A Raman Investigation of \( \text{PbZr}_{0.94}\text{Ti}_{0.06}\text{O}_3 \) Ceramics Under High-Pressures

A.G. Souza Filho\(^a\), P.T.C. Freire\(^a\), J.M. Sasaki\(^a\), I. Guedes\(^a\), J. Mendes Filho\(^a\), F.E.A. Melo\(^a\), E.B. Araújo\(^b\), and J.A. Eiras\(^b\)

\(^a\)Departamento de Física, Universidade Federal do Ceará, Caixa Postal 6030
Campus do Pici, 60455-970 Fortaleza, Ceará, Brazil, \(^b\)Universidade Federal de São Carlos, Departamento de Física, Grupo de Cerâmicas Ferroelétricas, Caixa Postal 676, 13565-670 São Carlos SP - Brazil

e-mail: agsf@fisica.ufc.br

We have investigated the behavior of the \( \text{PbZr}_{0.94}\text{Ti}_{0.06}\text{O}_3 \) Raman spectra as a function of hydrostatic pressures. The new structural phases were identified based on previous works performed in PZT system with different Ti concentrations at room- and high pressures. We showed that \( \text{PbZr}_{0.94}\text{Ti}_{0.06}\text{O}_3 \) exhibits a rich phase sequence up to 3.7 \( \text{GPa} \): rhombohedral(\( \text{LT} \)) \( \rightarrow \) orthorhombic(\( \text{I} \)) \( \rightarrow \) orthorhombic(\( \text{I}' \)). This sequence is different from that exhibited by \( \text{PbZr}_{0.90}\text{Ti}_{0.10}\text{O}_3 \) suggesting a very interesting concentration-pressure phase diagram for rich Zr-PZT system.

Keywords: A. insulators, D. phase transitions, E. inelastic light scattering, E. high pressure

I. INTRODUCTION

Lead zirconate titanate (PZT) is a solid solution of lead zirconate and lead titanate with molecular formula \( \text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3 \), known by their excellent pyroelectric, piezoelectric ferroelectric and properties. At room temperature, a variety of PZT forms (thin films, ceramics and single crystals) with different Ti concentrations have been widely studied by many experimental methods such as X-ray scattering \(^1\,^2\), neutron diffraction \(^3\), dielectric and pyroelectric measurements \(^4\,^5\) and Raman spectroscopy \(^6\,^7\).

Previous works have shown that PZT has several structures at room temperature depending on the \( x \) value. Among these structures PZT appears as tetragonal (\( C_{4v}^1 \)), orthorhombic (\( C_{2v}^3 \)) and rhombohedral (\( C_{3v}^6 \) and \( C_{3v}^8 \)) symmetries.

At high temperatures the material also presents a cubic symmetry, belonging to \( O_{h}^3 \) space group.

For PZT with \( x \leq 0.05 \) the structure at room temperature is orthorhombic (\( C_{2v}^3 \)). Increasing the temperature it undergoes two phase transitions: antiferroelectric orthorhombic \( \rightarrow \) high temperature ferroelectric rhombohedral \( \rightarrow \) paraelectric cubic. For Ti concentrations \( 0.05 \leq x \leq 0.48 \) the material, at room temperature, has a rhombohedral symmetry and can present two phases: (a) low temperature ferroelectric rhombohedral phase, \( F_R(\text{LT}) \), \( 0.05 \leq x \leq 0.37 \); (b) high temperature ferroelectric rhombohedral, \( F_R(\text{HT}) \), \( 0.37 \leq x \leq 0.48 \). Increasing the temperature and starting from \( T = 300K \) into \( F_R(\text{LT}) \) phase, it is observed a phase transition from \( F_R(\text{HT}) \) and a second phase transition to a paraelectric cubic phase. By other side, if \( x \geq 0.48 \) the PZT room temperature phase has tetragonal symmetry and increasing the temperature a phase transition to a paraelectric cubic phase is observed. A complete temperature-concentration diagram is given in Ref. 13.

In order to construct the concentration-temperature-pressure diagram for PZT, some investigations have been reported. Bauerle et. al. \(^14\) have studied \( \text{PbTi}_{0.10}\text{Zr}_{0.90}\text{O}_3 \) by Raman spectroscopy with pressures up to 6.85 \( \text{GPa} \). They showed that the material undergoes a phase transition at 0.57 \( \text{GPa} \) from the initial room temperature-room pressure (\( F_R(\text{LT}) \)) to a high-temperature rhombohedral phase. Between 0.8 and 0.91 \( \text{GPa} \), \( \text{PbTi}_{0.10}\text{Zr}_{0.90}\text{O}_3 \) goes to the orthorhombic antiferroelectric phase and between 3.97 and 4.2 \( \text{GPa} \) a new phase is reached, with a symmetry higher than that of the antiferroelectric phase.

