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# Infrared studies of the monoclinic–tetragonal phase transition in $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ ceramics

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## Abstract

Recently, the observation 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 was reported. Investigations of this new phase were reported using different techniques such as high-resolution synchrotron x-ray powder diffraction and Raman spectroscopy. In this work, the monoclinic  $\rightarrow$  tetragonal phase transition in  $\text{PbZr}_{0.50}\text{Ti}_{0.50}\text{O}_3$  ceramics was studied using infrared spectroscopy between 1000 and 400  $\text{cm}^{-1}$ . The four possible  $\nu_1$ -stretching modes (Ti–O and Zr–O stretch) in the  $\text{BO}_6$  octahedron in the  $\text{ABO}_3$  structure of PZT in this region were monitored as a function of temperature. The lower-frequency mode  $\nu_1$ -(Zr–O) remains practically unaltered, while both intermediate  $\nu_1$ -(Ti–O) modes decrease linearly as temperature increases from 89 to 263 K. In contrast, the higher-frequency  $\nu_1$ -(Ti–O) and  $\nu_1$ -(Zr–O) modes present anomalous behaviour around 178 K. The singularity observed at this mode was associated with the monoclinic  $\rightarrow$  tetragonal phase transition in  $\text{PbZr}_{0.50}\text{Ti}_{0.50}\text{O}_3$  ceramics.

## 1. Introduction

The solid solution of  $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ , known as lead zirconate titanate (PZT), is probably one of the most studied ferroelectric materials in the past 40 years, especially because of its excellent dielectric, ferroelectric and piezoelectric properties [1, 2]. The highest piezoelectric coefficients of PZT are found for compositions near the morphotropic phase boundary (MPB) between the tetragonal and rhombohedral regions of the composition–temperature phase diagram [1]. Until 1999, the MPB was interpreted as the coexistence, at room temperature, of the

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rhombohedral ( $F_R$ ) and tetragonal ( $F_T$ ) ferroelectric phases. However, experimental and theoretical results concerning the coexistence of these phases in the MPB region ( $0.46 \leq x \leq 0.49$ ) were considered to be controversial for several years.

Recently, especially in last three years, a great deal of attention has again been devoted to PZT because of the observation of a monoclinic phase near the MPB that was not predicted on the original phase diagram [3]. This monoclinic phase was initially studied using high-resolution synchrotron x-ray powder diffraction [4–7] and more recently using different techniques such as Raman spectroscopy [8, 9], dielectric measurements [10], and theoretical electromechanical studies [11].

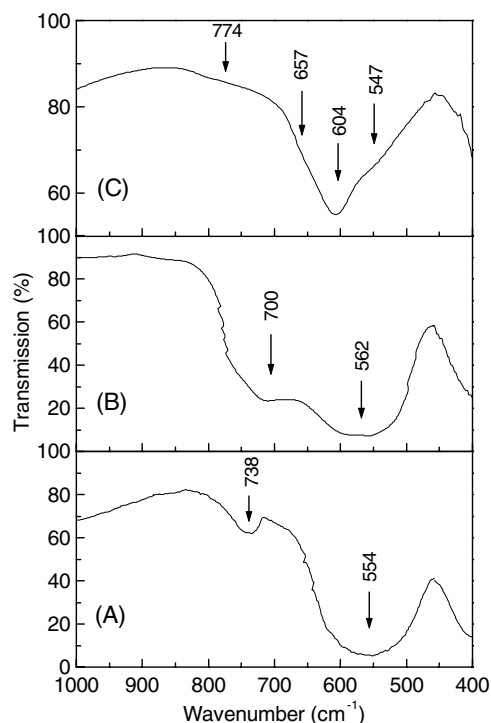
Some of these studies concerning the monoclinic phase in the PZT system have led to a new phase diagram around the MPB [7]. Thus, the monoclinic structure can be considered to be a ‘bridge’ between the tetragonal and rhombohedral phases in the PZT phase diagram [7]. However, the boundaries that define limits between rhombohedral–monoclinic–tetragonal phases remain unclear. Nowadays, the monoclinic phase has also been observed in a similar system that exhibits an analogous MPB such as  $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$  (PMN–PT) [12], but this system is characterized by complex phase behaviour. Comprehension of the monoclinic phase in systems such as PZT and PMN–PT around the MPB is complicated and requires systematic study to be understood correctly.

