# Dielectric and relaxation studies in hydrothermal processed PLZT ceramics

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$(Pb_{1-y}La_y)(Zr_{0.52}Ti_{0.48})O_3$ (PLZTy) powders were prepared using hydrothermal process and their structural and dielectric properties investigated. Increasing La content is shown to enhance crystallization of the raw samples and to transform the average symmetry to tetragonal one in the calcined ones. Two anomalies are observed on the real part of the permittivity on the sample with y = 0.03, at a relatively high temperatures ( ~ 180 °C, ~ 260 °C). The latter was interpreted as a transition from ferroelectric-rhombohedral phase to ferroelectric-quadratic phase. A quadratic law in temperature was used to study the temperature dependence of the dielectric constant of the samples showing the relaxation phenomenon and values of the fitting parameters such as the diffuseness parameter were calculated and discussed.
**Keywords:** PLZT; Dielectric anomalies; Relaxation, MPB; Diffuseness parameter

## I. INTRODUCTION

Ferroelectrics constitute an important class of materials that are used in the electronics industry. Studies devoted to these materials are mainly interested in polycrystalline ( ceramics) and thin film forms. Ferroelectric lead zirconate titanate $Pb(Zr_{1-x}Ti_x)O_3$ (PZT) are known to exhibit high piezoelectric and pyroelectric properties [1-3]. These materials are also known for their unusual phase boundary, called the morphotropic phase boundary (MPB)[4], which occurs at around 50 % Zr substitution for Ti in $PbTiO_3$, and which separates two structural phases rhombohedral ( Zr-rich region) and tetragonal ( Ti-rich region) structures; in particular, a very high piezoelectric response is recorded in the MPB. The occurrence of the MPB depends mainly on the procedure of preparation of the samples and the grain sizes [5,6]. Substitution of Lanthanum for Lead (PLZT) in these materials changes their macroscopic properties from normal ferroelectric to relaxor ferroelectric types; relaxation phenomenon affects deeply PLZT properties (anomalies). In particular, high values of dielectric permittivity and electromechanical and electro optic coefficients are recorded, which make these materials suitable for various applications such as capacitors, optoelectronic modulators,…[7-9]. These anomalies manifest themselves within a broad temperature region around a temperature, $T_m$, corresponding to the maximum in the dielectric permittivity; the phase transition is called 'diffuse phase transition' (DPT). Several models and approaches have been developed to interpret this DPT involving different mechanisms: chemical heterogeneities, superparaelectric behaving due to mesoscopic heterogeneities,…[10-14]. However, details concerning the physical process of the DPT remains not completely clear. As mentioned above, a maximum response of different characteristics, among them the electromechanical coupling coefficient, is obtained due to the coexistence of ferroelectric tetragonal and ferroelectric rhombohedral phases near the MPB. Based on this coexistence, different phase diagrams have been proposed [15, 16]. Moreover, this enhancement of the electromechanical response is suggested to be linked with the instability in the vicinity of the rhombohedral to tetragonal transition [16].

Low temperature dielectric measurements have revealed the presence of two anomalies in the real part of the dielectric constant of PZT materials near the MPB [17]. The occurrence of the anomaly corresponding to the lowest temperature was imputed to a tetragonal to monoclinic phase transition, which was supported by XRD studies of Noheda et al. [18]. The presence of such anomaly has also been reported in dielectric studies of PZT materials near the MPB [19]. With the aim of studying the effect of La addition on the structural and dielectric properties of the morphotropic phase boundary composition $Pb(Zr_{0.52}Ti_{0.18})O_3$ (PZT), we have prepared , using the hydrothermal process, $(Pb_{1-y}La_y)(Zr_{0.52}Ti_{0.48})O_3$ (PLZTy) powders, with y = 0, 0.015, 0.03, 0.06, 0.08, 0.10, 0.12, and 0.15. Indeed, addition of La ( La belongs to the so-called soft-dopants additives ) is known to improve permittivity and piezoelectric coupling coefficient of PZT materials [20]. Moreover, hydrothermal processing, contrary to other methods of preparation, in particular the solid-state reaction method, permits a good control of composition and morphology of the powder, does not necessitate any milling and calcinations operations and has lower agglomeration effects ( the latter having dramatic effects on the consolidation and densification behaviour of the powder) [21, 22]. The results

obtained from our studies were analysed and compared to those of the literature.

