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Pressure-induced phase transitions in Zr-rich $PbZr_{1-x}Ti_xO_3$ ceramics

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Abstract

A Raman study of structural changes in the Zr-rich $PbZr_{1-x}Ti_xO_3$ (PZT) system under hydrostatic pressures up to 5.0 GPa is presented. We observe that externally applied pressure induces several phase transitions in PZT ceramics among phases with orthorhombic (A_O), rhombohedral low-temperature (R_{LT}), and rhombohedral high-temperature (R_{HT}) symmetries (all found in PZT at ambient pressure and room temperature). Each of the compositions investigated ($0.02 \leqslant x \leqslant 0.14$) exhibits a high-pressure phase with orthorhombic ($O_{I'}$) symmetry. We further report a detailed study of the pressure dependence of Raman frequencies to elucidate the phase transitions and to provide a set of pressure coefficients for the high-pressure phases.

1. Introduction

Lead titanate zirconate $PbZr_{1-x}Ti_xO_3$ (PZT) is one of the most widely studied ferroelectric materials due to its potential technological applications. PZT has long been the subject of many experimental and theoretical research efforts to understand the physical origin of its striking ferroelectric properties. This system shows an interesting concentration–temperature (x–T) phase diagram and its physical properties can be associated with the various structural modifications found therein. The x–T phase diagram determined by Jaffe *et al* [1] shows a variety of phase transitions among ferroelectric, antiferroelectric, and paraelectric phases and, in particular, two regions in the x–T diagram are remarkable. One of them is well known as the morphotropic phase boundary (MPB), around $x = 0.47$, where PZT exhibits outstanding ferroelectric properties [1] whose physical basis was only recently identified as a result of the

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discovery of a new monoclinic phase close to the MPB [2, 3]. Another interesting part of the x–T diagram is the Zr-rich PZT region ($0.02 \leqslant x \leqslant 0.14$) which exhibits four phases. Two of them are antiferroelectric with orthorhombic (hereafter A_O) and tetragonal (hereafter A_T) symmetries, and the remaining two are ferroelectric with rhombohedral (low-temperature (hereafter R_{LT}) and high-temperature (hereafter R_{HT})) symmetries [1].

In contrast to the x–T phase diagram which is now well understood, the effects of pressure on the stable phase of PZT are still under investigation and only a few papers have been published on this subject. The earlier studies were limited to the $PbTiO_3$ [4] and $PbZr_{0.90}Ti_{0.10}O_3$ [5] compositions and more recent reports include high-pressure investigations through Raman and x-ray diffraction measurements on $PbZrO_3$ [6,7] and Raman measurements on $PbZr_{0.94}Ti_{0.06}O_3$ [8]. We here present a detailed Raman investigation of the pressure effects (up to 5.0 GPa) in the structural phases of Zr-rich PZT ceramics, building on our recent work [8]. Two groups of samples with different starting phases, rhombohedral (ferroelectric) and orthorhombic (antiferroelectric), were investigated and several structural phase transitions were observed. Furthermore, this study provides the pressure coefficients for different high-pressure phases in the Zr-rich PZT system, which yields important information for use when discussing strain in thin films.

2. Experimental procedure

The samples were prepared using a standard oxide mixture route. Stoichiometric amounts of 99.9% pure reagent-grade PbO, TiO_2, and ZrO_2 were mixed in a ball mill for 3.5 hours to achieve homogenization. The mixed powder was calcined at 850 °C for 2.5 hours. The samples were compacted using pressures of 400 MPa to form disc-shape samples. Finally, the discs were fired in covered alumina crucibles at a sintering temperature of 1250 °C for 4 hours. The atmosphere was enriched with PbO vapour, using $PbZrO_3$ powder around the discs, to prevent significant volatilization of PbO. At ambient pressure and room temperature, the PZT samples were characterized by micro-Raman spectroscopy at several points of the samples, and the recorded spectra were exactly the same from point to point, indicating excellent homogeneity of the samples.

