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Abstract. The ferroelectric ceramics have been one of the most studied compounds in the literature both in obtaining the same growth as in behavior of chemical and physical properties. In its growth the materials can go through other phases or to change their magnetic ferroelectric properties due to vacancies generated as $PbTiO_3$ material. This material structural changes its phase also applying pressure with temperature, concentration and allowing anharmonic study behavior [1]. Raman spectroscopy is a technique which provides high resolution in seconds chemical and structural information of almost any organic or inorganic compound. As a technique which does not require a special atmosphere or vacuum, is one technique that has been used extensively in the characterization of ferroelectric materials in particular of $PbTiO_3$.

1. Introduction

Lead titanate, $PbTiO_3$ (PT), is a known Perovskite kind of ferroelectric ceramic. The substitution of Pb^{2+} to de La^{3+} ions improves the mechanical and ferroelectric characteristics of PT. Due to its potential in technological applications, PLT has been widely studied [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15]. The physical properties of PLT depend mainly on the concentration of Lanthanum. It is also known that the particle size, the morphology and the crystal structure govern the ferroelectric structure in this material. PT has a high phase transition temperature from tetragonal ferroelectric to cubic paraelectric ($Tc = 770k$), but it decreases with increasing concentration of Lanthanum. The same thing occurs with hydrostatic pressure applied ($Tc = 12GPa$). These effects were verified in other published papers[16, 17, 15]. The Titanium of (PT) exhibits a negative thermal expansion (NTE), whose temperature depends on the lattice parameters which changes with La-concentration) [18].The phononic modes in PLT have been studied before [2, 4, 5]. However, besides the recent work by Joya and Ahart *et al* [1, 6], an evolution of Raman mode with the temperature and the pressure has not been documented in details.

2. Experimental

Raman scattering measurements were performed using a Jobin-Yvon T64000 triple monochromator with a CCD detector. The exciting light from an argon laser was focused
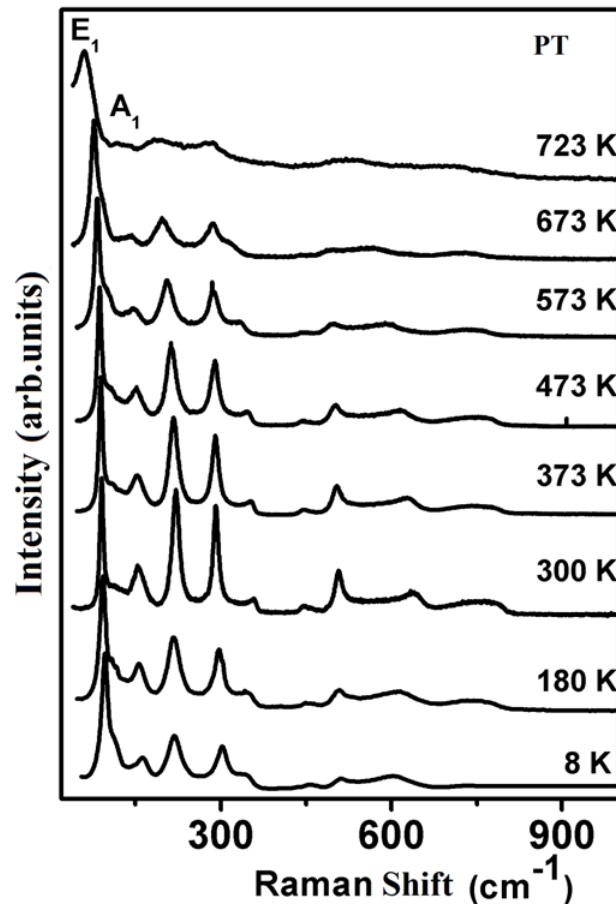
Figure 1. Raman spectra with temperature ($Pb_{1-x}La_xTiO_3$) for samples with La concentration, in this case $x = 2.5\%$.

on the samples with an optical microscope using a long working distance 50X objective. For the low temperature measurements, in the 10 K to 300 K range, a helium closed cycle cryostat was used while for high temperature, in the 300 K to 850 K range, an optical micro furnace was used. High pressure was applied on the samples using a diamond anvil cell (DAC), stainless steel gaskets with 100 micrometers thickness, and holes with a diameter of about 120 micrometers. Within our experimental conditions, we could not reach a pressure above 7.5 GPa, since the holes in the gaskets were deformed. The pressure transmitting medium was methanol-ethanol in the classic proportion 4:1. The frequency values of each vibrational mode were obtained by fitting asymmetric Lorentzian line shapes.

