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Microwave dielectric relaxation of ferroelectric PLZT ceramics in the range of 300–900 K

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Abstract. Dielectric response of PLZT(x/65/35) ceramics (with x = 0, 2, 4, 5) was studied using radio frequency and microwave techniques in the temperature range 300–900 K and with a frequency range of 10^2 Hz– 3×10^9 Hz. Dielectric relaxation appears around 1×10^9 Hz at room temperature. The relaxation frequency softens at T_c and the dielectric relaxation exists in both paraelectric and ferroelectric phases and depends on x the lanthanum concentration. A model of correlation chains gives some keys for understanding the frequency behaviour of such materials.

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1 Introduction

It has been shown recently that ceramics derived from BaTiO₃, Pb(Mg_{1/3}Nb_{2/3})O₃ [PMN] and PZT present a dielectric relaxation within the microwave range of around 1×10^9 Hz [1–3]. The methods used (cavity using an on-line transmission or wave guide methods) are suitable to determine the dielectric permittivities of homogeneous materials. A review of these methods is given in the literature [4–11]. The study of such relaxations requires the ability to work over both large frequency and temperature ranges: measurements using coaxial cells and network analysers at the moment can be used to cover a band of 10^7 Hz-2 $\times 10^{10}$ Hz. Up to now these measurements were limited to temperatures below 420 K due to experimental difficulties. It was the case for the study of $BaTiO_3$ and PMN type ceramics well suited because their Curie temperatures are relatively low (393 K and 266 K respectively).

It is possible to extend the range of dielectric measurements to 850 K thanks to development of a new device. This device has allowed us the study of ceramics at higher Curie temperatures. The present work deals with dielectric properties of lead lanthanum zirconate titanate [PLZT] ceramics whose Curie temperature varies from 500 to about 650 K.

2 Preparation of ceramics

The compositions $Pb_{(1-x)}La_x(Zr_{0.65}Ti_{0.35})(1_{-x/4})O_3$ were prepared by a solid state reaction from PbO, La_2O_3 , TiO₂ and ZrO₂ at 900 °C for 12 hours. The powder was then pressed isostatiscally in a latex container under 4000 bars for 10 min. The resulting cylindral sample measuring about 3 cm in diameter and 5 cm in height was sintered at 1200–1250 °C for 2 hours. Due to partial evaporation of volatile PbO mainly at the sample periphery, the latter was eliminated mechanically, leading to a cylinder of about 1 cm in diameter and 3 cm in height. A diamond wire saw was used to prepare disks of about 1 cm diameter and 1 mm thickness. The compactness (ratio of experimental density to theoretical density) was close to 0.97 for all samples [12].

3 Experimental technique

Heating of a sample could be achieved either by a conventional oven or by optical means using laser or image oven [13]. Within the frequency range used in this study, the sample was placed in a measuring cell connected through a coaxial line to a network analyser (HP8510B). A conventional oven has the disadvantage that the measuring cell and the connection between the cell and the coaxial line that provides the wave propagation are at high temperature. The standard materials that were used (especially the dielectrics presently used for the connections) did not allow temperatures above about 450 K. For this reason an optical method was chosen, a CO_2 laser emitting in the infrared at 10.6 μ m. The beam of this laser had a diameter of 1 cm and a divergence of 0.1 mrd. Its power was controlled by computer and variable from 20 to 200 W in steps of 0.1 W.

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The measuring cell was a open ended coaxial probe [14,15] fixed to the switchboard APC7 and made from Invar to limit dilatations. The central conductor of the coaxial line came into contact with the sample at one end, while the other end is connected to the network analysor. The sample was fixed against the coaxial constituting the cell by a system of springs. In the part that keeps the sample in place, a hole was made through which the laser beam passed to heat the sample. The laser beam was widened so that the heating of the sample on the rear face (the face in contact with the central conductor) was as uniform as possible ($\Delta T < 10$ K at T = 900 K). To get a homogeneous distribution of the laser power on the sample, the beam was spread over all of the rear face thanks to an infrared mirror system. In these conditions, the sample could be bring to high temperatures during a time long enough to avoid fractures, but short by comparison to the heating period in a conventional oven. Moreover the cell was heated only by the thermal transfer due to its contact with the sample and it remained at relatively low temperatures, which allowed the use of coaxial lines and APC7 connections in contact with the measuring cell. The sample temperature was measured using thermocouples or an optic pyrometer for temperature below 800 K and a sapphire fibre (ACCUFIBER) thermometer for higher temperatures.