## II. EXPERIMENT

The procedure of preparation of the samples was conducted in two-steps. In the first step, aqueous solutions of $ZrOCl_2$, $8H_2O$ 0.1M and $TiOCl_2$-xHCL (Ti: 15%) were mixed, with stirring, and 2M KOH was added until precipitation to obtain a precipitate (ZTO) which was then washed with distilled water for several times to obtain its neutrality. ZTO was put into an aqueous solution of 0.2M lead acetate and 0.5M lanthanum acetate. Thereafter, the solution obtained, which pH was raised to 11 by adding 2M KOH, was put into an autoclave ( Filling ratio superior to 80%) and heated at 200 °C during 12 hours. The resultant PLZT suspension was filtered and the remaining product was washed with distilled water for several times and finally dried at 70 °C in an oven. Annealing of the powders, at different temperatures, was done in air.

For dielectric measurements, PLZT powders were pressed into discs (diameter ~13 mm, ~1 mm thick) using poly (vinyl alcohol) as a binder. Dielectric constant ($\varepsilon_r$) and dissipation factor ( tan$\delta$) were measured using an impedance analyzer ( LCR) ( HP, Model 4284 A) in the frequency range 20 Hz - 1 MHz and for temperatures ranging from 30 to 450 °C. Scanning electron micrographs (SEM) were obtained using a JEOL – T330 microscope.

## III. RESULTS AND DISCUSSION

Fig. 1 displays XRD spectra of PLZTy samples, with y = 0, 0.015, 0.03, and 0.10 calcined at 700°C during 4 hours, which shows the coexistence of rhomohedral and tetragonal phases which is consistent with the fact that the compositions are near the MPB. Moreover, these figures clearly show the influence of addition of La on the structure of the samples prepared under the same conditions. Indeed, increasing La content seems to tend to transform the average symmetry to tetragonal one (Fig. 1) as indicated in the PLZT phase diagram [4]. Besides, no secondary phases (pyrochlore) have been detected. Dielectric measurements performed on samples annealed at 1100 °C ( y = 0, 0.03, 0.06, 0.08, 0.10, 0.12, 0.15, annealed during 2 H)) and 1200 °C ( y = 0.10 annealed at 1200 °C during 2 H and y = 0.12 annealed at 1200 °C during 2H and 5H) led to the curves given on figures 2, and 3, respectively. These figures revealed that the transition temperature from ferroelectric (FE) phase to paraelectric (PE) phase, corresponding to the maximum of the permittivity, $\varepsilon_r$ (Fig. 2a), of the undoped sample (PLZT0) is in agreement with the FE-PE phase boundary in the PZT phase diagram proposed by Jaffe et al. [4], and that increasing the annealing temperature, $T_a$, of the samples ameliorates $\varepsilon_r$ and gives a slight decrease of the temperature, $T_m$, of the maximum of $\varepsilon_r$ reaching low values for the samples with y = 0.10 (Fig. 3a) and 0.12 (Fig. 3b) and for $T_a$ = 1200 °C (Table 1). However, annealing of the sample with y = 0.12 at 1200 °C during 5H led to a deterioration of $\varepsilon_r$ (Table 1) which points out the role played by both annealing temperature and the duration, $t_a$, of the annealing process; dielectric properties depend strongly on the conditions of preparation and consequently on the microstructure of the samples as shown by SEM micrographs of Figs 4a and 4b corresponding to the samples with y = 0.10 and 0.12; Fig. 4b showing clear microstructural inhomogeneities.

Figures 2 and 3 show also that relaxation phenomenon takes place for y = 0.10, accompanied with a broad temperature region around $T_m$ (DPT), together with a decrease of $T_m$ (Fig. 2e). This phenomenon is more pronounced in the samples heated at 1200 °C (Fig. 3a).

