



Structural Transformation and Pressure-Induced Phase Transitions in PZT

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Abstract. Angle-dispersive X-ray diffraction, Raman scattering and dielectric spectroscopy measurements versus hydrostatic pressure were carried out to follow the crystalline-to-crystalline transformation occurring in $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ ceramic powders. Different PZT compositions under hydrostatic pressure up to 20 GPa were studied. Dielectric measurements versus pressure up to 2 GPa are discussed to bring new insights on the Pressure-composition (P-x) phase diagram. Based on these results, an updated version of the PZT (P-x) phase diagram is proposed.

Keywords: PZT, lead zirconate titanate, phase transition, high pressure, X-ray diffraction, Raman spectroscopy, dielectric properties

Introduction

For many years, the perovskite $\text{PbZr}_{(1-x)}\text{Ti}_x\text{O}_3$ solid solutions between lead zirconate and lead titanate have been the subject of extensive research in both experimental and theoretical physics. This rich and complex phase diagram exhibits a morphotropic phase boundary (MPB around $x = 0.48$) particularly interesting to study for both investigation of phase transitions and understanding of the origin of the peak observed in the relative permittivity and the piezoelectric coupling coefficient. Recently, Noheda et al. [1] discovered a new ferroelectric phase which adopts a monoclinic symmetry in the MPB region. This phase acts as a transitional bridge between the Ti-rich tetragonal and Zr-rich rhombohedral phases [1] and the polarization is changed in a continuous manner from the [001] to the [111] pseudo-cubic directions as the composition x decreases in the MPB region [2]. However, despite the high sensitivity of PZT to stress induced by external fields, only a few research have been reported on the pressure-induced phase transitions in these materials. In order to investigate the pressure-composition

phase diagram of the $\text{PbZr}_{(1-x)}\text{Ti}_x\text{O}_3$ solid solution, phase transitions versus hydrostatic pressure in the composition range $0.48 < x < 0.80$ have been studied by angle-dispersive X-ray diffraction and Raman scattering up to 20 GPa. Additional dielectric measurements versus hydrostatic pressure were carried out in order to characterize the polarization behaviour up to 2 GPa.

Experimental

$\text{PbZr}_{(1-x)}\text{Ti}_x\text{O}_3$ powder and ceramic samples in the composition range $0.48 < x < 0.80$ were prepared using a two-step solid-reaction technique described in our previous articles [6, 7]. Angle-dispersive X-ray diffraction data at high pressure on $\text{PbZr}_{(1-x)}\text{Ti}_x\text{O}_3$ powders were obtained at $T = 298$ K using a laboratory source for an average acquisition time of 48–60 h. The powder was loaded in gaskets between the anvils of the DAC (Diamond Anvil Cell). The 4:1 methanol: ethanol or 21:4:1 methanol: ethanol: H_2O (MEW) mixture were used as a pressure transmitting medium and powdered ruby or NaCl were added as pressure calibrants. Cell parameters were obtained by full profile refinement using the software Fullprof [4].

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High-pressure Raman experiments were performed in modified back-scattering geometry using a Jobin Yvon Model U 1000 double monochromator and a liquid nitrogen cooled CCD. The 647.1 nm line of an krypton ion laser was used for excitation and samples were loaded in a membrane-type DAC along with a ruby crystal as a pressure calibrant. The pressure-transmitting medium was argon. Dielectric measurements on ceramic pellets were performed with an Agilent 4294A impedance analyzer in a laboratory cell on the third stage of a Unipress gas compressor with petroleum as pressure transmitting medium. Both X-ray diffraction and Raman spectra after pressure release were identical to the initial recorded spectra, and the values of the dielectric constant after pressure cycling were the same.

Results and Discussion

Figure 1 presents the composition-pressure phase diagram of Ti-rich PZT as obtained from all experimental measurements. Whatever the composition in the studied hydrostatic pressure range, X-ray diffraction and Raman scattering experiments point out a series of phase transitions. In the Fig. 2 we have reported the cell-constant and volume change versus pressure obtained from full profile refinements for $\text{PbZr}_{0.40}\text{Ti}_{0.60}\text{O}_3$. Three different slope changes can be seen which correspond to the phase-transition sequence $T(P4mm) \rightarrow M^{\text{LP}}(Cm) \rightarrow M^{\text{HP}}(Cc) \rightarrow C$ as observed

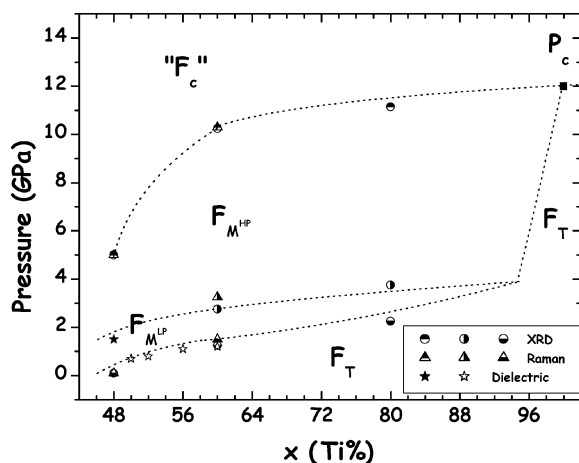


Fig. 1. Composition-Pressure phase diagram of Ti-rich PZT.