The Raman spectra were recorded with a Jobin-Yvon T64000 spectrometer, equipped with a N_2-cooled charge-coupled-device (CCD) detection system. The slits were set for a 2 cm^{-1} spectral resolution. The 514.5 nm line of an argon-ion laser was used for excitation. An Olympus microscope lens with a focal distance $f = 20.5$ mm and numeric aperture $NA = 0.35$ was used to focus the laser on the sample surface. The incident power density was of the order of 100 W cm^{-2}. High-pressure Raman experiments were performed using a diamond anvil cell (DAC) with 4:1 methanol–ethanol as the transmitting fluid. The pressure calibration was achieved using the well-known pressure shift of the ruby luminescence lines, using the relation [10]

$$P\ (\mathrm{GPa}) = \frac{\Delta\omega\ (\mathrm{cm}^{-1})}{7.535}.$$

The temperature within the laser spot was estimated by means of the Stokes/anti-Stokes intensity ratio and was found to be 25 ± 5 °C.

3. Results and discussion

Raman spectra of $PbZr_{0.98}Ti_{0.02}O_3$ as functions of hydrostatic pressure are shown in figure 1. At room temperature and ambient pressure, this composition has the A_O structure belonging to

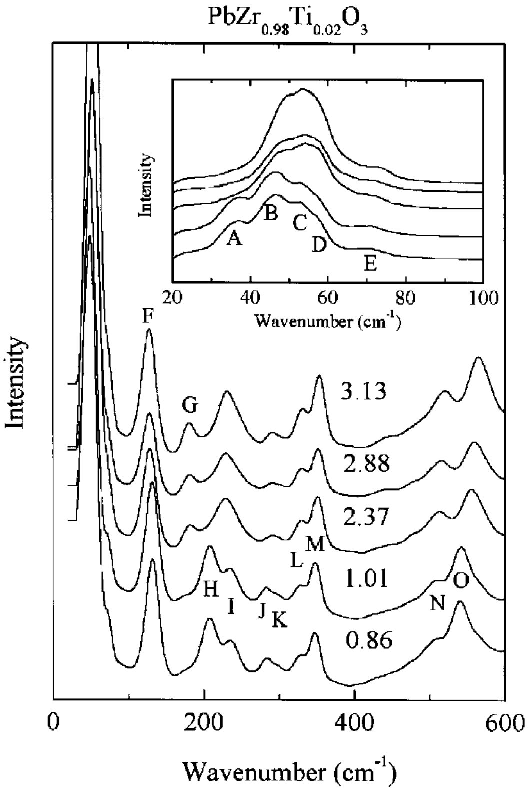

Figure 1. Raman spectra for $PbZr_{0.98}Ti_{0.02}O_3$ ceramics recorded at pressures up to 4.0 GPa. The inset depicts the low-frequency region. The numbers stand for pressure in units of GPa.

the space group C_{2v}^8, i.e., the same structure as $PbZrO_3$ [11]. The Raman spectra for PZT can be divided into two spectral regions, i.e., low- and high-frequency ones. The spectral region with $\omega \leqslant 100$ cm^{-1} contains the external modes related to the Pb-lattice modes [12]. In the high-frequency region, $100 \leqslant \omega \leqslant 1000$ cm^{-1}, internal modes related to the polyatomic groups of the material appear in the Raman spectra, namely: (i) the bands observed at 204 cm^{-1} (H), 232 cm^{-1} (I) associated with Zr–O bending; (ii) the bands observed at 285 cm^{-1} (K), 330 cm^{-1} (L), and 344 cm^{-1} (M) assigned to ZrO_3 torsion modes; and (iii) the highest-frequency modes at 501 cm^{-1} (N) and 532 cm^{-1} (O) associated with the Zr–O stretching. Those assignments are based on previously reported work for $PbZrO_3$ single crystals [11].

On applying pressure, first only minor differences are observed in the spectrum, mainly in the relative intensities of the various peaks, but then at higher pressures, more dramatic effects occur. At $P = 2.30$ GPa, the peak labelled A (32 cm^{-1} at ambient pressure) disappears. Also at the same pressure, the components of the doublet labelled H and I overlap, resulting in a single peak, which we have labelled I, for higher pressures. Upon increasing the pressure further, the new features gain intensity and the spectrum for $PbZr_{0.98}Ti_{0.02}O_3$ becomes similar to that related to the orthorhombic (I′) structure (hereafter $O_{I'}$) [6] in $PbZrO_3$. In comparison with the case for $PbZrO_3$, whose pressure-induced phase transitions were studied by Raman spectroscopy and are reported in reference [6], the phase transition from the A_O phase to the $O_{I'}$ phase in $PbZr_{0.98}Ti_{0.02}O_3$ takes place at a higher pressure value [9], reflecting the role of the Ti atoms in this phase transition.