In recent high-pressure works, Furuta et. al. showed by X-ray \(^15\) and Raman \(^16\) measurements that \( \text{PbZr}_3\text{O}_3 \) polycrystalline fine-powder sample undergoes two phase transitions up to 30 \( \text{GPa} \): from the antiferroelectric phase to an orthorhombic phase \( \Gamma' \) at 2.3 \( \text{GPa} \) and from an orthorhombic phase \( \Gamma' \) to an orthorhombic phase \( \Gamma'' \) at 17.5 \( \text{GPa} \).

The purpose of the present work is to present an investigation of the \( \text{PbZr}_{0.94}\text{Ti}_{0.06}\text{O}_3 \) by high-pressure Raman spectroscopy, in the pressure range between 0.0 and 3.7 \( \text{GPa} \). The results presented in this work yield new informations about the PZT pressure-concentration diagram and indicate that the sequence of pressure induced phase transitions in \( \text{PbZr}_{0.94}\text{Ti}_{0.06}\text{O}_3 \) is very different from those of \( \text{PbZr}_{0.90}\text{Ti}_{0.10}\text{O}_3 \), although the initial (atmospheric) phase are the same for both materials.
II. EXPERIMENTAL

The samples were prepared by the usual ceramic technique from 99.9% pure reagent grade PbO, ZrO$_2$ and TiO$_2$ oxides. Pb(Zr$_{1-x}$Ti$_x$)$_2$O$_3$ powder at 0.86 < x < 0.98 mol% were prepared. A mixture of the starting powders and distilled water was milled in a ball mill during 3.5 hours for homogenization. The mixture was calcined at 850 °C for 2.5 h. The fine powder obtained was pressed into disks of 20 mm diameter and 3 mm thickness at 4.9 x 10$^5$ Pa. Finally, the disks were fired in covered alumina crucibles at a sintering temperature of 1250 °C for 4 h. The atmosphere was enriched in PbO vapor using PbZrO$_3$ powder around the disks to prevent significant volatilization of PbO. PZT samples were microstructurally characterized by X-ray diffraction, using a RIGAKU diffractometer, model DMAXB, with a CuKα radiation (40 KV and 25 mA). Measurements were performed on the PZT powder using step mode (0.01 degrees/step) with 5 seconds for counting time per step in the range of 15 to 60 degrees.

Small pieces of samples with thickness of 100 μm were cut under a microscope to load the pressure cell. The pressure cell was a diamond anvil cell (DAC) with 4:1 methanol-ethanol as pressure-transmitting fluid. The pressure was measured by the frequency shift of the ruby luminescence lines. Excitation with 514.5 nm radiation from an argon ion laser working at 10 mW was employed. Backscattering configuration was the chosen geometry of this work. Raman spectra were obtained at room temperature by a Jobin Yvon Triplemate 64000 spectrometer equipped with N$_2$-cooled charge-coupled device (CCD) detection system. The slits were set for a 2 cm$^{-1}$ spectral resolution and a microscope lenses with f = 20, 5 mm was used to focus the laser on the sample.

III. RESULTS AND DISCUSSION

The PZT samples used in our experiments had Ti concentrations of 6%. At room temperature the structure has a rhombohedral (low temperature) symmetry, as observed by X-ray diffraction. In Fig. 1 we show Raman spectra of PZT taken at various pressures in the frequency range 25 to 200 cm$^{-1}$. This frequency region covers mainly the lattice modes of the material. The room pressure (0.0 GPa) spectrum, typical of the rhombohedral phase, displays three bands for frequencies lower than 200 cm$^{-1}$ at 52, 61 and 128 cm$^{-1}$. Fig. 2 shows Raman spectra of PZT taken at different pressures in the frequency range 150 - 750 cm$^{-1}$. In this spectral region it is expected to be observed some internal modes of certain groups of the material. In the 0.0 GPa spectrum it is observed bands at 207, 241 (Zr-O bending), 282 and 328 (ZrO$_3$ torsions), 535 (Zr-O stretching) and 670 cm$^{-1}$. The assignments of these bands were made based on the works in PbZrO$_3$ single crystals [4].

