Concentration-Pressure phase diagram for rich Zr PZT ceramics

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This work reports on the systematic high pressure Raman studies in the PbZr$_{1-x}$Ti$_x$O$_3$ (0.02 ≤ $x$ ≤ 0.14) ceramics performed at room temperature. The pressure dependence of the Raman spectra reveals the stable phases of the material under pressure variation. The results allowed us to propose a concentration-pressure phase diagram for rich Zr PZT system up to pressures of 5.0 GPa.

Lead Zirconate titanate, PbZr$_{1-x}$Ti$_x$O$_3$ is widely known for their technological importance in the field of electronic, sensors, and non-volatile ferroelectric memory devices. Due this, PZT system at different forms (ceramics, single crystals and thin films) is one of the most studied ferroelectric material for over 50 years by several experimental techniques such as X-ray and neutron diffraction, electric measurements, and Raman spectroscopy. Their dielectric, piroelectric, and ferroelectric properties are strongly dependent both on the structural phase and on the preparation method. Depending on the $x$ value PZT exhibits at atmospheric pressure and room temperature different phases as follows: For 0 ≤ $x$ ≤ 0.05, PZT presents an orthorhombic antiferroelectric structure belonging to the C$_{a0}$ space group. For $x$ varying from 0.05 to 0.37 (0.37 to 0.48) PZT presents rhombohedral ferroelectric low temperature phase F$_R$(LT) (rhombohedral ferroelectric high temperature phase F$_R$(HT)) belonging to the space group C$_{3v}$ ($C_{6v}$). The composition around $x = 0.48$ defines a region known as morphotropic phase boundary (MPB) which divides the rhombohedral from the tetragonal phases. From $x = 0.48$ to $x = 1.0$ the PZT exhibits a tetragonal structure belonging to the space group C$_{4v}$. Recently, new features on the MPB region were reported. Noheda et al. using high-resolution synchrotron X-ray powder diffraction and dielectric measurements, a new monoclinic ferroelectric phase belonging to the C$_{2}$ space group was discovered at low temperatures.

There are several number of theoretical and experimental efforts in order to determine the thermodynamically stable phase of PZT when pressure varies. Cerdeira et al. have studied the behavior of PbTiO$_3$ single crystal up to 80 kbar. The pressure dependence of the lowest E(TO) soft mode frequency obeys the Curie-Weiss law which predict that PbTiO$_3$ undergoes a structural phase transition from a ferroelectric tetragonal to a cubic paraelectric phase at pressure of about 90 kbar. Bauerle et al. have studied PbTi$_{0.10}$Zr$_{0.90}$O$_3$ ceramics by Raman spectroscopy with pressures up to 6.85 GPa. They showed that the material undergoes a phase transition at 0.57 GPa from the initial room temperature-atmospheric pressure (F$_R$(LT)) to a high-temperature rhombohedral phase. Between 0.8 and 0.91 GPa, PbTi$_{0.10}$Zr$_{0.90}$O$_3$ goes to the orthorhombic antiferroelectric phase and between 3.97 and 4.2 GPa a new phase is reached, with a symmetry higher than that of the antiferroelectric phase.

Recently, by means of dielectric, X-ray and Raman measurements, Furuta et al. showed that a PbZrO$_3$ polycrystalline fine-powder sample undergoes a rich phase transition sequence up to 30 GPa: from the antiferroelectric phase to an orthorhombic phase $\Gamma$ at 2.3 GPa, from an orthorhombic phase $\Gamma$ to an orthorhombic phase $\Gamma'$ at 17.5 GPa, and finally from an orthorhombic phase $\Gamma'$ to a monoclinic phase at 23 GPa. More recently, Souza Filho et al. have studied the PbZr$_{0.04}$Ti$_{0.96}$O$_3$, which besides presenting at room temperature the same phase that of PbZr$_{0.96}$Ti$_{0.04}$O$_3$, it presents a sequence of phase transitions very different from the latter. This fact points out to the richness of the PZT concentration-pressure phase diagram.

In spite of the variety of studies of PZT under temperature variation by several techniques, there is a limited number of Raman studies performed on the PZT system under pressure variation. The micro-Raman spectroscopy, which is quite useful to investigate a localized area in the probed sample with a spatial resolution of the order of $\mu$m, is one of the most powerful technique to investigate phase transition in condensed matter under pressure variation. The

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purpose of this work is to investigate through micro-Raman spectroscopy the structural properties of PbZr$_{1-x}$Ti$_x$O$_3$ ceramics under high hydrostatic pressure. A careful analysis of the Raman spectra of samples with six different $x$ values yielded information concerning the different stable phases of PbZr$_{1-x}$Ti$_x$O$_3$ under pressure variation. Based on previous Raman and X-ray investigations in PbZr$_{1-x}$Ti$_x$O$_3$ and PbZrO$_3$ we propose a concentration-pressure phase diagram for rich Zr PZT system up to pressures of 5.0 GPa for 0.02 $\leq x \leq$ 0.14.