Let us now analyse the phase transition related to the compositions ($0.06 \leqslant x \leqslant 0.14$), belonging to the R_{LT} starting phase, represented in figure 2 by $PbZr_{0.92}Ti_{0.08}O_3$. We observe that upon increasing the pressure, the Raman spectra remain qualitatively the same as at ambient pressure up to 0.50 GPa, thereby indicating the stability of the R_{LT} phase up to 0.50 GPa. However, for the spectrum taken at a pressure of 0.70 GPa, we observed several remarkable new spectral features. Both the appearance of new modes and abrupt changes in the relative intensity of these modes were observed, as can be seen in detail by examining the inset to figure 2. By comparing this spectrum with that recorded at ambient pressure for $PbZr_{0.98}Ti_{0.02}O_3$, there is no doubt that the starting R_{LT} phase changes to the A_O phase at 2.07 GPa. Upon increasing the pressure further, the $PbZr_{0.92}Ti_{0.08}O_3$ spectra present the same qualitative features as were observed for $PbZr_{0.98}Ti_{0.02}O_3$ except for the pressure value where the A_O–$O_{I'}$ transition takes place.

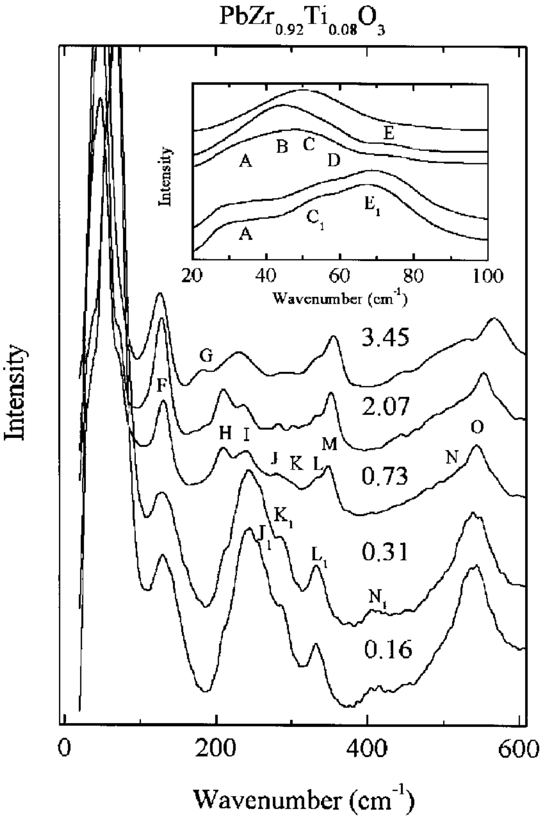

Figure 2. Raman spectra for $PbZr_{0.92}Ti_{0.08}O_3$ ceramics recorded at pressures up to 4.0 GPa. The inset depicts the low-frequency region. The numbers stand for pressure in units of GPa.

We also studied compositions up to a Ti content of $x = 0.14$. For the compositions with $x = 0.10$ and 0.14 there is a R_{HT} phase between R_{LT} and A_O. The effects of pressure on the structural phases in samples for the composition with $x = 0.10$ was reported earlier by Bäuerle *et al* [5]. The main change in the spectra at $P = 0.60$ GPa is the strongly increasing intensity of the mode located at about 36 cm^{-1}. The same authors observed a temperature-induced phase transition for the composition with $x = 0.10$ and they observed that the R_{LT}–R_{HT} phase transition is just marked by an increase in the intensity of the 40 cm^{-1}

