivity) vanish. With increasing frequency, the domain vibrations increase and, consequently, the imaginary component of dielectric permittivity starts to increase up to its maximum value. On the other hand, for a frequency higher than f_r, the dipoles are no longer able to follow the field variations and the real component of dielectric permittivity approaches ε_∞. In this frequency range, therefore, ε" passes through its maximum value and continuously decreases.

In order to characterize the dielectric response, the experimental points of ε´ and ε´´ were fitted by using the theoretical Debye relations (A). The shape of this relations, shown as dashed lines in Fig. 1, was found to be close to a

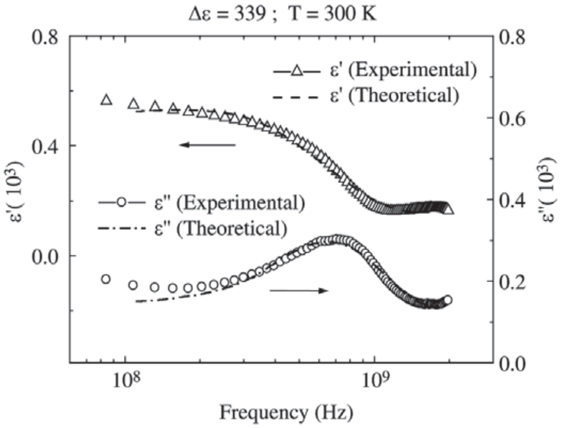

Figure 1. Dielectric dispersion for lanthanum modified lead titanate ceramic at room temperature. (symbol-experimental curves; dashed lines- theoretical curves).

relaxational behavior: there is a good agreement between the experimental points and theoretical curves.

$$\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_o - \varepsilon_\infty}{1+(\omega\tau)^2}\ ,\ \varepsilon'' = \frac{(\varepsilon_o - \varepsilon_\infty)\omega\tau}{1+(\omega\tau)^2} \qquad \text{(A)}$$

In these relations $\omega = 2\pi f$ is the measurement frequency; τ is the relaxation time (the relaxation frequency is defined by $f_r = 1/2\ \pi\tau$); ε_o and ε_∞ are the dielectric permittivities at frequencies lower ($f << f_r$) and higher ($f >> f_r$) than the relaxation frequency, respectively. The difference $\Delta\varepsilon = \varepsilon_o - \varepsilon_\infty$ is usually known as the relaxation strength. These characteristic parameters were obtained from the theoretical relations (A), resulting in: $\tau = 1.39\times10^{-9}$ *s*, $\varepsilon_o - \varepsilon_\infty = 339$ *and* $\varepsilon_\infty = 155$. It is important to outline that no appreciable dielectric relaxation is observed in the frequency range of 10^2 Hz - 10^7 Hz at room temperature.

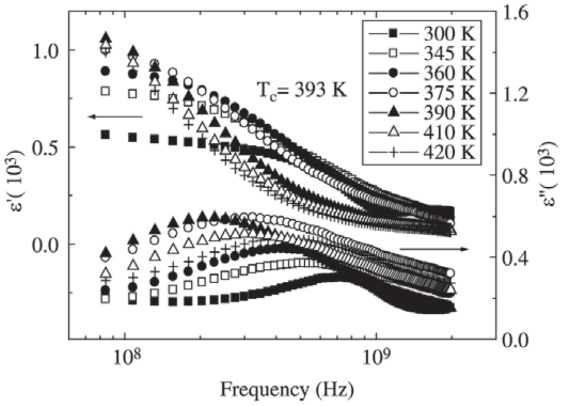

Figure 2. Frequency dependence of real and imaginary component of dielectric permittivity at various temperatures.

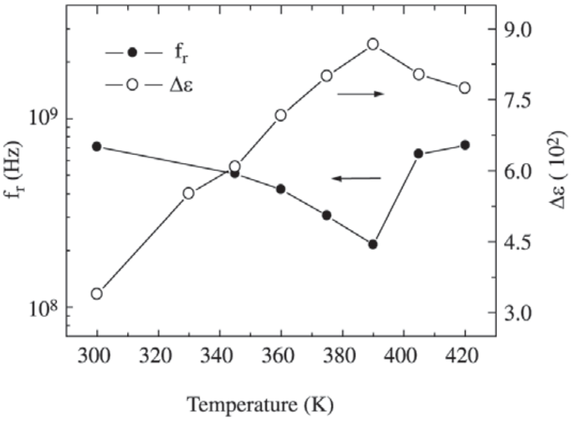

Figure 3. Temperature dependence of the relaxation strength ($\Delta\varepsilon$) and relaxation frequency (f_r).

As we earlier pointed out, the high frequency dielectric measurements were performed at various temperatures from room temperature up to 420 K, as shown in Fig. 2. Notice that the dielectric relaxation occurs not only in the ferroelectric region but also in the paraelectric one close to T_c. This could suggest the existence in the material of polar regions for temperatures higher than the transition temperature. It is not yet clear to us whether or not this fact could be one more evidence of the contribution from an "order-disorder" type ferroelectric-paraelectric phase transition in ABO_3 perovskite structures, as recently reported in the literature[13-15]. Further studies are in course in order to closely treat this question.

On the other hand, Fig. 3 displays the variation of the relaxation frequency and the relaxation strength versus temperature. The thermal evolution indicates that f_r goes to a minimum at the transition temperature as well as $\Delta\varepsilon$ passes through a maximum in the vicinity of the same temperature, which indicates that the maximum dielectric dispersion appears near the transition temperature.

4. Conclusions

The obtained results from the dielectric characterization in the microwave region, for the modified lead titanate ceramics, confirmed the existence of the dielectric relaxation behavior with a relaxation frequency about 7×10^8 Hz. This behavior may be associated to the effect produced by the ferroelectric domain walls vibrations in this frequency range. The fitting of the experimental points with the theoretical relations confirmed the dipolar character of the dielectric dispersion, showing a typical Debye relaxational behavior. On the other hand, dielectric relaxation appeared not only in the ferroelectric region but also in the paraelectric one close to T_c. This could involve the existence of polar regions for temperatures higher than the transition temperature and an "order-disorder" type ferroelectric-paraelectric phase transition (as proposed elsewhere by some authors), two facts that would however need further analysis.

5. Acknowledgements

The authors thank to CAPES, CNPq and FAPESP Brazilian agencies for financial support. The authors also thank Mr. Francisco J. Picon (DF-UFSCar) and Fabio L. Zabotto (DF-UFSCar) for technical assistance.

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