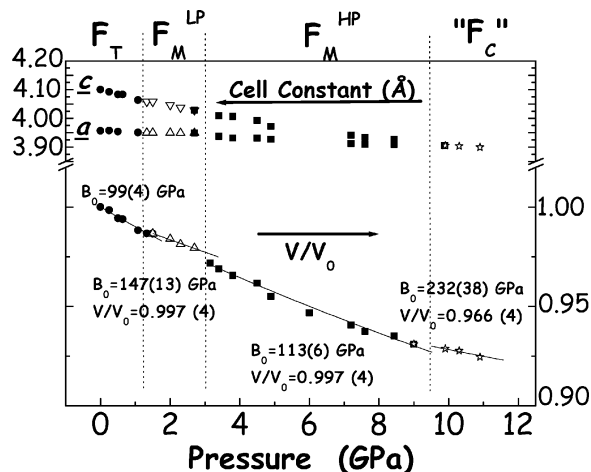


Fig. 2. Cell-constant and volume-change vs pressure of $\text{PbZr}_{0.40}\text{Ti}_{0.60}\text{O}_3$ at 298 K. The B_0 values are calculated with the Birch-Murnaghan state equation ($B'_0 = 4$).

by Raman spectroscopy. The two monoclinic phases correspond to the low pressure LP phase (similar to the high temperature monoclinic structure reported by Noheda et al. [1]) and the high pressure HP one. The appearance of new Raman modes at the $M^{\text{LP}} \rightarrow M^{\text{HP}}$ transition indicates a doubling of the unit cell as found for $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ [5]. The extended area (Fig. 1) of low pressure (respectively high pressure) monoclinic region is larger (respectively smaller) close to the MPB and shrinks (respectively increases) toward higher Ti contents. The composition at which the phase transition $T \rightarrow M^{\text{LP}}$ induced by an applied hydrostatic pressure disappears is speculative in the presented phase diagram. Indeed, the phase transition at 12 GPa observed in pure PbTiO_3 is a ferroelectric/tetragonal \rightarrow paraelectric/cubic phase transition [3] and more experimental measurements are needed to precisely draw the boundary of the low-pressure monoclinic phase in the Ti-rich region. The cubic phase "Fc" reached at high pressure is not a real paraelectric phase despite the cubic symmetry as indicated by X-ray diffraction data. Indeed, the associated Raman spectra show the presence of symmetry-breaking disorder and is similar to those observed for ferroelectric relaxors [6, 7]. These features emphasize the existence of a pressure-induced cross over from a long-range to a short-range order in pure PZT question the role of intrinsic instabilities toward pressure in the material. Finally, an increase of both pressure and Ti concentration progressively turns

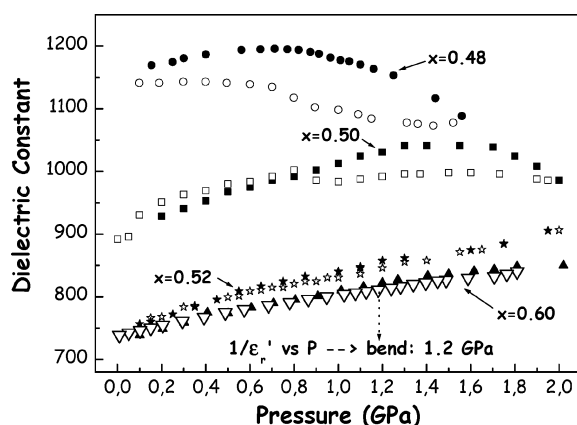


Fig. 3. Dielectric constant versus pressure of $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ for different compositions (x in the figure) measured at 100 kHz. For each composition a cycle of pressure was applied and solid symbols are the values for increasing pressure and empty symbols for decreasing pressure.

the locally-disordered F_c cubic into the paraelectric cubic one (P_c) in the cubic region. Dielectric measurements versus hydrostatic pressure (at $T = 298$ K) are reported in Fig. 3. The observed behaviour can be qualitatively explained taking into account the experimentally average strain (characterized in a first approximation by the value of cell parameters c/a) which acts on the magnitude of spontaneous polarization P_s [8]. For each ferroelectric species, conditions for the permitted orientations of P_s in the domain structure are dictated by the prototype symmetry [9]. Moreover it is well known that the ferroelectric domain structure (ferroelectric domains developed to minimise the electrostatic energy of depolarizing field and the elastic energy associated with mechanical constraints) and, in particular, the domain wall movement contribute considerably to the dielectric, piezoelectric and elastic properties of PZT ceramics [10]. If contiguous domains are strain-distinct, the conjoining ferroelectric-ferroelastic wall has only a limited family of possible orientations which are rigorously prescribed by the conditions for dimensional compatibility between the two domains along the wall plane. The switching behaviour of ferroelastic-ferroelectric walls markedly depends on the magnitude and the nature of the spontaneous domain strains.