mode. On the basis of this temperature-dependent study, Bäuerle *et al* [5] interpreted the pressure dependence of the mode at 36 cm^{-1} as an evidence of the R_{LT}–R_{HT} phase transition. In our pressure measurements we observed in the same pressure range an increase in the intensity of such a mode, indicating good agreement between our results and those reported in reference [5]. For the composition with $x = 0.14$ (see figure 3), the pressure-induced phase transition sequence was very similar to that observed for the $x = 0.10$ sample except for the appearance of a mode at about 100 cm^{-1} (labelled F_1 in figure 3) in the spectrum taken at 1.19 GPa and the presence of strong elastic scattering. The F_1 mode remains present in the spectra up to a pressure of 1.89 GPa where a new phase transition is clearly observed [9], and the elastic scattering intensity is decreased considerably, becoming similar to the spectrum taken at ambient pressure and room temperature. This result suggests that the structural phase in the 1.18–1.89 GPa pressure range should have either fluctuations of the polarization or a randomly arranged local polarization [13], thereby indicating that such a structural phase is possibly disordered and this new mode (F_1) can be activated by the disorder in the lattice. For the $x = 0.10$ sample, we also observed a weaker elastic scattering effect, but there was no evidence for an F_1 mode in the Raman spectra. This result suggests that the degree or type of disorder depends on the Zr content, similarly to the case for Zr-rich Nb-doped PZT [13]. The new phase above $P = 1.80$ GPa, for $x = 0.14$, is easily identified as being of A_O symmetry owing to its very peculiar Raman spectra compared with those of all the other PZT phases.

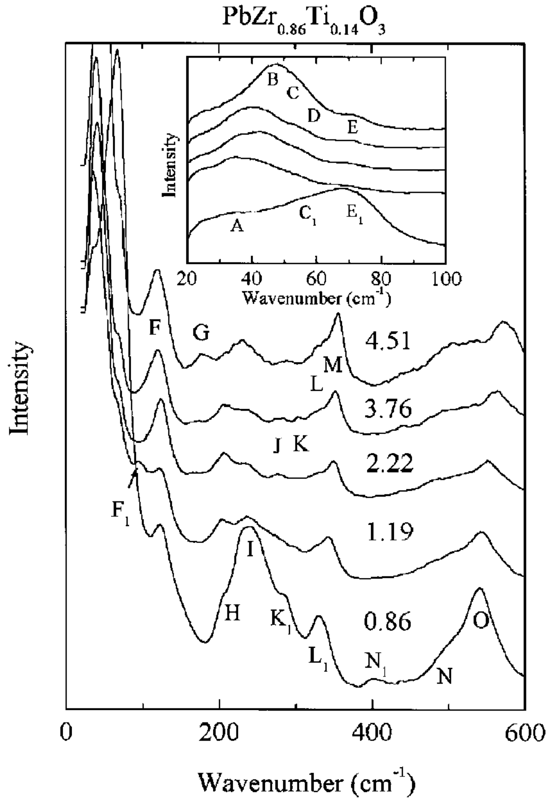

Figure 3. Raman spectra for $PbZr_{0.86}Ti_{0.14}O_3$ ceramics recorded at pressures up to 5.0 GPa. The inset depicts the low-frequency region. The numbers stand for pressure in units of GPa.