4 Permittivity measurements

Modes matching methods allowed the calculation of the reflection coefficient (or the admittance) of the interface between the coaxial line and the cylindrical structure containing the material to be studied [16–18]. The numerical methods used for modes matching showed that this type of interface was associated with an admittance Y = G+jB and that it could therefore be represented by an equivalent circuit RC [14,15,19]. In the method used here, the elements R and C of the equivalent circuit were determined from measurements on reference samples of known permittivities. The complex permittivity of a sample was measured using numerical inversion of the measured reflection coefficient S_{11} at the interface coaxial-sample.

For low frequencies $(10^2 \text{ Hz}-13 \times 10^6 \text{ Hz})$ and at room temperature, measurements were made using a general radio frequency cell connected to an impedance analyzer HP4192A (or HP4291A). For frequencies greater than 10^8 Hz , the cell used was an open-ended coaxial probe connected to a network analyzer HP8510B. In this frequency range the equivalent circuit reduces to a capacity C, since the conductance G is very small, and consequently has no effect in the calculation of the reflection coefficient [20]. Figure 1 shows the results obtained for a PLZT (5/65/35) ceramic and the good agreement between the results coming from the three different apparatus.

5 Experimental results

Figures 2 and 3 show the thermal evolution of the real permittivity ε' as a function of frequency and

temperature for PbZr_{0.65}Ti_{0.35}O₃ (PZT(0/65/35)) and Pb_{0.95}La_{0.05}Zr_{0.65}Ti_{0.35}O₃ (PLZT(5/65/35)) ceramics. A maximum of ε' occurs at the Curie temperature $T_{\rm c}$ ($T_{\rm c}(0/65/35) = 630$ K and $T_{\rm c}(5/65/35) = 505$ K). Figure 4 shows the variations of ε' for compositions corresponding to the following values of x: 0, 2, 4 and 5.

The frequency variations of ε' and ε'' show the characteristic behavior of a dielectric relaxation, a decrease in ε' and a maximum in ε'' at the relaxation frequency near to 10⁹ Hz (Figs. 5 and 6). The dielectric relaxation can also be characterised by a Cole-Cole response function of dipolar elements [21,22]:

$$\varepsilon^*(\omega) = \varepsilon_{\infty} + \Delta \varepsilon \left[1 + (i\omega\tau)^{(1-\alpha)} \right]^{-1}$$

 ω is the angular frequency ($\omega = 2\pi f$), τ is a relaxation time, the relaxation frequency is defined by $f_{\rm r} = 1/2\pi\tau$ and is experimentally given by the frequency at the maximum of ε'' . α is a positive constant $(0 \le a < 1)$ and is a characteristic parameter of the Cole-Cole diagram that can be determined from the function $\varepsilon''(\varepsilon')$, ε_{∞} is the permittivity at frequencies greater than the relaxation frequency $f_{\rm r}$, $\Delta \varepsilon$ is the amplitude of the variations of ε from low to high values of the ratio $f/f_{\rm r}$. For all the compositions (x = 0, 2, 4 and 5%), the study of the thermal evolution indicates that the relaxation frequency f_r goes through a minimum close to the phase transition temperature $T_{\rm c}$ and that the dielectric dispersion $\Delta \varepsilon$ presents a maximum (Figs. 7 and 8). Figures 9 and 10 show Cole and Cole diagrams of the PZT ceramic (x = 0) and Figure 11 the variations of the α parameter as a function of the temperature and lanthanum concentration x.

6 Discussion

The lead zirconate titanate (PZT 65/35) and lanthanummodified lead zirconate titanate (PLZT x/65/35) ceramics are characterised by a dielectric response that is strongly dependent on temperature and frequency.

They present similarities with the $BaTiO_3$ type ceramics with respect to the following features:

- existence of dielectric relaxation of Cole-Cole type at microwave frequencies for both ferroelectric and paraelectric phases;
- existence of a minimum of relaxation frequency at the phase transition.

However it is different by three main points:

- whatever the temperature, the values of the relaxation frequency $f_{\rm r}$ are significantly higher in the case of the PZT;
- values of the permittivity ε' of the PZT ceramics are lower than those obtained for the BaTiO₃ type ceramics with similar compactnesses;
- the parameter α increases for $T > T_c$ and in particular when x = 0. This behaviour was also observed in the PMN ceramics. It is related to local fluctuations in x [2] and to the existence of domains with composition different from the mean composition (x/35/65).



