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Monoclinic–tetragonal phase transition in $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ studied by infrared spectroscopy

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Abstract

The discovery of a new monoclinic phase in the $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ (PZT) system in the vicinity of the morphotropic phase boundary (MPB), previously considered as a region where the rhombohedral and tetragonal phases of PZT coexist, was recently reported. Investigations of this new phase were reported using different techniques such as high-resolution synchrotron x-ray powder diffraction and Raman spectroscopy. The main objective has been to define a new phase diagram of PZT. In this context, infrared spectroscopic studies were performed in the vicinity of the MPB and studies were initially centred on a PZT sample with $x = 0.49$ mol% Ti content. Results suggested that the *monoclinic* \rightarrow *tetragonal* phase transition occurs at 237 K, confirming the use of IR as a useful technique to investigate this phase transition.

Since 1999, when Noheda *et al* [1] reported the discovery of a new monoclinic phase in the $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ (known as PZT) phase diagram, initially established by Jaffe *et al* [2], the ferroelectric PZT has been extensively studied to understand what happens around the morphotropic phase boundary (MPB). Consequently, a new phase diagram for PZT must be proposed. In this way, new features of the MPB region were reported and this new monoclinic ferroelectric phase was explored by different techniques, initially by high-resolution synchrotron x-ray powder diffraction [3–6] and Raman spectroscopy [7, 8]. More recently, dielectric measurements [9] and theoretical electromechanical studies [10] were used to try to understand the behaviour of this new monoclinic phase. However, one question still remains: what are the boundaries that define the separation between the rhombohedral, tetragonal and monoclinic phases in the PZT phase diagram? Recently, Noheda *et al* [6] proposed a new PZT phase diagram including the new monoclinic phase. Considering room

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temperature (≈ 300 K), Noheda *et al* [6] proposed the existence of the monoclinic phase for PZT with $0.45 < x < 0.48$ (see figure 7 in [6]), where the $F_R \rightarrow F_M \rightarrow F_T$ transition occurs with increasing Ti content. Considering a fixed PZT composition, the suggested transition as a function of temperature has the sequence $F_M \rightarrow F_M + F_T \rightarrow F_T$ (see figure 6 in [6]), indicating the possible coexistence of the monoclinic and tetragonal phases in the MPB region. Therefore, the monoclinic structure can be considered as a 'bridge' between the tetragonal and rhombohedral phases in PZT [6]. However, the boundaries that define the limits between rhombohedral–monoclinic–tetragonal phases remain unclear. Probably the use of combined techniques will provide a well defined PZT phase diagram as soon as possible.

Among the above-cited techniques which were used for exploration of the new ferroelectric monoclinic phase in PZT, spectroscopic techniques, such as Raman and infrared spectroscopy (IR), are useful tools to investigate phase transitions in polycrystalline materials. The IR technique can be used to study ferroelectric phase transitions because infrared vibrational frequencies, and consequently the interatomic forces, are affected by the onset of the ferroelectric state due to temperature phase transitions. The main purpose of this work is to use the IR technique to explore the recently discovered *monoclinic* \rightarrow *tetragonal* phase transition at PZT compositions around the MPB, offering additional information to construct the correct phase diagram for the PZT around the MPB.

The present investigation of the PZT phase diagram near the MPB requires samples of high quality in terms of chemical homogeneity. Samples of $\text{PbZr}_{0.51}\text{Ti}_{0.49}\text{O}_3$, or simply PZT49 ($x = 49$ mol% of Ti content), were obtained through the solid-state reaction from 99.9% pure reagent grade PbO , ZrO_2 and TiO_2 oxides. The starting powders and distilled water were mixed and milled for 3.5 h for powder homogenization. The mixture was calcined at 850°C for 2.5 h and it was pressed at 400 MPa, giving rise to PZT ceramic discs with 10 mm diameter and 5 mm thickness. Finally, the discs were sintered at a temperature of 1250°C for 4 h and an excellent homogeneity was obtained. The sintering atmosphere was enriched in PbO vapour by using $\text{PbZrO}_3 + 5$ wt% ZrO_2 powder around the discs inside a covered alumina crucible in order to avoid significant volatilization of PbO . The weight loss due to possible PbO escape was $\approx 0.1\%$, and the sintered densities were in excess of $\approx 97\%$ of the theoretical density. Thus, samples under high stoichiometry and homogeneity control were obtained.