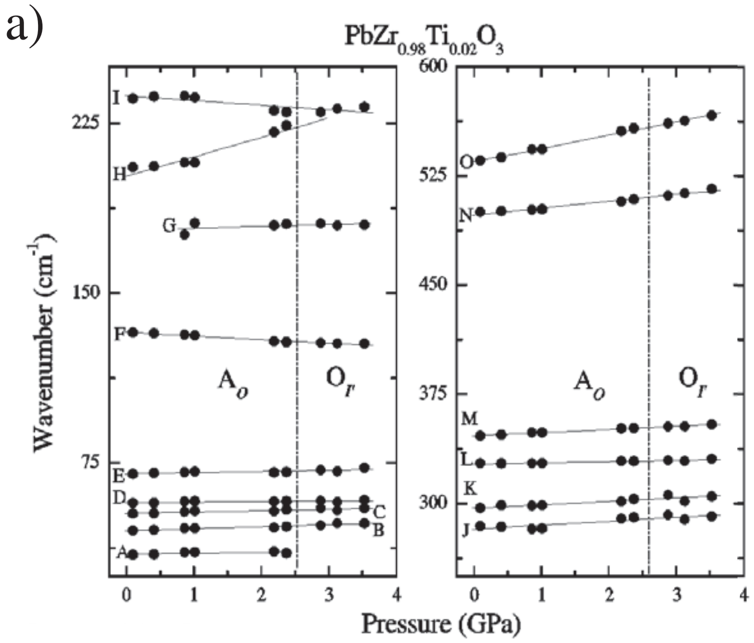

Figure 4. Frequency of the Raman modes as a function of pressure for the compositions (a) $PbZr_{0.98}Ti_{0.02}O_3$, (b) $PbZr_{0.92}Ti_{0.08}O_3$, and (c) $PbZr_{0.86}Ti_{0.14}O_3$. The solid lines are linear fits of the data to $\omega(P) = \omega_0 + \alpha P$. The vertical dotted lines represent the points at which the phase transitions between the rhombohedral low-temperature (R_{LT}), rhombohedral high-temperature (R_{HT}), antiferroelectric orthorhombic (A_O), and orthorhombic I′ ($O_{I'}$) phases occur. The open and filled circles in (c) correspond to two different sets of measurements.

Upon increasing the pressure, the behaviour of the modes labelled H and I indicates a phase transition from the A_O phase to the $O_{I'}$ phase, as in $PbZrO_3$ [6] and the $x = 0.02$ (figure 1), 0.06 [8], and 0.08 (figure 2) samples.

In order to understand the pressure dependence of these Raman modes in detail, we deconvolved the spectra into several peaks with Lorentzian line shapes, and frequency versus pressure (ω versus P) plots were then constructed. A linear behaviour was observed for all the ω versus P plots and the data were fitted accordingly ($\omega(P) = \omega_0+\alpha P$), using the least-squares technique, and the results are shown in figures 4(a)–4(c) for $PbZr_{0.98}Ti_{0.02}O_3$, $PbZr_{0.92}Ti_{0.08}O_3$, and $PbZr_{0.86}Ti_{0.14}O_3$ respectively, as solid lines. The values found for the intercept ω_0 and the linear pressure coefficients α are listed in tables 1 and 2, corresponding to the results for $PbZr_{0.98}Ti_{0.02}O_3$ and $PbZr_{0.92}Ti_{0.02}O_3$ and those for $PbZr_{0.86}Ti_{0.14}O_3$, respectively. Of interest is the pressure behaviour of the F mode that is present in all phases, i.e., its frequency decreases with increasing pressure. The observed transitions can be seen clearly by observing the ω versus P plot (figure 4), where the discontinuities are emphasized by the vertical dotted lines. The intensities of some modes plotted in figure 4 depend on the Zr content. This effect is probably associated with changes in the polarizabilities that arise from the replacement of the Ti atoms by the Zr atoms. The weak G mode for compositions with $x = 0.02$ and $x = 0.08$ is present in both the A_O and $O_{I'}$ phases, but for $x = 0.14$ it could be observed only in the $O_{I'}$ high-pressure phase. A similar behaviour is observed for the J_1 mode that is present for $x = 0.08$, but absent for $x = 0.14$. From examining figure 4(c), which corresponds to $PbZr_{0.86}Ti_{0.14}O_3$, it is very clear that there is a phase transition around $P = 1.0$ GPa where we