Fig. 1. Frequency dependence of permittivity ε' and dielectric losses ε'' of the (5/65/35) PLZT ceramic, at room temperature.



Fig. 2. Temperature dependence of permittivity ε' at various frequencies of the (0/65/35) PZT ceramic.

Many theories, including some related to intrinsic and extrinsic mechanisms, have been put forward to explain the origin of the high frequency dielectric relaxation in the case of the ferroelectric perovskites of $BaTiO_3$ type:

- the dielectric relaxation is caused by the piezoelectric resonance of grains in the ceramics [23,24];
- the dielectric dispersion is correlated with the piezoelectric resonance of ferroelectric domains in both crystals and ceramics [25,26];
- the dielectric dispersion is related to the jump of the Ti⁴⁺ ions, in octahedron site, between different wells of potential [27].

But these models are not able to explain the dielectric relaxation at high frequencies [1]. A microscopic relaxation mechanism was proposed [28,29]. This model offers a microscopic description of the dielectric relaxation mechanism in the BaTiO₃ based on the fact that a Ti⁴⁺ ion which is displaced out of the centre of an oxygen



Fig. 3. Temperature dependence of permittivity ε' at various frequencies of the (5/65/35) PLZT ceramic.



Fig. 4. Temperature dependence of permittivity ε' of the (x/65/35) PLZT ceramic (with x = 0, 24 and 5) at 1 GHz.

octahedron can occupy different potential wells. The relaxation process is associated with the cooperative jumps of Ti⁴⁺ between these different wells and the formation of correlation chains. The shift of the Ti⁴⁺ ion would be coherent at a length l_c corresponding to a correlation chain. The increase of l_c when T tends to T_c leads to an increase in $\Delta \varepsilon$ and a decrease in f_r : indeed the elementary dipolar moment is not that of a crystallographic unit cell, but that of the correlation chain and in a simplified model neglecting dipole interactions: $\Delta \varepsilon = n \frac{p^2}{3\varepsilon_0 kT}$, where n is the number of correlation chains per unit volume and p is the dipolar moment of the correlation chains. This model explains the very high values of the measured permittivity. When considering the model of correlation chains, the first point to emphasize is that the cooperative motion between the Zr⁴⁺ and Ti⁴⁺ ions in the PZT ceramic is coherent for a length l_c shorter than that corresponding to Ti⁴⁺ ions in the BaTiO₃ and so f_r (PZT) > f_r (BaTiO₃) at T_c . Firstly the substitution Zr⁴⁺-Ti⁴⁺ in lead-free ceramics causes a small decrease in the f_r value at T_c ($f_r(BaTiO_3) \sim 10^8$ Hz; $f_r(BaTiO_8Zr_{0.2}O_3) \sim 7 \times 10^7$ Hz): the Zr⁴⁺ ions fulfill the role of relaying the Ti⁴⁺ ion in the BaTi_{1-x}Zr_xO₃ solid solution. On the contrary, the Pb²⁺-Ba²⁺ substitution leads to an increase of f_r at T_c (f_r (Ba_{0.95}Pb_{0.05}TiO₃) $\sim 3 \times 10^8$ Hz) [30,31]. The Pb²⁺ ion and its $6(sp)^2$ lone pair cause a stronger distortion of the crystalline system compared to the Ba²⁺ ion. The



Fig. 5. Frequency dependence of permittivity ε' and dielectric losses ε'' of the (0/65/35) PLZT ceramic, at room temperature.



Fig. 6. Frequency dependence of permittivity ε' and dielectric losses ε'' of the (5/65/35) PLZT ceramic, at room temperature.



Fig. 7. Temperature dependence of relaxation frequency and dielectric dispersion $\Delta \varepsilon$ of the (0/65/35) PZT ceramic.



Fig. 8. Temperature dependence of relaxation frequency and dielectric dispersion $\Delta \varepsilon$ of the (0/65/35) PZT ceramic.



Fig. 9. Cole-Cole diagram of the PZT ceramic (x = 0) below the ferro-paraelectric transition temperature.

strong distortion in the PZT goes with an important tetragonality (c/a > 1) which allows the Ti⁴⁺ and Zr⁴⁺ ions to have displacements from the octahedron center that are clearly different owing to a steric effect due to the different sizes of these two cations. The role of the Zr⁴⁺ ion as a relay in the correlation chain will be made more difficult, the correlation chains will be more short and the value of f_r higher.

