Relaxation and transport mechanisms in $(Pb_{.79}La_{.21}Ti_{.95})O_3$ ceramic

K. Limame, M. Kellati, S. Sayouri
LPTA, Département de Physique, B. P. 1796, Fès-Atlas, Morocco

Variations of the dielectric constant and the relaxation time of La- doped $PbTiO_3$ ceramic, as functions of frequency, are studied using the well- known model of Debye. The conductivity of the material is also studied and the variation of the activation energy as function of frequency is discussed.

I. EXPERIMENTAL

Lead titane ($PbTiO_3$; PT), a ferroelectric material, is known for its interesting properties ; high Curie temperature, pyroelectric coefficient, and spontaneous polarization , and low dielectric constant. These properties make it suitable for numerous applications : ultrason transducers [1] thermistors, optical electronic devices and satellite detection [2], etc. At room temperature, PT has a tetragonal perovskite structure [3,4], and combined with other oxides it forms materials such as (Pb, La)TiO_3, (PLT), Pb (Zr, Ti)O_3, (PZT), and (Pb, La)(Zr,Ti)O_3(PLZT) whose very wide range of applications is well know: non-volatile random access memory (NVRAM) and dynamic random access memory (DRAM) devices [5,6], infrared sensors [7], etc. These materials have been prepared using different methods, among them the sol gel process, possessing some advantages; low processing temperature, high purity, chemical homogeneity and stoichiometry control, etc. In addition, the sol gel method permits the fabrication of amorphous materials, which cannot be realized using other methods. PLT ceramics belong to the family of ferroelectric relaxors: frequency dispersion of the dielectric permittivity, ε_r , and a large maximum of ε_r at a temperature, T_m, which is shifted towards high values with increasing frequency; the corresponding phase transition is called diffuse phase transition.

Recently, we have prepared using the sol gel method a series of $(Pb_{1-x}, La_x)Ti_{1-x/4}O_3$ powder samples (PLTx), corresponding to the concentrations, x (at. %), in La equal to 0, 7, 14, 21, and 28, and have studied the effect of temperature on the evolution of PLT21 using Fourier transform infrared (FTIR) spectroscopy, thermal gravimetric analysis (TGA), differential thermal analysis (DTA) and X-ray diffraction (XRD)[8]. The effect of La-doping concentration was also investigated; in particular, it was shown that the crystallization of PLT occurred at 600°C, which temperature is inferior to that reported for the same composition prepared by the traditional solid-state reaction technique [9]. Besides, we have used XRD and scanning electron microscopy (SEM) to study the synthesis process and the characteristics of the hole series of samples prepared, and their dielectric permittivity were measured in the temperature range of 20 - 550 °C, and in the frequency range of 0.1– 1000 kHz. The results of this experimental study showed that the dielectric properties and the phase transition in PLT ceramics are strongly influenced by the La content, the heat treatment conditions, and the microstructure (homogeneity and densification of the powders related to the method of preparation,…) [10- 12] .

In the present study, we try to interpret dielectric results relative to PLT21, which showed the highest value of the dielectric constant, using the well-known model of Debye, pointing out the role played by the transport phenomenon in these materials.

II. EXPERIMENTAL [8, 10]

The following precursors were used to prepare the PLT powders: lead acetate ($Pb(CH_3COO)_2$, $3H_2O$, purity 99.9 %, Johnson Matthey GmbH Alfa, Karlsrube, Germany), lanthanum acetate ($La(CH_3COO)_3$, xH_2O) (purity 99.9 %, x = 1.5, Johnson Matthey GmbH Alfa, Karlsrube, Germany), and titanium alcoxide (97 % (Assay) Johnson Matthey GmbH Alfa, Karlsrube, Germany). Bidistilled water was used as solvent.