Spectroscopic techniques, such as Raman and infrared spectroscopy (IR), are useful tools for investigating phase transitions in polycrystalline materials and single crystals. Infrared spectroscopy 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. This study is a consequence of our previous work [13] using the IR technique to explore the monoclinic  $\rightarrow$  tetragonal phase transition of PZT in order to better understand the role of the monoclinic phase in this complex system around the MPB.

## 2. Experimental details

The study of the  $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$  phase diagram near the MPB requires samples of high quality in terms of chemical homogeneity. In this work  $\text{PbTiO}_3$  powder and  $\text{PbZr}_{0.50}\text{Ti}_{0.50}\text{O}_3$  ceramics ( $x = 50$  mol% of Ti content) were prepared (obtained through the solid-state reaction from 99.9%-pure reagent-grade  $\text{PbO}$ ,  $\text{ZrO}_2$  and  $\text{TiO}_2$  oxides). The starting powders and distilled water were initially mixed and milled for 3.5 h for homogenization. The mixture was calcined at  $850^\circ\text{C}$  for 2.5 h and then pressed at 400 MPa, to produce PZT ceramic disks with a diameter of 10 mm and thickness of 5 mm. Finally, the disks were sintered at a temperature of  $1250^\circ\text{C}$  for 4 h and an excellent homogeneity was obtained. The sintering atmosphere was enriched in  $\text{PbO}$  vapour by using  $\text{PbZrO}_3 + 5$  wt%  $\text{ZrO}_2$  powder around the disks inside a covered alumina crucible to compensate for  $\text{PbO}$  volatilization. The weight loss due to possible  $\text{PbO}$  escape was  $\approx 0.1\%$  and the sintered densities were in excess of  $\approx 97\%$  of the theoretical density. Finally, samples with high stoichiometry and homogeneity control were obtained.

Using  $\text{PbZr}_{0.50}\text{Ti}_{0.50}\text{O}_3$  powders dispersed in pressed KBr discs, infrared measurements were performed with a Nicolet Nexus 870 FT–IR spectrometer from  $1000$  to  $400\text{ cm}^{-1}$  (each IR spectrum was recorded with  $2\text{ cm}^{-1}$  resolution). 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  $\pm 2\text{ K}$  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.



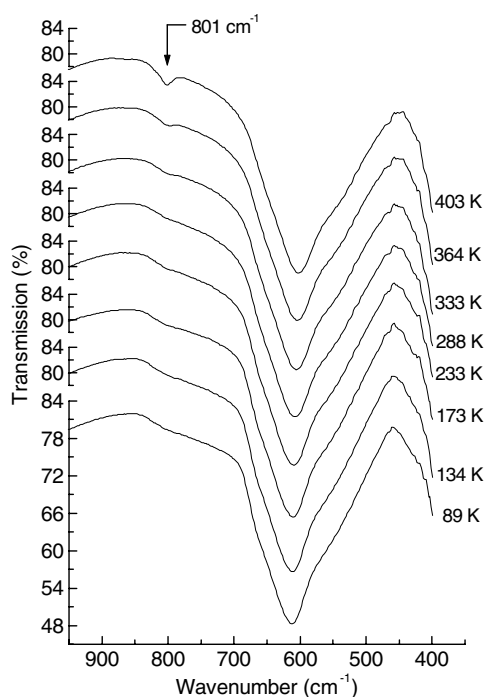
**Figure 1.** Infrared spectra recorded at room temperature of the  $\text{PbZrO}_3$  (A) [14],  $\text{PbTiO}_3$  (B) [14] and  $\text{PbZr}_{0.50}\text{Ti}_{0.50}\text{O}_3$  (C) (this work).