Concerning the progressive replacement of Pb^{2+} by La^{3+} , the weak quantities that are introduced seem to play no noticeable role on the variation of f_r at T_c that remains close to 1 GHz for all the lanthanum concertrations (Figs. 7 and 8). On the contrary, the value of $\varepsilon'(T_c)$ increases with the amount of lanthanum (Fig. 4); in this case it is the quality of the compactness of the ceramics that is responsible. Indeed the addition of lanthanum allows

transparent ceramics to be obtained (compactness = 1), which is important in view of electrooptic applications.

The parameter α , a phenomenological parameter that describes the dielectric relaxation, varies also with the temperature (Fig. 11). In fact, this parameter is linked to the dynamic motions of polar elements. In the ferroelectric phase, $\alpha \approx 0$, demonstrating thus the existence of only a simple dipolar reorientation mechanism (Debye relaxation). The response function is exponential $\varphi(t) \propto e^{-t/\tau}$. This implies a simple mechanism, internal to the correlation chains and not dependent on their size (α is independent of the temperature in this region). In contrast, when $T > T_c$, α depends on the temperature. Therefore the dipolar reorientation mechanism becomes more complex (Cole-Cole relaxation). The presence of couplings inside short correlation chains becomes highly likely together with the interaction with long range



Fig. 10. Cole-Cole diagram of the PZT ceramic (x = 0) below the ferro-paraelectric transition temperature.



Fig. 11. Temperature dependence of Cole-Cole parameter α of the (x/65/35) PLZT ceramic (with x = 0, 2, 4 and 5).

polarisation of the environment of these chains. That is to say that interactions over long distances are going to appear (between correlation chains and/or between different composition zones). In the time domain, this behaviour can be described by means of the Kohlrausch-Williams-Watts stretched exponential function [32] which can be derived $\varphi(t) \propto \exp[-(t/\tau)^{\beta}]$ from different theoretical models and where β is a shape parameter that lies between 0 and 1. In the frequency domain, the most general form that has been proposed to describe the non-Debye behaviour is the Havriliak-Negami relaxation function $\Phi(\omega) = [1 + (i\omega\tau)^{(1-\alpha)}]^{\gamma}$ [33], where α and γ are both shape parameters that lie in the range $0 < \alpha, |\gamma| < 1$ ($\gamma =$ $-1, \alpha = 0$: Debye relaxation, $\gamma = -1, -\alpha \neq 0$: Cole-Cole relaxation, 0 > γ > -1, 0 < α < 1: Cole-Davidson relaxation [34]), and τ is a relaxation time. These functions characterize different interaction mechanisms at short and

long range in the paraelectric phases. It is remarkable that the small amount of lanthanum (a few percent) does not modify the relaxation frequency but introduces a new mechanism of interaction in the ferroelectric phase since PZT presents a Debye relaxation, and PLZT (with x = 2 to 5%) a Cole-Cole relaxation.

7 Conclusion

The development of a microwave dielectric measuring device, able to operate at high temperatures, has allowed the study of ceramics with composition $Pb_{(1-x)}La_x(Zr_{0.65}Ti_{0.35})(1-x/4)O_3$ (PLZT) around their Curie temperature (505 $\leq T_c \leq 630$ K). The value of T_c decreases with x most notably due to of the reduction in the amount of Pb²⁺, this latter generally resulting in

ferroelectric distortions caused by the existence of the $6(sp)^2$ lone pair. Studies of frequency variations showed a dispersion of permittivity that comes from a Debye type relaxation close to 10^9 Hz. This relaxation exists in both the paraelectric and ferroelectric regions and the frequency of relaxation shows a minimum at the Curie temperature $T_{\rm c}$. As for BaTiO₃, this relaxation can be clarified by a potential model of double potential wells. The value of $f_{\rm r}$ at $T_{\rm c}~(\sim 9 \times 10^8 {\rm ~Hz})$ for PLZT ceramics is greater than that earlier obtained from ceramics of BaTiO₃ ($f_{\rm r} \sim 10^8$ Hz). This result implies that the cooperative motion between Ti^{4+} and Zr^{4+} ions in PLZT ceramics is coherent within a shorter length of correlation chains l_c than that for only the Ti⁴⁺ ions in BaTiO₃ ceramics. Thanks to its particular configuration it is the Pb^{2+} ion that plays an indirect but fundamental role. The replacement of Pb^{2+} by La^{3+} has no effect on the relaxation frequency, but modifies the long range interactions as well in the ferroelectric phase as in the paraelectric phase.

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