Preparation of the samples was needed two steps. The first step consisted of a preparation of a colloidal solution of TiO_2. Titanium alcoxide was added to 0.5M lactic acid aqueous solutions. A white precipitate was then obtained under stirring, at 80 °C, during 12 hours, which transforms into a clear solution. The latter was adjusted, by adding water, to 1M Ti solution. A rapid stirring was necessary to obtain a homogeneous solution (colloidal solution). In a second step were added to the latter colloidal solution, in stoichiometric amounts, lead and lanthanum acetates. Due to Pb loss during annealing process, 5 mol. % excess lead acetate was added.

Phase identification of the samples was performed using X-ray diffraction (Cu K_α ray, λ= 1.5418 A).
The obtained powders were pressed into discs (diameter: ~13 mm, thickness: ~1.5 mm) and annealed at different temperatures; annealing was performed after coating the discs with PZT powder prepared by the conventional solid-state reaction method.
Dielectric measurements were carried out in the frequency range of 100 Hz to 1 MHz using an inductance – capacitance – resistance (LCR) bridge (HP, Model 4284 A). Scanning electron micrographs (SEM) were obtained using a JEOL – T330 microscope.

III. RESULTS AND DISCUSSION

Fig. 1 shows the variation of the dielectric constant of PLT21 as a function of temperature [10]: a high value was recorded for this sample for a temperature equal to 230 °C. An optimum value of the concentration in La enhances the dielectric constant as observed en other works [13,14] due essentially to the method of preparation and the optimisation of heating parameters (Annealing temperature and the duration of the annealing process which lead to better homogeneity of the powder (fine powder)) [4,8,10,15].
All the features corresponding to a diffuse phase transition are present for the sample studied. Moreover a relaxation phenomenon is also clear from figure 1. The relaxation occurring in these types of materials is generally attributed to various effects [16-18]: frustration, topological disorder, A- and B-site heterogeneities in the (BO_6) and (AO_{12}) octahedron, respectively, anharmonic motion of desordered ions. Besides, this phenomenon is characterized by a relaxation time which is mainly influenced by the type of interactions [17] and the grain size and which expression is given by [19]:

$$\tau_r = \frac{d_g}{d_{jg}} \frac{\varepsilon_0 \varepsilon_{jg}}{\sigma_g}$$

where d_g and d_{jg} denote the grain and grain boundaries, diameters, respectively.
To interpret the results relative to the dielectric constant, we have used the well- known Debye's relation given by:

$$\varepsilon(\omega) = \varepsilon_{hf} + \frac{\varepsilon_{bf} - \varepsilon_{hf}}{1 + (j\omega\tau)^{1-\alpha}}$$

where ε_{hf} , ε_{bf} are the dielectric constants at high and low frequencies respectively, τ the relaxation time, and where α traduces the dispersion of τ, and have used the least square method for the procedure of fitting. Fig 2 displays the variation of the relaxation time as a function of frequency, and table 1 gathers values of the activation energy (E_a), for a temperature ranging between 100 and 200 °C, deduced from this analysis, of figure 3, showing the variation of $\ln(T\sigma)$ as function of (1/T). E_a decreases with frequency and has relatively weak values which traduces the good cristallinity in the cubic phase as observed from XRD spectra [8, 10, 20]. Moreover, for $\nu > 10^4$Hz, E_a becomes practically constant. Figure 4 and 5 show the variation of the dielectric constant (ε) and the dielectric losses ($tg\,\delta$) as functions of frequency (ν), at T=160°C. The rapid and sharp decrease of these two parameters recorded for $\nu < 10^4$ Hz may be due the space charge polarization [21]. For $\nu > 10^4$ Hz the pronounced attenuation of this behaviour my be comes from oxygen vacancies, introduced to compensate for the excess charge in the perovskite lattice [22- 25]. It can be noticed that other studies using Raman spectroscopy, have shown that the local disorder created by La-doping may be linked to the phenomenon of relaxation which occurs in these materials [4] and/or to the grain boundaries and the interfacial polarization [26].The conductivity, σ , of the material, which follows the relation:

$\sigma = \frac{qn}{kT} e^{-E_a/kT}$, increases with increasing frequency; this tendency being more pronounced for $\nu > 10^4$ Hz (Fig. 6). σ also increases with temperature as shown in figure 7; the mechanism of conduction in PLT21 at high frequencies and relatively high temperatures results mainly from the presence of oxygen vacancies and the structural disorder generated by La doping [4]. In the case where $\nu < 10^4$ Hz migration of the space charge is mainly responsible of the observed behaviour of σ.