At the beginning of the pressure cycle, the values of the dielectric constant raise due to the increase of stresses in the material which influence the motion of the domain walls, while in the same time the spontaneous polarization is affected by the evolution of the

ratio c/a when it approaches the value 1 (cubic structure). So the balance of the two effects gives rise to a peak which depends on the crystal structure, on the magnitude of spontaneous polarization and on the level of stress/strain. If we refer to the numerous studies concerning the grain size effects in ferroelectric ceramics with perovskite structure [10], it has been shown that the increase of permittivity observed in fine-grained ferroelectric ceramics is due to an “internal pressure effect” equivalent to an external compressive one. However, if the dielectric permittivity rises and peaks by decreasing the grain size, one can observe a rapid decrease after the maximum as the grain size tends towards the critical grain-size below which the material becomes cubic. The extrinsic contribution of the applied hydrostatic pressure seems to play a similar role.

Composition in the MPB region (Fig. 3) exhibits a huge pressure-hysteresis of the dielectric constant in the whole pressure range. In the limited range of pressure where the dielectric measurements are performed, the $M^{\text{LP}}(\text{Cm}) \rightarrow M^{\text{HP}}(\text{Cc})$ phase transition is likely reached and the pressure hysteresis has to be related to the dielectric properties of the high-pressure monoclinic phase or/and the nature of $M^{\text{LP}} \rightarrow M^{\text{HP}}$ phase transition. Frantti et al. [11, 12], in the description of phase transition as a function of temperature and composition, suggested it may not be adequate to describe PZT phase near MPB as a one phase system. A two-phase model is more suitable because of the presence of the locally-distorted region. The phase transition from the tetragonal phase to the monoclinic phase was assumed to occur via these local crystalline regions, as suggested by Raman and neutron diffraction data [11]. In the case of the pressure-induced phase transition, the pressure hysteresis suggests a gradual phase transition and support the results obtained by Frantti et al. [11] in the Ti rich region. For the $\text{PbZr}_{0.40}\text{Ti}_{0.60}\text{O}_3$ ceramic composition (Fig. 3) it seems that the pressure hysteresis starts just above the tetragonal-monoclinic phase transition for $P \approx 1.5$ GPa (in $1/\epsilon'$ versus P representation, this is the magnitude of pressure at which the slope changes). Similar results have been found for intermediate compositions ($0.48 < x < 0.60$).

The high values of the dielectric constant for $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ emphasize the role of the monoclinic phase on dielectric properties. Bellaïche et al. [2] showed that the dielectric susceptibility χ_{33} peaked near the monoclinic-to-rhombohedral transition and is much larger in the rhombohedral phase than in the tetragonal structure whereas the dielectric

susceptibility χ_{11} exhibits peaks at both transitions and its magnitude is very large in the monoclinic phase.

It is also interesting to note that the magnitude of dielectric constant decreases as the Ti concentration raises. This can be understood by the pressure stability of the tetragonal phase in the Ti-rich region and/or by the different contribution of Zr and Ti cations to the rotation of the total spontaneous polarization in the monoclinic phase [2].

Conclusion

The P-x phase diagram of PZT in the Ti rich region exhibits phase transitions induced by applied hydrostatic pressure. The existence of two kinds of monoclinic phases is reported and dielectric measurements of PZT ceramics under pressure emphasize the pressure-induced phase transitions between the tetragonal and the monoclinic phases. Because of the coexistence of local structures and stresses, the dielectric constant versus pressure of monoclinic PZT shows a huge-pressure hysteresis cycle which supports the strain/stress effects related to a metastable state due to the presence of a locally-distorted structure.

Note added in proof

In very recent study [11] of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ by X-ray diffraction, Raman spectroscopy and theoretical methods, a different high-pressure transition sequence was proposed: $M(\text{Cm}) \rightarrow R1(\text{R}3\text{m}) \rightarrow R2(\text{R}3\text{c})$. Neutron diffraction data [12], however, confirm the $M^{\text{LP}}(\text{Cm}) \rightarrow M^{\text{HP}}(\text{Cc})$ transition in both $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ and $\text{PbZr}_{0.40}\text{Ti}_{0.60}\text{O}_3$ due to the presence of superlattice reflections, which indicate a doubling of the unit cell arising from octahedral tilting. These reflections

are too weak to be observed by X-ray diffraction. The neutron diffraction results indicate that the pseudo-cubic phase will probably also have a low-symmetry space group. No transitions to rhombohedral forms were observed.

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