Near the DPT (around $T_m$) the dielectric constant behaves as a function of temperature in conformity with the following equation:

$$1/\varepsilon=1/\varepsilon_{max}(1+(T-T_m)^{\gamma}/2\delta^2) \qquad (1)$$

where $\gamma$is a parameter which values are such as $1 < \gamma < 2$.In the ideal case of a Curie- Weiss behavior, $\gamma$ equals 1, and it takes the value 2 for relaxor behavior. $\delta$ is a parameter traducing the broadening of the phase transition; indeed doping with La has a strong influence on the broadening. Fig. 5, where the reduced dielectric constant $\varepsilon_{max}/\varepsilon$ is plotted as a function of the reduced temperature $(T - T_m)/T_m$ clearly shows this influence; the width of these curves, representing the width of the broadening, increases with increasing La content. As expected from fitting of experimental data corresponding to PLZTy, with y = 0, 0.08, 0.12 and 0.15, with the help of Eq. (1), a linear fit is obtained (Figs. 6).

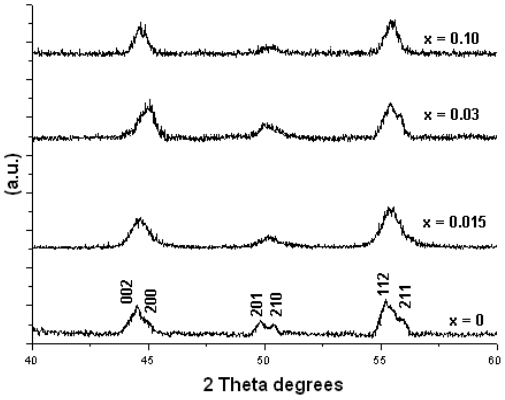


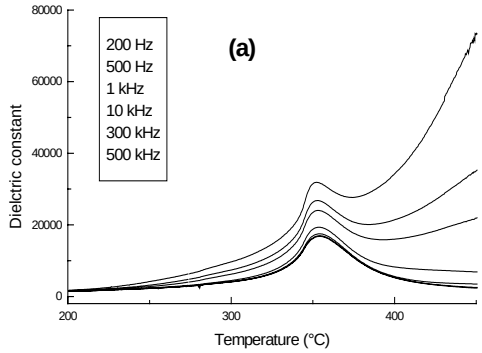

**Fig.1**: XRD patterns of PLZTy samples calcined at 700°C during 4 hours showing the gradual transformation from the MPB phase to quadratic phase

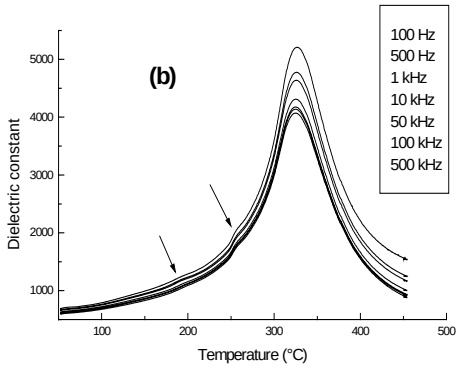
| PLZTy | f (Hz) | $T_a$ (°C) (in hour | $\varepsilon_m$ | $T_m$ |
|---|---|---|---|---|
| PZT (y = 0) | 200 | 1100 (2 | 31800 | 352 |
| PLZT0.03 | 100 | 1100 (2 | 5210 | 326 |
| PLZT0.06 | 100 | 1100 (2 | 3750 | 267 |
| PLZT0.08 | 100 | 1100 (2 | 2300 | 253 |
| PLZT0.10 | 200 | 1100 (2 | 5807 | 159 |
| PLZT0.10 | 100 | 1200 (2 | 7098 | 144 |
| PLZT0.12 | 100 | 1100 (2 | 6976 | 167 |
| PLZT0.12 | 100 | 1200 (2 | 7989 | 100 |
| PLZT0.12 | 100 | 1200 (5 | 3740 | 109 |
| PLZT0.15 | 100 | 1100 (2 | 2554 | 120 |

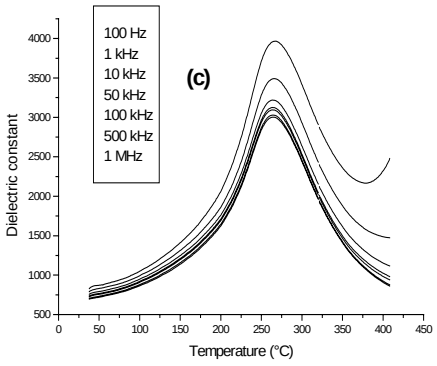
**Table 1:** $T_m$ and $\varepsilon$ values, for different PLZT compositions.