Table 1:

Frequency (Hz)	10^2	10^3	10^4	10^5	10^6
E_d(eV)	0.46	0.40	0.39	0.30	0.30

IV. CONCLUSION

The model of Debye has been used to interpret dielectric results deduced from the study of the ferroelectric relaxor PLT21 sample and the behaviour of the relaxation time discussed. The conductivity has also been investigated and shows a behaviour, which is consistent with previous works. Besides, variation of the activation energy as a function of frequency reflects the good structural characteristics of the sample. Grain boundaries and space charge effects seem to have great influence on the above parameters traducing the transport phenomenon.

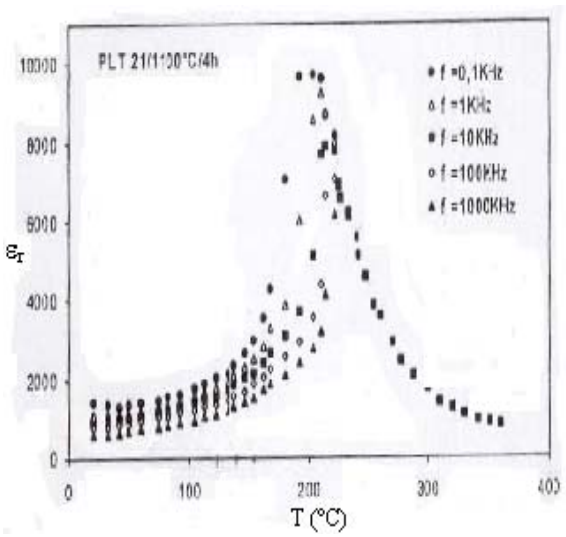

Fig.1. Temperature dependence of dielectric constant of (PLT21) sample [10]