### 3. Results and discussion

Figure 1 shows infrared spectra of powdered  $\text{PbZrO}_3$  and  $\text{PbTiO}_3$  collected from literature [14] and  $\text{PbZr}_{0.50}\text{Ti}_{0.50}\text{O}_3$  prepared in this work. Two absorption bands were observed in  $\text{PbZrO}_3$  (figure 1(A)) in the observed range. The higher frequency has a centre at  $738\text{ cm}^{-1}$  and the lower frequency extends from  $716$  to  $460\text{ cm}^{-1}$ , with a centre at  $554\text{ cm}^{-1}$ . The  $\text{PbTiO}_3$  (figure 1(B)) presents a broad band with a centre at  $562\text{ cm}^{-1}$  and a shoulder at about  $700\text{ cm}^{-1}$ . Figure 1(C) shows an infrared spectrum of  $\text{PbZr}_{0.50}\text{Ti}_{0.50}\text{O}_3$ , studied in this work. This spectrum presents a broad band that extends from  $870$  to  $452\text{ cm}^{-1}$  with a maximum absorption at  $604\text{ cm}^{-1}$  and shoulder at  $547\text{ cm}^{-1}$ . The asymmetric band in figure 1(C) suggests, in principle, a composite of both isolated  $\text{PbTiO}_3$  and  $\text{PbZrO}_3$  spectra, whose frequencies may be located at  $547$ ,  $604$ ,  $657$  and  $774\text{ cm}^{-1}$ .

Several infrared measurements were recorded in the temperature range  $89$ – $403\text{ K}$ , with the intention of studying the structural phase transition in  $\text{PbZr}_{0.50}\text{Ti}_{0.50}\text{O}_3$ . Figure 2 shows infrared spectra for selected temperatures in the region  $400$ – $1000\text{ cm}^{-1}$ . In this figure, we can see that no appreciable changes were observed in the spectra for frequencies below  $700\text{ cm}^{-1}$ . However, with increasing temperature we note that a well defined absorption appears with a centre at  $801\text{ cm}^{-1}$ , but the precise temperature at which this occurs is not clear. The observed change in the spectrum may most likely be interpreted as a result of the monoclinic  $\rightarrow$  tetragonal phase transition for  $\text{PbZr}_{0.50}\text{Ti}_{0.50}\text{O}_3$ .

At this stage, some discussion of these results is useful to understand and interpret each IR spectrum as a function of temperature. The PZT is a solid solution of



**Figure 2.** Infrared spectra of  $\text{PbZr}_{0.50}\text{Ti}_{0.50}\text{O}_3$ , recorded for several temperatures in the range 89–403 K. The band at  $801\text{ cm}^{-1}$  is associated with the  $\nu_1$ -(Zr–O) higher-frequency mode of the  $\text{BO}_6$  octahedron in PZT's  $\text{ABO}_3$  structure (discussion in the text).

$\text{PbTiO}_3$ – $\text{PbZrO}_3$  formed by a reaction sequence from  $\text{PbO} + \text{TiO}_2 \rightarrow \text{PbTiO}_3$ , followed by the step  $\text{PbO} + \text{PbTiO}_3 + \text{ZrO}_2 \rightarrow \text{PbO}(\text{solid solution}) + \text{PbTiO}_3 + \text{ZrO}_2 \rightarrow \text{Pb}(\text{Zr, Ti})\text{O}_3$  (PZT) [15, 16]. The PZT obtained presents an  $\text{ABO}_3$  perovskite structure and different phases, depending on the Zr/Ti ratio. The infrared vibrations for the titanate family, which include classical perovskites such as  $\text{BaTiO}_3$ ,  $\text{SrTiO}_3$ ,  $\text{PbTiO}_3$  and  $\text{PbZrO}_3$ , may be explained on the basis of the vibrations of the  $\text{TiO}_6$  octahedron [17–19]. In these structures, the  $\text{TiO}_6$  octahedron presents four distinct modes of vibration: higher-frequency  $\nu_1$ -stretching and lower-frequency  $\nu_2$ -torsion,  $\nu_3$ -bending and  $\nu_4$ -cation-( $\text{TiO}_3$ ) vibrations [19]. Considering the  $\text{TiO}_6$  octahedron and the frequency range studied, the  $\nu_1$ -stretching vibration occurs at higher frequencies than the  $\nu_3$ -bending vibration, as expected from a comparison of the changes in potential energy due to repulsive forces between ions in the two normal vibrations [17].