Using PZT49 powder samples dispersed in pressed KBr discs, infrared measurements were performed with a Nicolet Nexus 870 FT-IR spectrometer from 1400 to 400 cm^{-1} (each IR spectrum was recorded with $\pm 1\text{ cm}^{-1}$ precision). For low-temperature studies, the KBr disc was mounted in a cryostat with KBr windows capable of going up to liquid-nitrogen temperature. The temperature was controlled manually within ± 2 K accuracy. To certify the homogeneity in temperature of the KBr pellets, and consequently the PZT temperature, each spectrum was collected after 1 h under stable temperature.

Systematic infrared measurements were carried out for different temperatures in order to study the PZT *monoclinic* \rightarrow *tetragonal* phase transition. The spectra of the PZT49 sample, measured at 98 and 273 K, are shown in figure 1 in the region from 400 to 1400 cm^{-1} . Both spectra showed a band centred at 613 cm^{-1} , with a shoulder at 770 and 549 cm^{-1} and another at 534 cm^{-1} . Possibly the observed change in the IR spectra at different temperatures (figure 1) may be interpreted as a result of the expected phase transition.

To understand and interpret each IR spectrum it is important to remember that PZT is a PbTiO_3 – PbZrO_3 solid solution formed by a reaction sequence from PbO (orthorhombic), TiO_2 (tetragonal) and ZrO_2 (monoclinic) [11, 12], and presents a ABO_3 perovskite structure like BaTiO_3 and SrTiO_3 . The infrared vibrations for the titanate family, which include perovskites such as BaTiO_3 , SrTiO_3 , PbTiO_3 and ZrTiO_3 , may be explained based on vibrations of the TiO_6 octahedron [13, 14]. In these structures, the TiO_6 octahedron presents two

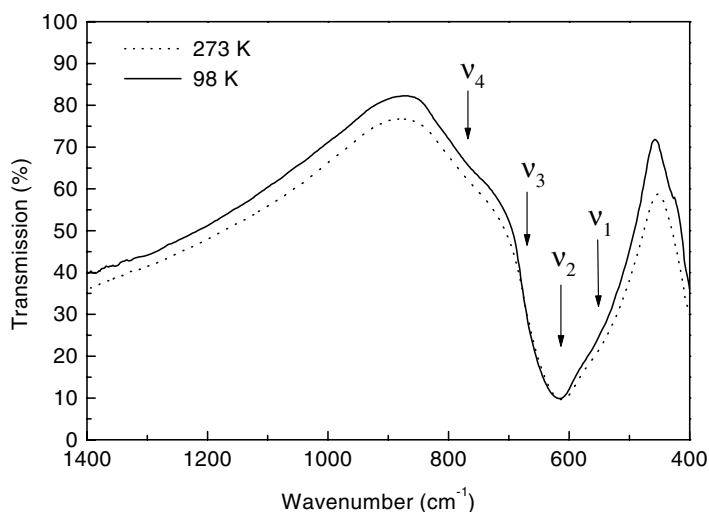


Figure 1. Infrared spectra of powdered $\text{PbZr}_{0.51}\text{Ti}_{0.49}\text{O}_3$ dispersed in a pressed KBr disc. This figure shows only two spectra, recorded at 98 K (solid curve) and 273 K (dot curve).

distinct vibration modes: lower-frequency (ν_i) *bending* vibration and higher-frequency (ν_j) *stretching* vibration. Considering the TiO_6 octahedron, the *stretching* vibration occurs at higher frequencies than *bending* vibration, as expected, from a comparison of the change in potential energy due to repulsive forces between ions in the two normal vibrations [13]. Thus, each infrared spectrum of PbTiO_3 or ZrTiO_3 presents two normal modes active in the infrared region [15]. In figure 1, ν_1 and ν_2 represent *bending* modes while ν_3 and ν_4 represent *stretching* modes in the BO_6 (TiO_3 and ZrO_3) octahedron in ABO_3 structure. These ν_j frequencies shown in figure 1 were determined by theoretical fitting of each IR spectrum recorded as a function of temperature, as will be described below.

From the point of view of group representation, cubic symmetry, point group O_h , presents an F_{1u} species and a single band structure is expected. When the cubic phase transforms into the tetragonal phase, the point group is C_{4v} , presenting E and A_1 species. In this way, a double-band structure is expected for the tetragonal phase. Finally, the E and A_1 transform into A' and A'' species when the symmetry changes from tetragonal to monoclinic [16]. Thus, a double-band structure is also expected for the monoclinic phase.