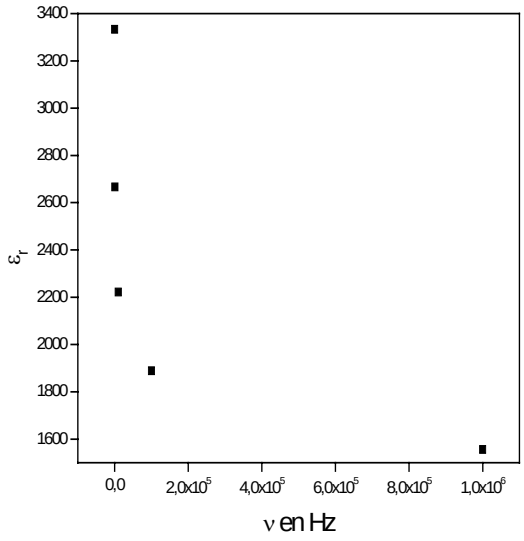

Fig.3. Inverse temperature dependence of ln(σT)of (PLT21) at various frequencies

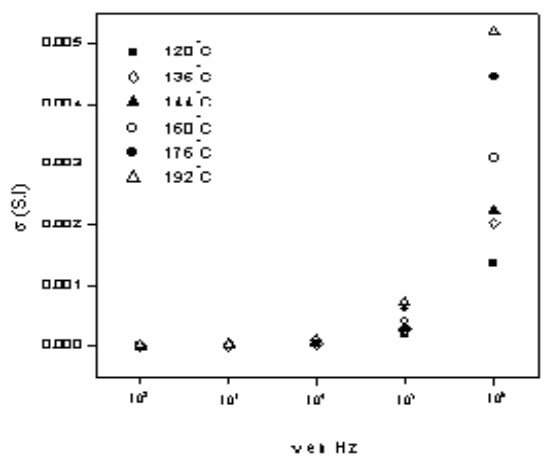

Fig.2. Frequency dependence of relaxation time at various temperatures of PLT21

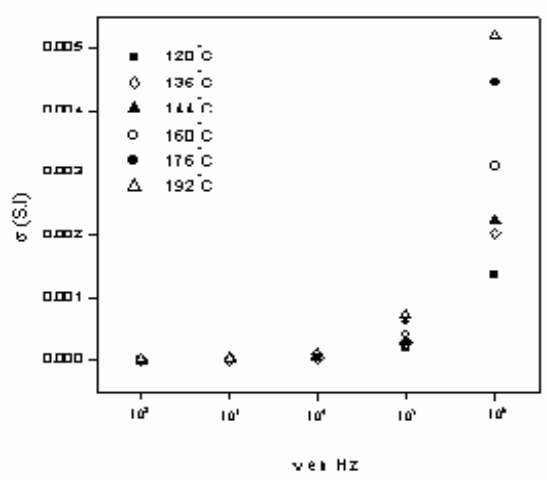

Fig.4. Frequency dependence of dielectric constant of (PLT21) a temperature of T=160°C

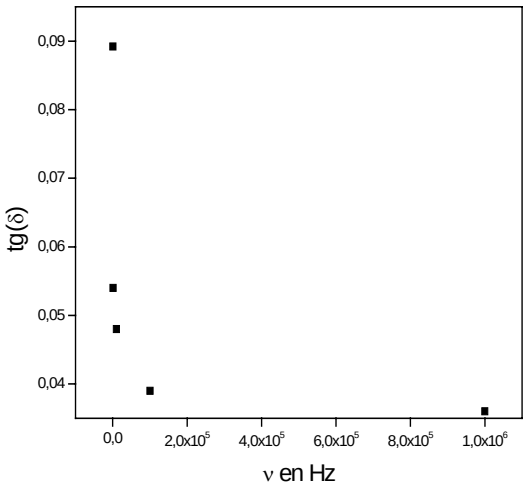

Fig.5. Frequency dependence of tangent losse constant of (PLT21) a temperature of T=160°C

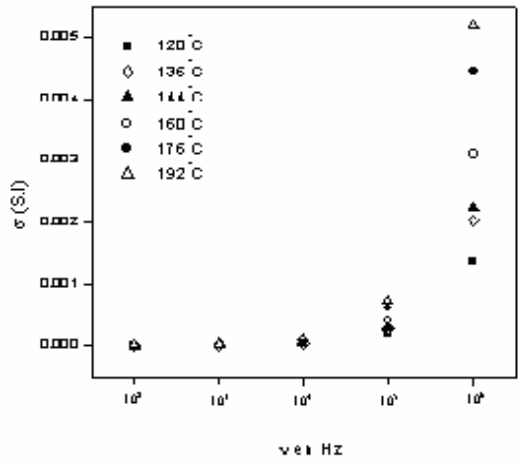

Fig.6. Frequency dependence of conductivity of (PLT21) at various temperatures.

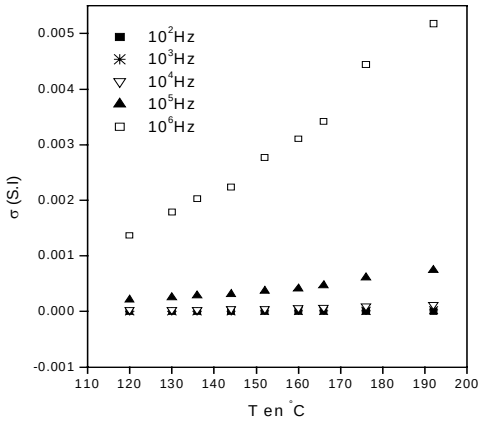

Fig.7. Temperature dependence of conductivity of (PLT21) sample at various frequencies

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