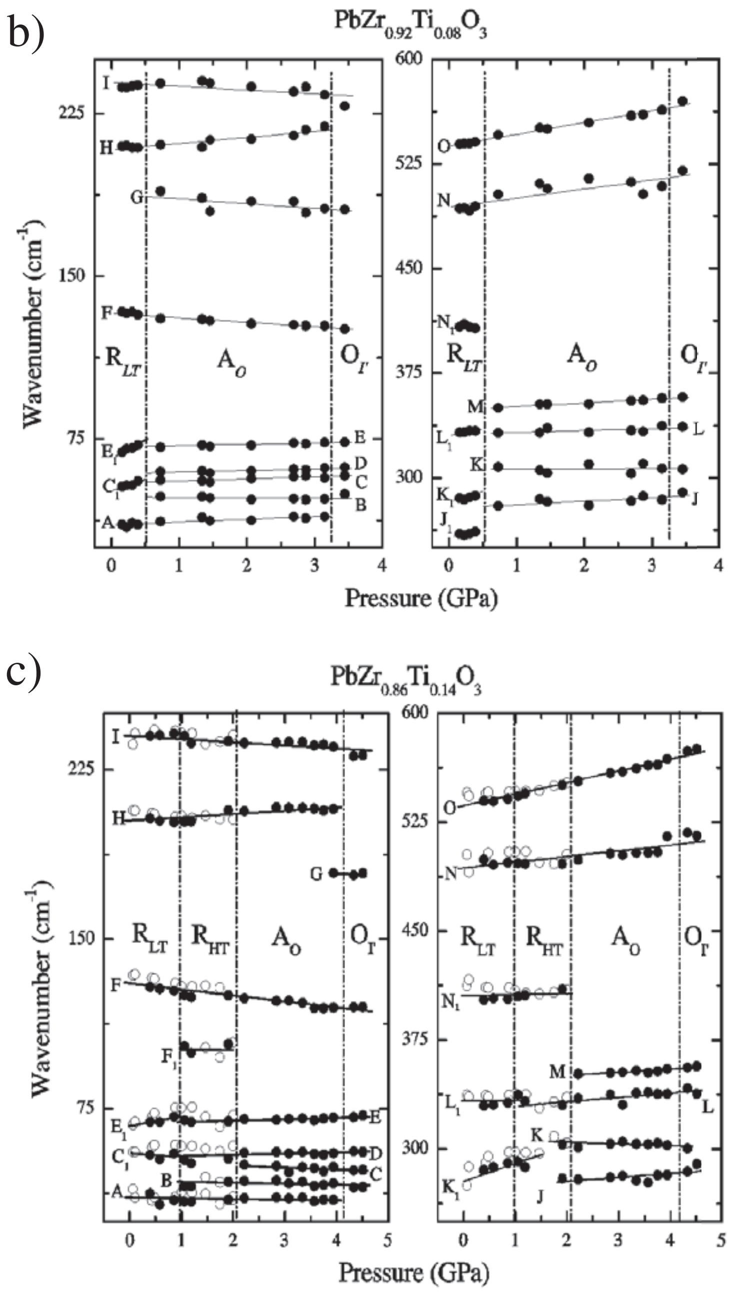

Figure 4. (Continued)

first observe the appearance of the F$_1$ mode. Finally, knowledge of the pressure dependence of the Raman frequencies, shown in tables 1 and 2, makes it possible to obtain the strain in PbZr$_{1-x}$Ti$_x$O$_3$ ($0.02 \leqslant x \leqslant 0.14$) thin films built on different substrates. The strain can be estimated by comparing the frequency shift of the Raman modes measured in PZT thin films at ambient pressure with those obtained in PZT under high pressure.

Table 1. Values of the frequency intercept ω_0 (cm^{-1}) and pressure coefficients α (cm^{-1} GPa^{-1}) for $PbZr_{0.98}Ti_{0.02}O_3$ and $PbZr_{0.92}Ti_{0.08}O_3$.

	$PbZr_{0.98}Ti_{0.02}O_3$				$PbZr_{0.92}Ti_{0.08}O_3$			
	A_O		$O_{I'}$		R_{LT}		A_O	
Modes	ω_0	α	ω_0	α	ω_0	α	ω_0	α
A	34.7	0.4			35.5	1.2	35.5	1.2
B	45.1	0.9	45.1	0.9			48.2	−0.1
C_1					51.2	10.1		
C	52.7	0.6	52.7	0.6			54.6	1.0
D	57.5	0.2	57.5	0.2			58.9	0.8
E_1					66.9	13.7		
E	70.2	0.5	70.2	0.5			71.4	0.6
F	132.7	−1.6	132.7	−1.6	133.0	−2.1	133.0	−2.1
G	177.8	0.8	177.8	0.8			187.9	−2.2
H	201.6	8.6			207.5	3.9	207.5	3.9
I	237.1	−2.0	237.1	−2.0	238.9	−1.5	238.9	−1.5
J_1					257.9	7.0		
K_1					283.2	9.2		
J	282.3	2.7	282.3	2.7			278.1	2.5
K	296.9	2.2	296.9	2.2			306.0	0.2
L_1					331.2	1.3		
L	326.9	0.8	326.9	0.8			331.6	5.3
M	346.4	2.2	346.4	2.2			348.4	2.6
N_1					411.3	10.0		
N	498.3	4.6	498.3	4.6	494.1	6.5	494.1	6.5
O	534.6	9.2	534.6	9.2	537.9	8.5	537.9	8.5

