Structural study of the $PbZr_{0.52}Ti_{0.48}O_3$ under hydrostatic pressure

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Abstract

Piezoelectric Lead zirconate titanate perovskite $PbZr_{0.52}Ti_{0.48}O_3$ (PZT) prepared by the hydrothermal method is investigated by Energy Dispersion X-Ray Diffraction (EDXRD) as function of pressure and by dielectric measurements as function of temperature. The energy dispersion patterns investigated up to 42.80GPa show peaks that are assigned to the pseudo cubic structure and show that all peaks remain visible for the whole domain of pressure. By else, the dielectric behaviour of PZT ceramics shows two anomalies or modes at 180°C and 260°C which are interpreted as due to the predominance of the tetragonal phase and a complete structural transition rhombohedral-tetragonal, respectively.

1. Introduction

Lead zirconate titanate Pb $(Ti_{1-x}Zr_x)O_3$ (PZT) ceramics exhibit high piezoelectric and pyroelectric properties and thus are widely used as sensors and actuators[1] and numerous investigations of chemical and physical properties of the solid solution have been paid[2,3]. These materials are 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 the structural rhombohedral phase of the Zr rich region and the structural tetragonal phase of the Ti-rich region. The two phases coexist without a solubility gap [4]. PZT ceramics usually exhibit their maximum values of dielectric permittivity and piezoelectric coefficients close to 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. In PLZT, relaxation deeply affects its properties with an increase of the dielectric permittivity, the electromechanic and electrooptic coefficients, which allows considering various additional applications such as capacitors or optoelectronic modulators [7,8].

2. Experimental results and discussion

$PbZr_{0.52}Ti_{0.48}O_3$ and $Pb_{1-y}La_y(Zr_{0.52}Ti_{0.48})_{1-y/4}O_3$ powders, with y= 0, 0.015 and 0.03 have been prepared by the hydrothermal process [9] and pressed into discs with a diameter equal to 12 mm and a width equal to1mm. The $PLZT_y$ powders have been treated at 850°C (y=0) and 1100°C (y= 0.03) for 2 hours.

The effect of La in PLZT powders on the dielectric properties of the MPB composition has been evaluated by XRD, EDXRD under hydrostatic pressure, and by dielectric measurements versus temperature at different frequencies.

We have report the temperature dependence of the dielectric constant ε_r for different frequencies (fr) in figures 1 and 2 for PZT sintered at 850°C during 2H and for $PLZT_{0.03}$, sintered at 1100°C, respectively. We can see for PZT (Fig.1) that ε_r increases with the temperature and that two dielectric modes occur at about 180°C and 260°C with an amplitude that decreases when frequency increases. The existence of these two modes was already

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reported in literature [10]. For $PLZT_{0.03}$ (Fig.2), the dielectric response for all frequencies indicates that the amplitude of the two modes decreases when concentration of La and/or the sintered temperature increase.

The origin of the two observed dielectric anomalies was explain by Mishra et al. [12], which attributed the first mode observed at 180°C to the predominance of the tetragonal phase and the second mode observed at 260°C to the complete structural transition from rhombohedral to tetragonal phases. Within the new experimental results obtained during the present study, the earlier propositions for indexation of the modes will be discussed below.

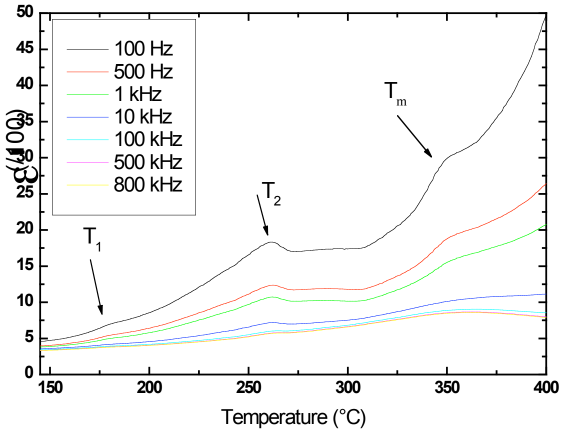

Figure: 1. Dielectric constant as a function of temperature for PZT, sintered at 850°C during 2H (frequency increases from top to bottom).