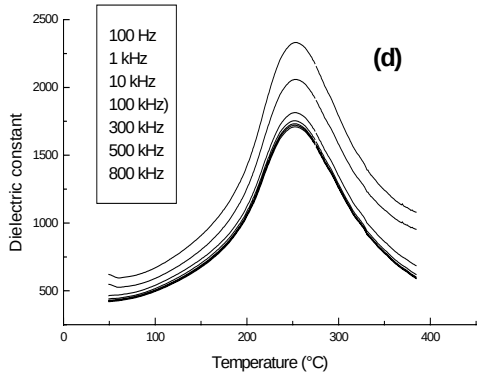
| PLZTy | $T_a$ (°C) ,$t_a$ (in hours)) | $\delta$ | $\gamma$ |
|---|---|---|---|
| PZT(y=0) | 1100 (2) | 1.6 | 11.1 |
| PLZT0.03 | 1100 (2) | 1.5 | 13.9 |
| PLZT0.06 | 1100 (2) | 1.45 | 19.3 |
| PLZT0.08 | 1100 (2) | 1.45 | 19.6 |
| PLZT0.10 | 1100 (2) | 2 | 58.5 |
| PLZT0.10 | 1200 (2) | 2 | 65.0 |
| PLZT0.12 | 1100 (2) | 2 | 53.3 |
| PLZT0.12 | 1200 (2) | 2 | 75.0 |
| PLZT0.12 | 1200 (5) | 2 | 78.0 |
| PLZT0.15 | 1100 (2) | 2 | 68.0 |

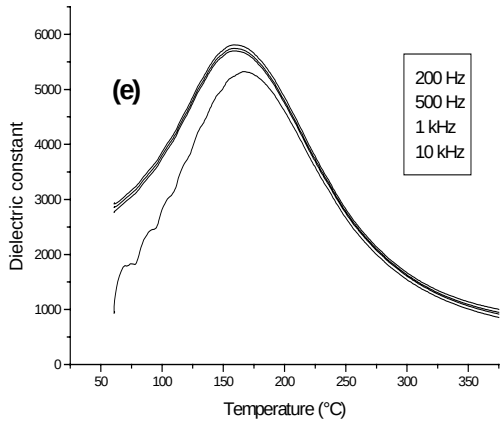
**Table 2**: $\delta$ and $\gamma$ values, for different PLZT compositions at 10 kHz