Considering preceding discussions, several fits were performed using infrared spectra recorded at temperatures between 98 and 308 K. Particular attention was devoted to mode ν_1 in figure 1 because the observed asymmetry in infrared spectra may be a consequence of this mode in particular. To study the behaviour of this mode ν_1 , each IR spectrum recorded as a function of temperature was fitted by the least-squares method using two pairs of Lorentzian peaks. The number of Lorentzian peaks used was assigned based on the four possible vibration modes in PZT described above. Thus, the fitted mode ν_1 is plotted in figure 2 as a function of temperature with the associated error bars, which were determined based on χ -square values. As observed in figure 2, when temperature increases the mode ν_1 shifts from 532 to 528 cm^{-1} , presenting an inflection point at 237 K. This behaviour clearly suggests the expected *monoclinic* \rightarrow *tetragonal* phase transition at this temperature. Figure 3 shows this point, at $\text{PbZr}_{0.51}\text{Ti}_{0.49}\text{O}_3$ ($x = 0.49$ mol% Ti), added to the new PZT phase diagram around the MPB, recently proposed by Noheda *et al* [6]. As we can see, this specific point was not previously determined in the PZT phase diagram but its position in the diagram suggest a good

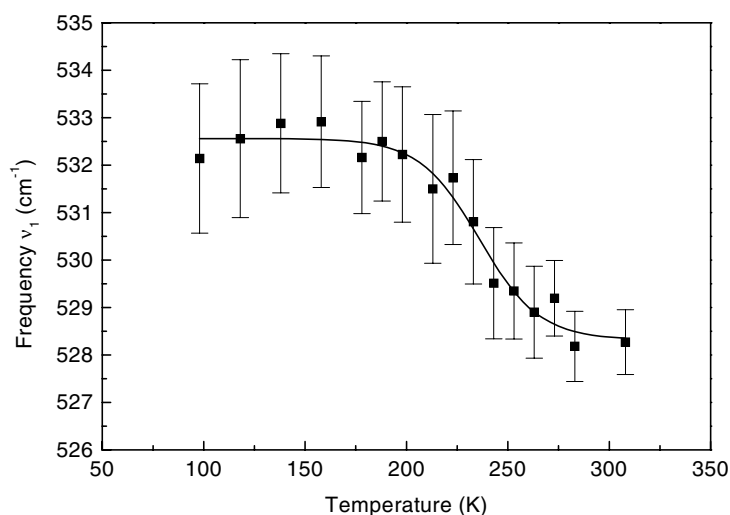


Figure 2. Variation of the infrared mode ν_1 of $\text{PbZr}_{0.51}\text{Ti}_{0.49}\text{O}_3$ as a function of temperature in the range 98–308 K (the curve is just a guide for the eye).

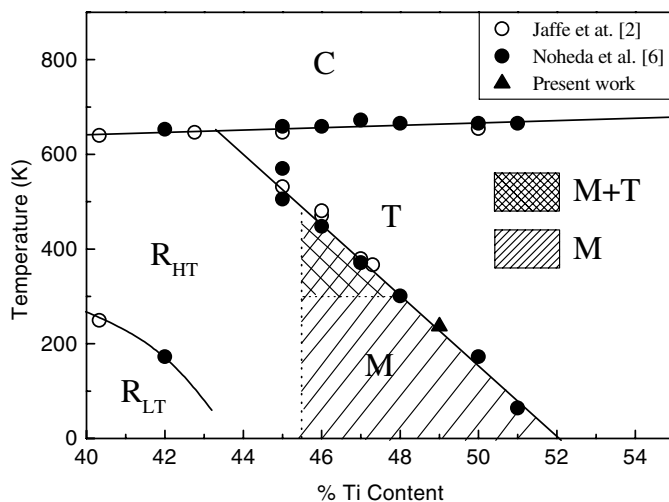


Figure 3. New PZT phase diagram around the MPB proposed by Noheda *et al* [6]. Open circles represent data obtained from Jaffe *et al* [2], solid circles were obtained from Noheda *et al* [6] and the solid triangle results from IR in current work for $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ ($x = 0.49$).

agreement with expected results. This result, obtained here from IR, demonstrates that IR could be a useful tool to investigate this phase transition in PZT ceramics. Further work using IR involving compositions of PZT around the MPB is in progress.

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