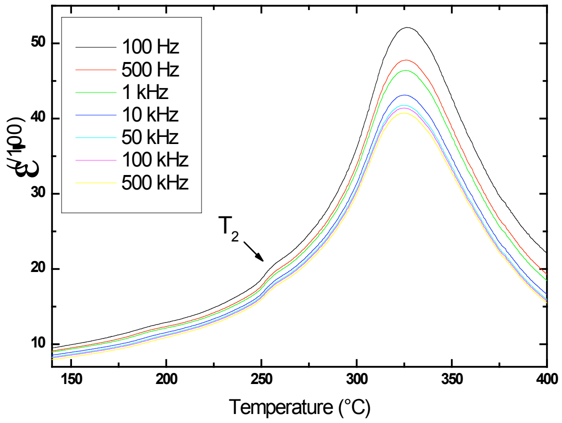

Figure: 2. Dielectric constant as a function of temperature for $PLZT_{0.03}$, sintered at 1100°C during 2H (frequency increases from top to bottom).

It is known that the pressure often decreases the ferroelectric-paraelectric temperature transition. Thus, to confirm the origin of these modes, we studied the PZT ceramics under high hydrostatic pressure by X-Ray diffraction.

We have reported in figures 3, 4 the XRD spectra at room temperature of PZT and $PLZT_y$ (y=0, 0.015 and 0.03) respectively, calcined at various temperatures between 700°C and 1100°C. Spectra in figure 3-a presents a shoulder (200) in the peak, which indicates the presence of the morphotropic phase boundary due to the coexistence of rhombohedral and tetragonal phases. As shown by the curves of Fig. 3-c for samples heated at 1100°C, the tetragonal phase only remains. This can also be observed in Figs. 3 and 4 when the temperature of calcination increases, where the reflection peak at (200) splits into two peaks, (200)T and (002)T [13,14]. We can deduce that the tetragonal structure, for $PLZT_y$, becomes stable with heating at 1100°C. These results are in good agreement with those reported in literature [15].

Now, we consider experimental results of XRD spectra for $PLZT_y$ (y=0, y =0.015 and y= 0.03) calcined at 1100°C for 2 hours as represented in Fig.5. We can observe, first that the addition of La leads to the reduction of the coexistence of both phases tetragonal-rhombohedral. At second, we can observe that, as seen by the respective amplitude of the two peaks when the sintering temperature increases up to 1100°C, the addition of La also leads to the reduction of the tetragonal phase. We see that PZT samples calcined at 850°C, present at room temperature the morphotropic phase and the anomaly T_1 observed at 180°C is due to the beginning of the predominance of the tetragonal phase on the rhombohedral one. On another hand, addition of La or increasing of the temperature of calcination reinforces the tetragonal phase, so that the $PLZT_{0.03}$ calcined at 1100°C is in the tetragonal phase at room temperature and thus, cannot present a phase transition to the rhombohedral phase when the temperature

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increases. Only a transition to a high temperature cubic phase can exist. So the observed mode T_2 at 230°C cannot be attributed to a R-T (total) phase transition.