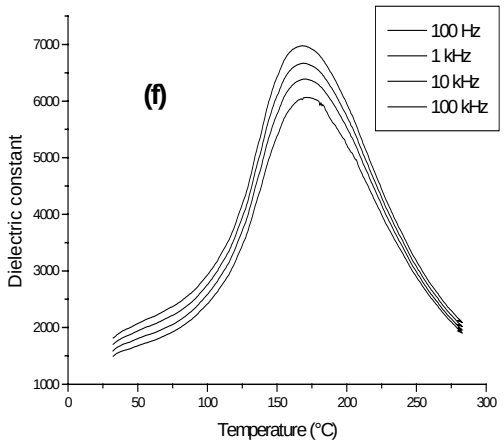




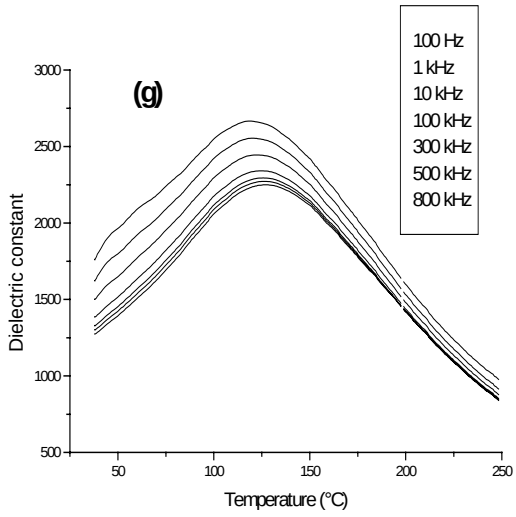
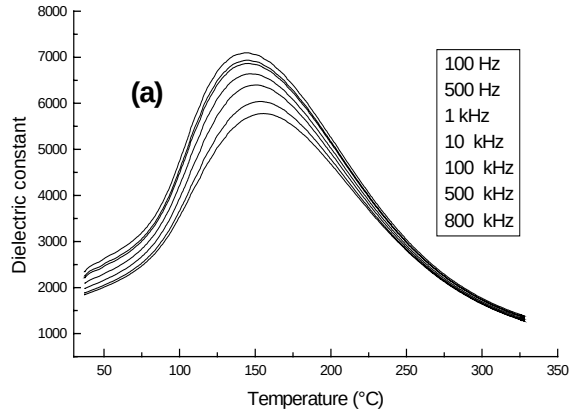
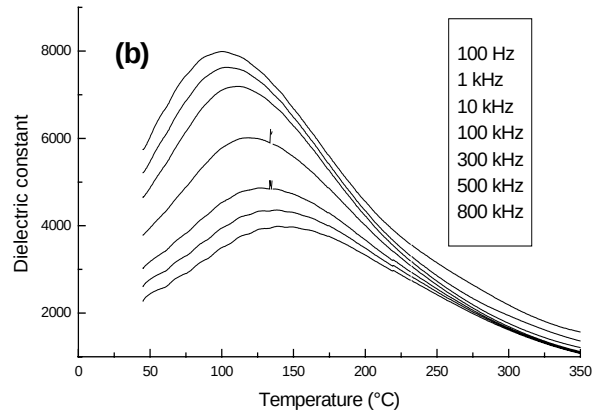




**Fig.2 :** Dielectric constant variation as a function of temperature for PLZTy, y = 0 (a), 0.03 (b), 0.06 (c), 0.08(d), 0.10 (e), 0.12 (f), 0.15 (g), annealed at 1100°C during 2H (frequency increases from top to bottom)



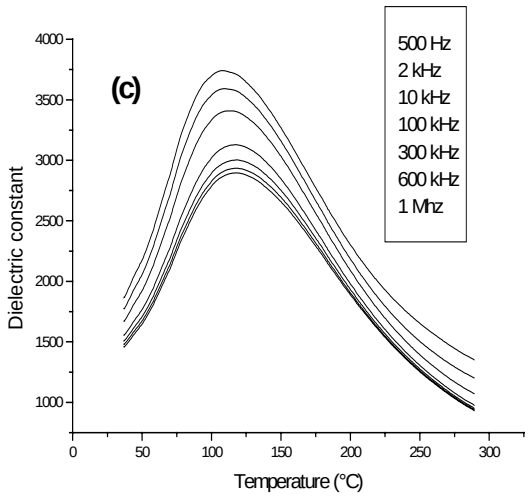




**Fig. 3**: Dielectric constant variation as a function of temperature for PLZTy, (a) PLZT0.10 annealed at 1200°C during 2h, (b) PLZT0.12 annealed at 1200°C during 2h, (c) PLZT0.12 annealed at 1200°C during 5h (frequency increases from top to bottom)

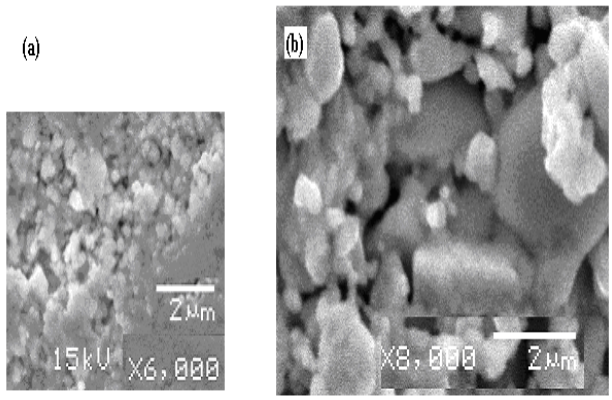



**Fig.4:** SEM micrographs of PLZTy samples
(a) PLZT0.10 annealed at 1100°C during 2 H
(a) PLZT0.12 annealed at 1100°C during 5 H