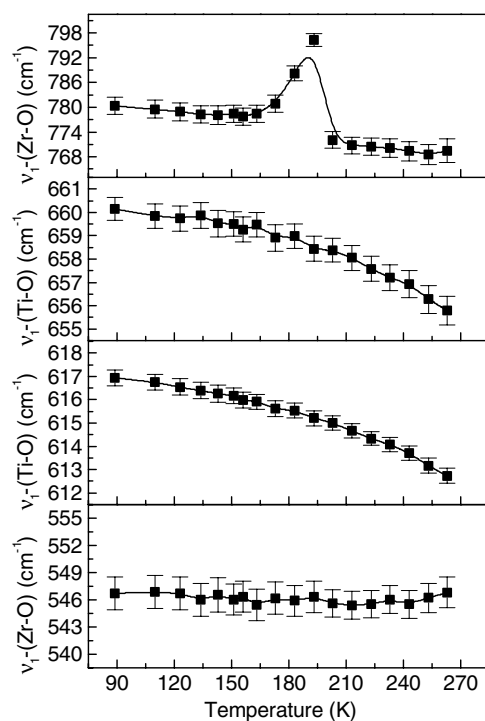
In figures 1(A) and (B), the modes assigned for  $\text{PbZrO}_3$  ( $554$  and  $738\text{ cm}^{-1}$ ) and  $\text{PbTiO}_3$  ( $562$  and  $700\text{ cm}^{-1}$ ) are associated with  $\nu_1$ -stretching modes (Ti–O and Zr–O stretch) in the  $\text{BO}_6$  octahedron of the  $\text{ABO}_3$  structure. For  $\text{PbZrO}_3$  and  $\text{PbTiO}_3$ , the  $\nu_2$ -torsion (Ti– $\text{O}_3$  and Zr– $\text{O}_3$  torsion),  $\nu_3$ -bending (O–Ti–O and O–Zr–O bend) and  $\nu_4$ -cation-( $\text{TiO}_3$ ) modes are below  $400\text{ cm}^{-1}$  [19, 20]. The  $\nu_2$ ,  $\nu_3$  and  $\nu_4$  bands occur below the available experimental range used in this work and will not be considered in our discussion.

The preceding discussion was centred on the vibrational nature of the  $\text{BO}_3$  group, which consists of a central Zr or Ti atom surrounded octahedrally by six O half-atoms. From the point of view of group representation, this octahedron has the symmetry of the point group  $\text{O}_h$ . In cubic symmetry, point group  $\text{O}_h$  presents an  $\text{F}_{1u}$  species and a single triply degenerate band structure is expected, since three equivalent axes exist in the case of the cubic lattice. When the

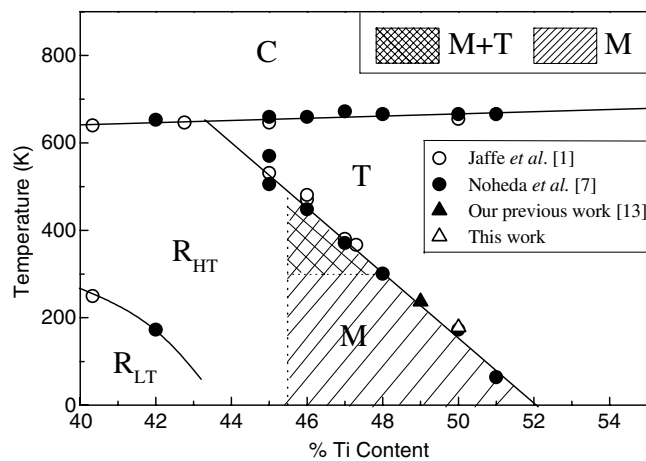
cubic phase transforms into the tetragonal phase, point group  $C_{4v}$  presents E and  $A_1$  species with cubic triple degeneracy partially removed. In this way, a double band structure is expected for the tetragonal phase. Finally, the E and  $A_1$  species transform into  $A'$  and  $A''$  species when the symmetry changes from tetragonal to monoclinic [21]. Thus, a double partially degenerate band structure is also expected for the monoclinic phase.