The preparation of our samples is described elsewhere. Raman microprobe spectroscopy experiments were performed at room temperature in the backscattering geometry using the 514.5 nm radiation line of a Ar-ion laser for excitation. The backscattered light was analyzed using a Jobin Yvon Triplemate 64000. A N$_2$-cooled Charge Coupled Device (CCD) detector was used to detect the Raman signal. The spectrometer slits were set for a 2 cm$^{-1}$ spectral resolution. An Olympus microscope lens and an objective with a numerical aperture NA = 0.80 were employed to focus the laser beam at the polished sample surface. The laser power impinging on the samples surface was of the order of 10 mW. The pressure transmitting fluid used was 4:1 methanol-ethanol and pressure calibration was achieved with the well known pressure shift of the ruby luminescence lines.

**Orthorhombic Antiferroelectric Phase - PbZr$_{1-x}$Ti$_x$O$_3$ with 0.02 $\leq x \leq$ 0.04** - Figure 1 shows the unpolarized Raman spectra for PbZr$_{0.98}$Ti$_{0.02}$O$_3$. At room temperature and room pressure, this composition has an orthorhombic structure belonging to the space group $C_{6v}^2$ as PbZrO$_3$. Below 150 cm$^{-1}$ (spectral region depicted in the insert of Fig. 1) six modes at frequencies of 35, 44, 55, 70, and 132 cm$^{-1}$ are observed. This spectral region contains the external modes related to Pb- lattice modes. In the high frequency region, 150 $\leq \omega \leq$ 1000 cm$^{-1}$ some internal modes related to certain polyatomic groups of the material appears in the Raman spectra. In the 0.0 GPa spectrum, bands at 204, 232 (Zr-O bending), 285, 330, and 344 (ZrO$_3$ torsions), 501, and 532 cm$^{-1}$ (Zr-O stretching) are also observed. The assignments of these bands were made based on the works in PbZrO$_3$ single crystals.

To understand the pressure dependence of Raman spectra for PbZr$_{0.98}$Ti$_{0.02}$O$_3$, let us remember the main results obtained by Furuta et. al. in PbZrO$_3$ polycrystalline up to pressure of 5.0 GPa. These authors showed that the left-hand side mode of doublet located at about 210 cm$^{-1}$ disappears at pressures higher than 2.3 GPa and that the right side mode increases in intensity. This spectral discontinuity is attributed to the orthorhombic(I) antiferroelectric phase $\rightarrow$ orthorhombic(I') phase transition already determined by means of high-pressure X-ray diffraction measurements. For PbZr$_{0.98}$Ti$_{0.02}$O$_3$ the doublet mode is characterized by bands at 207 (labeled with a in the Fig. 1) and 232 cm$^{-1}$ (labeled with b in the Fig. 1). Upon increasing pressures, the spectral features for the doublet is the same that was found in PbZrO$_3$. This spectral discontinuity observed for PbZr$_{0.98}$Ti$_{0.02}$O$_3$ around 2.18 GPa indicates the orthorhombic(I) antiferroelectric phase $\rightarrow$ orthorhombic(I') phase transition. Moreover, the transition can be clearly identified by drastic changes in the lattice mode region (insert in Fig. 1), in particular through the observation of a band (marked with an arrow) that disappears in the spectra of high pressure phase.

For pressures above 2.18 GPa and up to 4.0 GPa, the Raman spectra remain the same which could suggest that the material did not undergoes additional structural phase transitions as occur for the PbZrO$_3$. The Raman spectra of PbZr$_{0.96}$Ti$_{0.04}$O$_3$ are qualitatively similar to those of PbZr$_{0.98}$Ti$_{0.02}$O$_3$. The only difference is that the pressure where the phase transition orthorhombic phase (I) $\rightarrow$ orthorhombic phase (I') occurs is 2.4 for the PbZr$_{0.96}$Ti$_{0.04}$O$_3$.