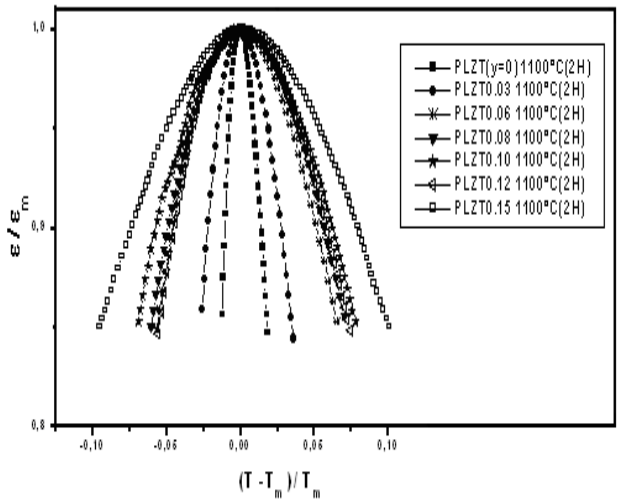



Fig.5.: Reduced dielectric constant $\varepsilon / \varepsilon_m$ vs reduced temperature $\tau$ for different PLZT compositions

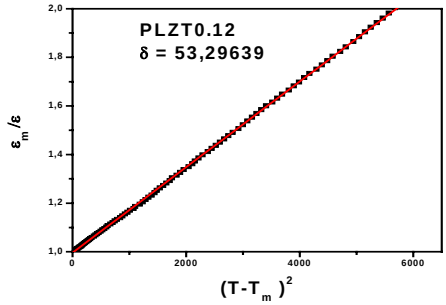



Fig. 6a.

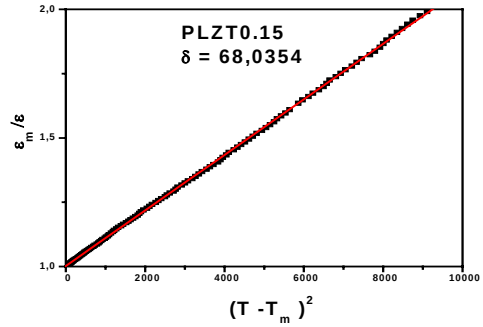



Fig.6b

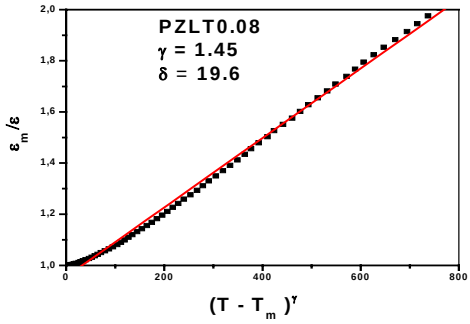



Fig. 6c.

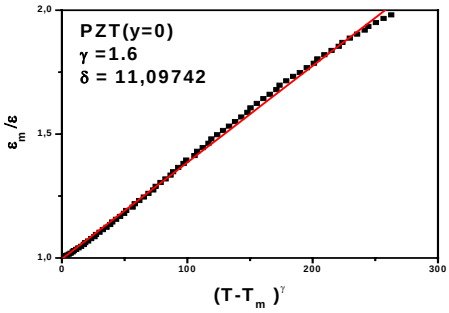



Fig. 6d.

Fig.6: Reduced dielectric constant $\varepsilon_m/\varepsilon$ vs reduced temperature $(T-T_m)^{\gamma}$ for different PLZT compositions

The corresponding values of the two parameters ($\gamma$ and $\delta$) are gathered in table 2. $\gamma$ equals 2 for relaxor behavior (Figs. 6a and 6b) (samples annealed at 1100 °C with y = 0.12, 0.15) and is inferior to 2 for normal behavior (Fig. 6c and 6d) (samples annealed at 1100 °C, with y = 0, 0.08). It is interesting to note that the parameter $\delta$ increases with increasing annealing temperature pointing out the crucial role played by the microstructure itself influenced by factors such as structural chemical defects.