Increasing the pressure the Raman spectra remain qualitatively the same of the room temperature pressure up to 0.3 GPa. This means that the rhombohedral phase is stable up to that pressure. However, in the spectrum taken at 0.3 GPa, completely different bands are observed. Fig. 1 shows that in the 0.3 GPa spectrum, new bands appear at 36, 45 and 56 cm$^{-1}$. At the same time a band with frequency of 61 cm$^{-1}$ in the 0.26 GPa spectrum disappears. Fig. 2 also shows drastic changes in the Raman spectra between 0.26 and 0.3 GPa. The 207 cm$^{-1}$ band grows in intensity; the 241 cm$^{-1}$ jumps to lower frequency (235 cm$^{-1}$) and decreases in intensity; the 328 cm$^{-1}$ band decreases in intensity and a new band, at 346 cm$^{-1}$, appears. The discontinuities both in the number of bands and in the band frequencies and the changes in the band’s intensities point to a phase transition from the rhombohedral structure to a different one. In Fig. 3 we present the frequencies of all bands observed in our PZT Raman spectra as a function of pressure in the range 0.0 to 3.7 GPa, where the discontinuities outlined above can be clearly seen. We remember that for PbZr$_{0.9}$Ti$_{0.1}$O$_3$, this material undergoes three different phase transitions from a F$_{R}$ (HT) to a rhombohedral phase, F$_{R}$ (LT), from that to an orthorhombic phase and, finally, to a phase of high symmetry [4].

It should be observed that the initial phase of the material studied in this work is the same of PbZr$_{0.90}$Ti$_{0.10}$O$_3$. However, are the sequence of phase transition in PbZr$_{0.90}$Ti$_{0.10}$O$_3$ and PbZr$_{0.94}$Ti$_{0.06}$O$_3$ the same? In order to determine the sequence of phase transitions of PbZr$_{0.94}$Ti$_{0.06}$O$_3$ one has to search the various phases presented by the material. Let us now try to provide the correct structure of the new phase observed in the PZT for P ≥ 0.3 GPa. The standard process would be to perform X-ray measurements simultaneously with our Raman measurements. However, our experimental setup does not allow us to do X-ray measurements at high-pressure. Another possibility it is to compare the Raman spectra taken in the new phase with the Raman spectra of PbZr$_{1-x}$Ti$_x$O$_3$ with different Ti concentrations, but with well-known phases.
FIG. 1. Raman spectra of $PbZr_{0.94}Ti_{0.06}O_3$ at various pressures in the low frequency region.

FIG. 2. Raman spectra of $PbZr_{0.94}Ti_{0.06}O_3$ at various pressures in the high frequency region.
We performed a series of both Raman and X-ray measurements in PbZr$_{1-x}$Ti$_x$O$_3$ with different Ti concentrations at room temperature and atmospheric pressure. The Raman spectra of Fig. 1 and Fig. 2 obtained at pressure P=0.3 GPa (the new phase) is the same that we observed for Ti concentrations of 0.02 and 0.04; in those cases X-ray diffraction showed that at room temperature, the phase of the material is orthorhombic, as pointed by other works in the literature. Also, the Raman spectrum is the same reported to PbZrO$_3$ single crystal that belongs to orthorhombic structure [17]. We can conclude that the new phase presented by PbZr$_{0.94}$Ti$_{0.06}$O$_3$ is an orthorhombic one and the first phase transitions we are observing is from a rhombohedral $F_r$(LT) to an orthorhombic phase.

Fig. 3 shows that this new phase is stable over a large range of pressure; in the figure the two dashed lines limit the orthorhombic phase region from 0.3 to 2.7 GPa. Some features of the orthorhombic phase Raman spectra, as a function of pressure, can be described as follows: (a) the frequencies of bands change only slightly; (b) the band at 36 and 50 cm$^{-1}$ decrease slowly in intensity up to 2.7 GPa; (c) the band at 70 cm$^{-1}$ increases slowly in intensity as pressure is increased.

FIG. 3. Pressure dependence of the Raman bands of PbZr$_{0.94}$Ti$_{0.06}$O$_3$ at room temperature. The dashed lines represent the phase transition pressures

However, for pressures higher than 2.9 GPa, different Raman spectra are observed. Particularly clear is the disappearing of both a band in the lattice region of spectra (Fig. 1) and two bands marked by squares in Fig. 2. Fig. 3 also shows these discontinuities in the frequency of Raman bands. For frequencies lower than 150 cm$^{-1}$ six bands are observed in the spectra for pressure ranging from 0.3 to 2.7 GPa. For pressures higher than 2.7 GPa just five bands are observed. The band whose intensity goes to zero for P $\geq$ 2.7 GPa was found in the 0.3 GPa spectrum at 56 cm$^{-1}$. As pressure increases, its frequency increases and its intensity decreases. This intensity decreasing is slow, associated with the continuous change from the intermediate structure to the structure of higher pressure (P $\geq$ 2.7 GPa).