**Rhombohedral Ferroelectric Phase - PbZr$_{1-x}$Ti$_x$O$_3$ with 0.10 $\leq x \leq$ 0.14** - This set of samples presents at room temperature and atmospheric pressure a rhombohedral structure belonging to the $C_{6h}$ space group. First, let us describe the pressure dependence of Raman spectra for PbZr$_{0.94}$Ti$_{0.06}$O$_3$ and PbZr$_{0.92}$Ti$_{0.08}$O$_3$. The former was the subject of our recent work where we have shown that PbZr$_{0.94}$Ti$_{0.06}$O$_3$ undergoes two different phase transitions up to 3.7 GPa as follow: rhombohedral(LT)$\rightarrow^{0.57GPa}$orthorhombic(I)$\rightarrow^{3.06GPa}$orthorhombic(I'). These phase transitions and the pressure dependence of Raman active modes were described in details elsewhere. It should be pointed that composition PbZr$_{0.92}$Ti$_{0.08}$O$_3$ have exactly the same pressure dependence and the transitions rhombohedral(LT)$\rightarrow$ orthorhombic(I) occur at 0.5 and 3.4 GPa, respectively.

Figure 2 shows the Raman spectra for PbZr$_{0.96}$Ti$_{0.10}$O$_3$ recorded at different pressures. Baüerle er. al. have reported for PbZr$_{0.96}$Ti$_{0.10}$O$_3$ composition the following sequence of pressure-induced phase transitions: rhombohedral(LT)$\rightarrow^{0.57GPa}$rhombohedral (HT)$\rightarrow^{0.85GPa}$orthorhombic(I)$\rightarrow^{3.9GPa}$higher symmetry phase (probably cubic). Our results agree in part with those reported in Ref. 20: in the pressure range of 0.0 - 1.0 GPa, we found the same sequence of phase transitions. Unfortunately, Baüerle et al. did not report the spectral region above 200 cm$^{-1}$. By observing the double bands (labeled with a and b) of the spectra in the insert of Figure 2, it is clear that the stable phase above 4.2 GPa for PbZr$_{0.90}$Ti$_{0.10}$O$_3$ is the orthorhombic phase I' as already depicted in this paper and in the works of Refs. 22 and 23. Thus, the transition observed in PbZr$_{0.90}$Ti$_{0.10}$O$_3$ at 3.9 GPa is from an antiferroelectric orthorhombic phase to the orthorhombic I' instead of antiferroelectric orthorhombic to a paraelectric cubic phase as proposed by Baüerle et al.

For the compositions PbZr$_{0.86}$Ti$_{0.14}$O$_3$ (see Fig. 3) and PbZr$_{0.88}$Ti$_{0.12}$O$_3$ it was observed the almost the same qualitative features that was found for PbZr$_{0.90}$Ti$_{0.10}$O$_3$. It was found an increase in the rhombohedral(LT)$\rightarrow$ rhombohedral(HT) $\rightarrow$ orthorhombic(I) phase transition pressures and surprisingly a decreasing in the orthorhombic(I)
orthorhombic(I') transition pressure. Finally, the results of all compositions investigated in this work can be summarized in the equilibrium phase diagram (concentration-pressure) for Zr rich PZT ceramics depicted in Fig. 4.

In conclusion, we have performed a systematic high-pressure Raman study on several PbZr$_{1-x}$Ti$_x$O$_3$ samples in order to reveal the effects of the pressure on the stable phases of Zr rich PZT ceramics. We detected the existence of a triple point which limit the antiferroelectric, rhombohedral low temperature phase, and rhombohedral high temperature phase for Ti concentration around 0.09. Also, it should be pointed out the possibility of the existence of another triple point in the phase diagram that would be determined by the extension limit of antiferroelectric phase.

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FIG. 1. Raman spectra for PbZr$_{0.98}$Ti$_{0.02}$O$_3$ ceramics recorded at pressures up to 5.0 GPa. The insert depicted the external region mode.

FIG. 2. Raman spectra for PbZr$_{0.90}$Ti$_{0.10}$O$_3$ ceramics recorded at pressures up to 5.0 GPa. The insert show that a doublet mode behavior indicating a orthorhombic(I) $\rightarrow$ orthorhombic(I’) phase transition.
FIG. 3. Raman spectra for PbZr$_{0.86}$Ti$_{0.14}$O$_3$ ceramics recorded at pressures up to 5.0 GPa.

FIG. 4. Plot of Concentration-Pressure phase diagram for Zr rich PZT system. The open triangle and open squares are data taken from Furuta et al. and Baierle et al., respectively. For all points, the error bar was of order of 0.15 GPa. The dashed lines are visual guides.