Concerning the variation of $\varepsilon_r$ as a function of temperature, this constant increases with increasing La reaches a maximum for y = 0.12 and then decreases (Table 1). Gupta et al.[23] obtained a maximum of $\varepsilon_r$ at y = 0.02, however relaxation occurs at a concentration ( y = 0.08) close to ours.

Moreover, two anomalies are observed at about 180 °C and 260 °C on PLZT0.03 (Fig. 2b) heated at 1100 °C. The existence of such anomalies has been reported in the literature; however, other studies have not revealed them [23]. Ragini et al. [17] have observed two anomalies at low temperatures (197 K and 253 K) on PZT samples ($PbZr_xTi_{1-x}O_3$, x = 0.52 and x = 0.515), which they imputed, based on the work of Noheda et al. [24], to a transition from tetragonal to monoclinic phase for the first anomaly (located at about 197 K) and to a cell-doubling transition [24] for the second anomaly (located at about 253 K). Sheen and Kim [19] have also observed an anomaly on PZT thin films, which they interpreted as a transition from tetragonal to monoclinic symmetry with decreasing temperature ( $PbZr_{1-x}Ti_xO_3$, x = 0.46, 0.48, 0.49, where the anomaly occurs at about 490 K, 325 K, and 235 K, respectively). Our results reveal the existence of anomalies at relatively high temperatures in comparison with those mentioned above. Bouzid studied the effect of Niobium and Potassium doping on the anelastic behavior and on the dielectric response of Pb $(Zr_{0.54}Ti_{0.46})O_3$ (PZT54/46) samples prepared using the conventional mixed-oxide method [25, 26]. From dielectric measurements, Bouzid observed two anomalies, at relatively high temperatures, on undoped PZT54/46 samples and on those doped with Nb and K. These two anomalies were interpreted as being due to a rhombohedral to quadratic phase transition for that located at a temperature of about 180 °C (undoped sample), and to a quadratic to cubic phase transition for that occurring at about 370 °C (undoped sample). This interpretation was based on the correlation made between mechanical losses and dielectric losses [25, 26]. Indeed, anelastic behavior (mechanical losses and elastic modulus) studies showed the existence, for the undoped and doped samples, of two minimums of the elastic modulus [26], which indicates the occurrence of two phase transitions [26]: rhombohedral to quadratic phase and quadratic to cubic phase. Moreover, these observations are supported by the work of Gerthsen et al. [27] pointing out the correlation existing between mechanical and dielectric losses.

Concerning the anomalies we have observed from dielectric studies of our samples, one may infer from comparison of our results to those mentioned above that the anomaly (located at about 180 °C) is due to a transition from ferroelectric- rhombohedral phase to ferroelectric-quadratic phase. it can be noticed that the existence of such anomaly has not been reported in other works on PZT ceramics prepared by other methods [23]. The anomaly located at about 260 °C, which disappears in the sample with y = 0.06, may be due to an "intrinsic" phenomenon and needs more investigation to clarify its origin.

## IV. CONCLUSION

PLZT ceramics with compositions near the morphotropic boundary phase have been prepared and their structural and dielectric properties investigated. Addition of La seems to enhance crystallization of the raw powders and moves the structural phase towards tetragonal one. Moreover, no secondary phase has been detected. Dielectric measurements revealed the existence of two anomalies at relatively high temperatures T≈180 °C and T≈260 °C. The former, which presence is consistent with a previous work, is interpreted as the temperature at which the transition from ferroelectric-rhombohedral phase to ferroelectric-quadratic phase occurs. The existence of these two anomalies seems to be dependent on the method of preparation of the samples. Relaxation occurs in our samples at about y = 0.10, and the dielectric constant reaches its maximum for y ≈ 0.12, which value is different from other studies where this maximum occurs at low values of y. In the vicinity of the (diffuse) phase transition from ferroelectric to paraelectric phase, the dielectric constant follows a quadratic law in temperature in the case of relaxor behavior and the broadening of the phase transition is shown to increase with La content.

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