The Raman spectra for frequencies higher than 100 cm$^{-1}$ at 3.3 GPa can all be identified on the basis of previous work performed on PbZrO$_3$ [16]. If we compare the Raman spectrum at 3.3 GPa in Fig. 3, we observe that it is similar to the spectrum of PbZrO$_3$ at 2.3 GPa. At this pressure PbZrO$_3$ belongs to an orthorhombic phase(I') [16], different from the original orthorhombic phase(I), where dielectric hysteresis measurements show to be an antiferroelectric phase [13]. This indicates that in PbZr$_{0.94}$Ti$_{0.06}$O$_3$, there is a phase transition from an orthorhombic phase(I) to an orthorhombic phase(I') at about 2.9 GPa.

In summary, the results Raman measurements presented here have showed that PbZr$_{0.94}$Ti$_{0.06}$O$_3$ undergoes two
different phase transitions up to 3.7 GPa: *rhombohedral* ($LT_{0.3GPa}$) $\rightarrow$ *orthorhombic* ($I_{2.9GPa}$) $\rightarrow$ *orthorhombic* ($I'$).

These results point to the richness of concentration-pressure phase diagram because the sequence of phase transitions observed are very different from the $PbZr_{0.90}Ti_{0.10}O_3$ [14] and $PbZrO_3$ [16].

**Acknowledgments:** A. G. Souza Filho is grateful for Fundação Cearense de Amparo a Pesquisa (FUNCAP) for fellowship program. The authors would like to thank CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico) and FUNCAP (Fundação Cearense de Amparo a Pesquisa) Brazilian funding agencies for financial support.

[1] H. Zhang, S. Leppavuori, and P. Karjalainen, J. Appl. Phys., 77, (1995) 2691.
[2] A. Pignolet, L. Wang, M. Proctor, F. Levy, and P.E. Schmid, J. Appl. Phys., 74, (1993) 6625.
[3] H. Fujishita and S. Katano, J. Phys. Soc. Jpn, 66, (1997) 3484.
[4] Z. Ujma, J. Handerek, H. Hassan, G.E. Kugel, and M. Pawelezyk, J. Phys: Condens. Matter, 7, (1995) 895.
[5] J. Handerek and Z. Ujma, J. Phys: Condens. Matter., 7, (1995) 1721.
[6] I. El-Harrad, P. Becker, C. Carbatos-Nedelec, J. Handerek, Z. Ujma and D. Dimytrov, J. Appl. Phys., 78, (1995) 5581.
[7] D. Baurele, Y. Yacoby, and W. Richler, Solid State Commun., 14, (1974) 1137.
[8] D.C. Agrawal, S.B. Majumder, Y.N. Mohapatra, S. Sathaiah, H.D. Bist, R.S. Katiyar, E. Ching-Prado, and A. Reyes, J. Raman Spectroscopy, 24, (1993) 459.
[9] K. Rolender, G.E. Kugel, M.D. Fontana, J. Handerek, S. Lahlon and C. Carbatos-Nedelec, J. Phys: Condens. Matter, 1 (1989) 2257.
[10] G. Burns, and B.A. Scott, Phys. Rev Lett., 25, (1970) 167.
[11] G. Burns, and B.A. Scott, Phys. Rev Lett., 25, (1970) 1191.
[12] J.F. Meng, R.S. Katiyar, G.T. Zou, and X.H. Wang, phys. stat. sol.(a), 164, (1997) 851.
[13] B. Jaffe, W.R. Cook, and H. Jaffe, Piezoelectric Ceramic, Academic Press, New York, 1971, pg. 139.
[14] D. Bauerle, W.B. Holzapfel, A. Pinczuk and Y. Yacoby, phys. stat. sol., 83, (1977) 99.
[15] Y. Kobayashi, S. Endo, L.C. Ming, K. Deguchi, T. Ashida and H. Fujishita, J. Phys. Chem. Solids, 60, (1999) 57.
[16] H. Furuta, S. Endo, L.C. Ming and H. Fujishita, J. Phys. Chem. Solids, 60, (1999) 65.
[17] A.E. Pasto, and R.E. Condrate, J. Am. Ceram. Soc., 56, (1973) 436.