The pressure dependence of the Zr-rich PZT system can be discussed on the basis of recent results, obtained by means of first-principles calculations for some perovskites [14]. Classical ferroelectric systems, such as $PbTiO_3$ and $BaTiO_3$, show a high-pressure phase with cubic symmetry. This is not the case for $PbZrO_3$, which up to 80 GPa shows high-pressure phases with orthorhombic and monoclinic symmetries [7]. It is well known that phonon instabilities such as mode softening are often closely related to a structural phase transition in ferroelectric systems. These instabilities may occur for wave vectors belonging either to the centre or to the zone boundary or even belonging to any point in the first Brillouin zone. As all of them are Raman active (as happens with the C_{2v} point group), the optical modes belonging to the centre of the first Brillouin zone were measured and no soft modes were found in the pressure range used in the present work. Following the theoretical results of Cockayne and Rabe [14], the fact that Zr-rich PZT does not become a cubic paraelectric under pressure is due to the existence of instabilities over the entire range of pressure that has been studied, thereby implying more deformable octahedra. This is closely related to the observed pressure dependence, in agreement with experimental Raman results for $PbZrO_3$ [6, 7] and Zr-rich PZT [5, 8, 9]. The authors argued that the ferroelectric–antiferroelectric phase transition (observed in our work for compositions starting with the R_{LT} phase ($0.06 \leqslant x \leqslant 0.14$)) must be due to one or more competing instabilities. However, theoretical results for $PbZrO_3$ [14] indicate that some modes belonging to the boundary of the Brillouin zone have such instabilities and they can account for the phase transitions found in [14]. For compositions near $x = 0.50$ there is a competition between ferroelectric and rotational instabilities, thereby leading to a strong ferroelectric instability [16]. Similarly to the case for $PbZrO_3$, these instabilities are

Table 2. Values of the frequency intercept ω_0 (cm^{-1}) and pressure coefficients α (cm^{-1} GPa^{-1}) for $PbZr_{0.86}Ti_{0.14}O_3$.

	$PbZr_{0.86}Ti_{0.14}O_3$					
	R_{LT}		R_{HT}		A_O	
Modes	ω_0	α	ω_0	α	ω_0	α
A	35.7	−0.3	35.7	−0.3	35.7	−0.3
B					43.0	−0.4
C_1	51.5	−0.9				
C					55.3	−1.7
D					53.6	0.5
E_1	67.3	4.2	67.3	4.2		
E	68.5	0.6	68.5	0.6		
F_1			101.4	−0.2		
F	130.4	−2.6	130.4	−2.6	130.4	−2.6
G					181.6	−0.6
H	202.6	1.4	202.6	1.4		
I	240.0	−1.4	240.0	−1.4		
K_1	277.7	12.3	277.7	12.3		
J					272.3	2.7
K					307.2	−1.3
L_1	333.0	0.4	333.0	0.4		
L					326.4	3.0
M					345.9	2.3
N_1	405.5	0.7				
N	493.4	3.9	493.4	3.9	493.4	3.9
O	536.3	8.0	536.3	8.0	536.3	8.0

strongly pressure dependent, thus furnishing a possible mechanism for the R_{LT}–R_{HT} phase transition induced by pressure. We recall this discussion because these are the only theoretical results that have been available up to now to provide an understanding of the phase transition of PZT under high pressure.

In summary, a detailed study of the pressure-induced phase transition in Zr-rich $PbZr_{1-x}Ti_xO_3$ up to a pressure of 5.0 GPa is reported here. Our experimental Raman results are consistent with theoretical calculations [14], which have predicted strong phonon instabilities for $PbZrO_3$, thus implying more deformable octahedra, which is closely related to the effects of hydrostatic pressure on the Raman spectra observed here. This explains why several phase transitions are observed for the Zr-rich PZT system. Finally, an analysis of the pressure dependence of the frequencies was performed in order to provide a set of pressure coefficients which provide valuable information for obtaining the internal strains in PZT thin films.

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