3. Results
In Figure 1 shows the Raman spectra as a function of temperature, normal modes of vibration go towards low frequencies with increasing temperature.The temperature affects the population of the different levels for each normal mode due to the non- equidistance in levels of energy, since the average position of atoms changes. However, in both cases, the change in the network parameters is attributed to the potential anharmonicity. On the other hand, the variations of the half-width of Raman bands under the effect of temperature or pressure are attributed to the decay to the decay of a given phonon into two or three phonons [19].

In figure 2 the softening of all the Raman peaks is due to the increase of chemical and
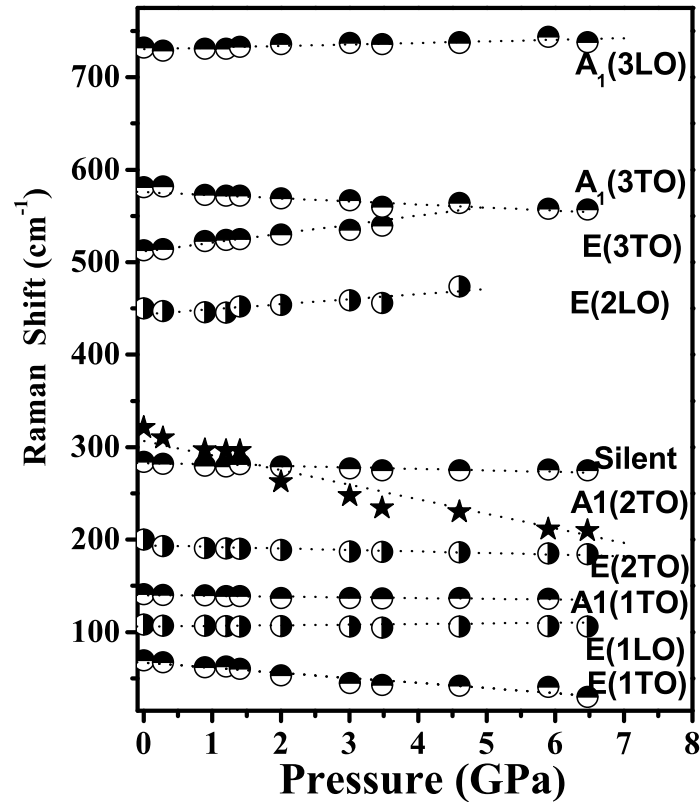
Figure 2. The Raman spectra for the region low frequency for the 2.5% La sample. This figure shows the softening evolution of the E1(TO) mode with increasing applied hydrostatic pressure.

structural disorders. Similar frequency behavior shifts and broadening were observed for the other La concentrations. The peak softening could be due to the defects and dislocations present in the lattice, local symmetry breakdown for the impurities and vacancies. All these effects in the lattice can lead to a breakdown of the Raman selection rules, this effect is observed in the damping of the vibration modes. Where P is the pressure, α the thermal expansion, $d\omega$ the shift of Raman bands, T the temperature, and α the Coefficient of thermal expansion. This equation can be written as a function of bulk modulus [20, 21, 22]:

$$\left(\frac{\partial \omega}{\partial T}\right)_P = -B\alpha \left(\frac{\partial \omega}{\partial P}\right)_T + \left(\frac{\partial \omega}{\partial T}\right)_V \Rightarrow \left(\frac{\partial \omega}{\partial T}\right)_V = B\alpha \left(\frac{\partial \omega}{\partial P}\right)_T + \left(\frac{\partial \omega}{\partial T}\right)_P \qquad (1)$$

The first term $\left(\frac{\partial \omega}{\partial T}\right)_V$ in equation 1 denotes the phonon-phonon interaction, or is the so-called explicit contribution of anharmonicity. To the right of the equation the volume-dependent implicit term $\left(\frac{\partial \omega}{\partial P}\right)_T$ can be obtained by measuring the Raman spectrum under pressure at constant temperature. The term $\left(\frac{\partial \omega}{\partial T}\right)_P$ can be determined by measuring the spectrum as a function of the temperature at constant pressure. The coefficients $(dw/dp)_T$ are related through the coefficient of thermal expansibility and compressibility of the materials.

As can be observed data found in other work [19], with increasing concentration the coefficient also increases to an absolute value. In this case, we were unable to calculate the coefficient for 15 and 20% La concentration, since the bulk modulus values have not been reported in the literature. In table 1 the result of the coefficient of anharmonicity for the pure material is comparable to that of literature obtained by simulation of the molecular dynamic [23].

Table 1. Calculation of $\left(\frac{\partial \omega}{\partial T}\right)_V$ coefficients at constant volume. Explicit contribution of anharmonicity.

PLT ($E1$)	0% La	2.5%La	5%	10% La
$\left(\frac{\partial \omega}{\partial T}\right)_V$ (cm^{-1})	-0.039	-0.054	-0.06	-0.08

Acknowledgements

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