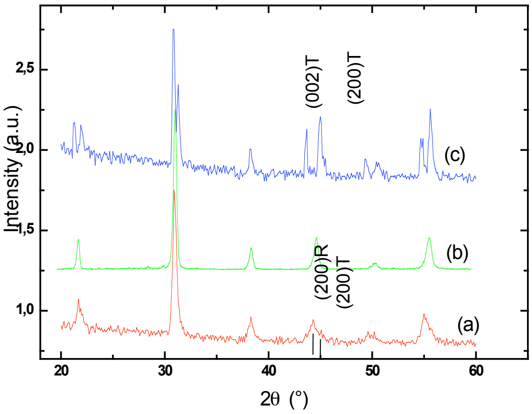

Figure 3: XRD spectra for PZT calcined at (a) 700°C, (b) 850°C (c) 1100°C

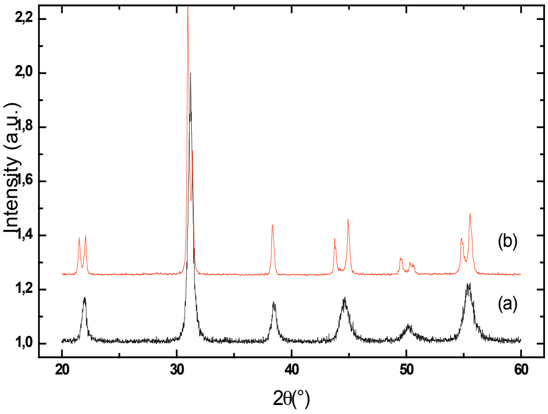

Figure 4: XRD spectra for $PLZT_{0.015}$ calcined at (a) 700°C, (b) 1100°C

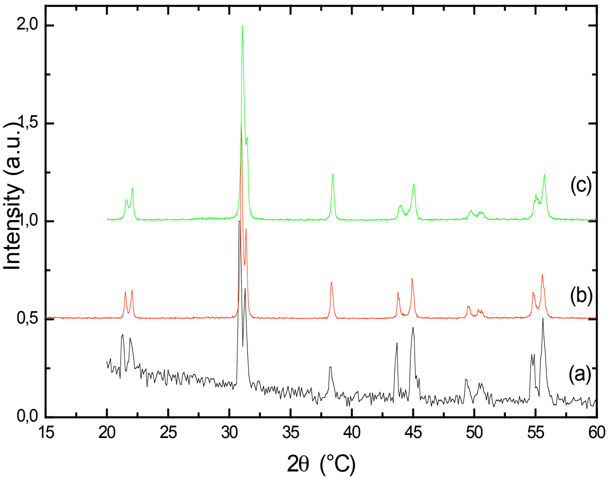

Figure 5: XRD spectra for $PLZT_y$ calcined at 1100°C for 2 hours (a) y=0, (b) y =0.015 and (c) y= 0.03

To evaluate the critical pressure threshold responsible of structural transformations, we investigate the powders under high hydrostatic pressure with the EDXRD measurements method at room temperature. PZT powdered samples are pressurized using a gasketed diamond anvil cell (DAC).

Fig. 6 shows the energy dispersion XRD patterns collected at different pressures up to 42.80 GPa for the hydrothermal PZT calcined at 700°C during 4 hours and heated 2 hours at 850°C. All peaks are assigned to the pseudo cubic structure. Note that upon compression, all peaks remain visible until the highest pressure reached in this study. Results plot in Fig. 6 also show that the compression induces a shift of peaks reflection that is reversible when the pressure decreases from 42.80 GPa to 1 atm. No additional peaks due to other phases can be identified proving that the pseudo cubic structure is more stabilized by high pressure.

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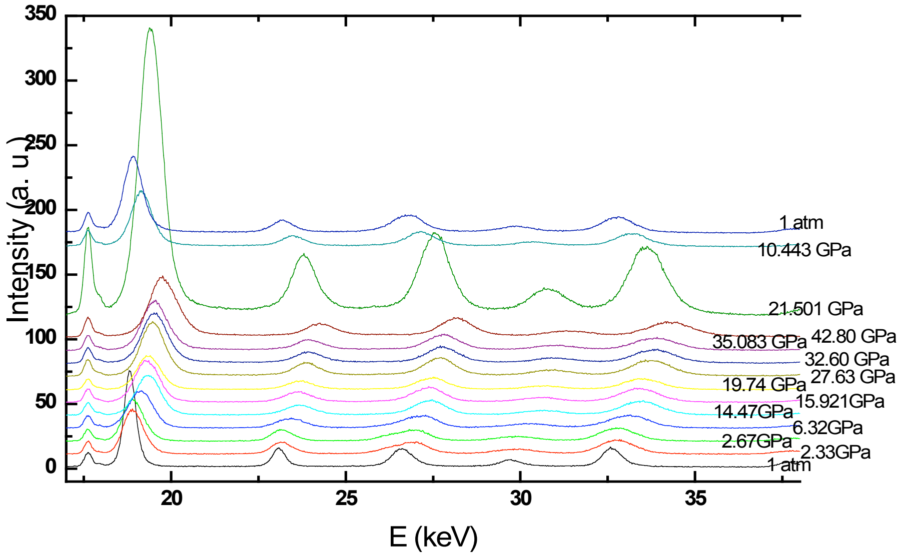

Figure 6:. Energy dispersion XRD patterns of PZT to pressure up to 42.80 GPa and decrease pressure at 1 atm.

4. Conclusion

$PLZT_y$ ceramics with compositions near the morphotropic phase boundary ($Pb_{1-y}La_y(Zr_{0.52}Ti_{0.48})O_3$) have been prepared using the hydrothermal process and investigated. The present study focuses on the influence of La content and sintering temperature on structure and dielectric properties of $PLZT_y$ (y=0, 0.015 and 0.03). It shows that PLZT presents two modes or anomalies in the ferroelectric domain. These modes are affected by the La concentration and the sintering temperature. The anomaly observed at 180°C is attributed to a predominance of the tetragonal phase on the rhombohedral phase, the second anomaly which occurs at 260°C can not be attributed to the structural transition rhombohedral-tetragonal because the tetragonal structure was stabilised at high temperature around 1000°C. Studies at high pressure do not reveal a new structural transition, but on the contrary confirm that the pseudo cubic structure is stabilized by high pressure.

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