Under the above considerations, several fits were performed using infrared spectra recorded at temperatures of 89–263 K. The experimental data obtained were fitted by the least-square method using two couples of Lorentzian curves. The number of Lorentzian curves that were used was assigned on the basis of four possible vibrational modes in PZT, as described above: two modes for  $\nu_1$ -TiO<sub>3</sub> and two modes for  $\nu_1$ -ZrO<sub>3</sub> (see figure 1(C)). Thus, the four fitted modes were plotted in figure 3 as a function of temperature, with associated error bars that were determined on the basis of  $\chi$ -square values. As observed in figure 3, when the temperature increases, the mode  $\nu_1$ -(Zr–O) at 546 cm<sup>-1</sup> remains practically unchanged and both modes  $\nu_1$ -(Ti–O), starting at 617 and 660 cm<sup>-1</sup>, decrease linearly. The observed decrease in these  $\nu_1$ -(Ti–O) modes, as a function of increasing temperature, can be explained by an inverse relationship between atomic separation and vibrational frequency if there is no structural phase transition in the observed temperature range. Thus, these modes were insensitive to the expected monoclinic  $\rightarrow$  tetragonal phase transition at PbZr<sub>0.50</sub>Ti<sub>0.50</sub>O<sub>3</sub>. On the other hand, the higher-frequency  $\nu_1$ -(Zr–O) mode decreases linearly from 780 to 778 cm<sup>-1</sup> when the temperature increases from 89 to 156 K. After 156 K, this mode presents anomalous behaviour with a maximum at 796 cm<sup>-1</sup> for 193 K and then presents a linear decrease between 203 and 263 K. The higher-frequency  $\nu_1$ -(Ti–O) mode also presents anomalous behaviour around 180 K, but it is almost imperceptible. The singularity observed at these modes may be associated with the monoclinic  $\rightarrow$  tetragonal phase transition, which in principle can be associated with distortions associated with a unit cell of the monoclinic and tetragonal phases during the phase transition. The anomalous behaviour of the higher-frequency  $\nu_1$ -(Zr–O) and  $\nu_1$ -(Ti–O) peaks in figure 3 can be associated with the temperature at which the monoclinic  $\rightarrow$  tetragonal phase transition occurs. This value was added to the new phase diagram that was proposed by Noheda *et al* [7] around the MPB (figure 4). As we can see, this result is in good agreement with the results obtained from other techniques, such as dielectric measurements and high-resolution synchrotron x-ray powder diffraction [7], that lead to values around 174 K.

To understand the structural phase transitions in the PZT system that were studied by infrared spectroscopy, it is necessary to consider the behaviour of each constituent of the solid solution (PbTiO<sub>3</sub> and PbZrO<sub>3</sub>) as a function of temperature. At room temperature ( $\sim$ 300 K), PbZrO<sub>3</sub> presents an orthorhombic structure, while PbTiO<sub>3</sub> shows a tetragonal structure. The corresponding spectra are shown in figures 1(A) and (B). As the orthorhombic structure possesses lower symmetry than the tetragonal structure, the PbZrO<sub>3</sub> bands shown in figure 1(A) are separated more than those in PbTiO<sub>3</sub>, as shown in figure 1(B). In these constituents, considering the phase transitions from lower-to-higher-symmetry structures, the bands located at high frequencies will shift to lower frequencies, where they are superposed on the low-frequency bands and become triply degenerate in the cubic structure. Analogous behaviour is expected in the structural phase transitions of the solid solution PbZrO<sub>3</sub>–PbTiO<sub>3</sub> (PZT). In this way, it is expected that, for PbZr<sub>0.50</sub>Ti<sub>0.50</sub>O<sub>3</sub>, the high-frequency bands associated with the octahedra ZrO<sub>6</sub> and TiO<sub>6</sub>, which are around 780 and 660 cm<sup>-1</sup> respectively (as shown in figure 3), will be shifted to low frequency when the monoclinic  $\rightarrow$  tetragonal transition occur. These shifts were observed clearly in the  $\nu_1$ -(Zr–O) mode and weakly in the  $\nu_1$ -(Ti–O) mode. On the other hand, no anomalous behaviour was observed in the evolution of the low-frequency modes  $\nu_1$ -(Zr–O) and  $\nu_1$ -(Ti–O) as a function of temperature. Therefore, the anomalies observed in the vibrational modes are caused by the monoclinic  $\rightarrow$  tetragonal transition in the PZT system.



**Figure 3.** The behaviour of the  $\nu_1$ -stretching modes (Ti-O and Zr-O stretch) in the  $\text{BO}_6$  octahedron of PZT's  $\text{ABO}_3$  structure as a function of temperature.



**Figure 4.** The new PZT phase diagram around the MPB proposed by Noheda *et al* [7]. The open circles represent data obtained from [1], solid circles from [7], and solid triangles from infrared spectroscopy in our previous work [13]. The open triangles are a result of the studies in the present work for  $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$  ( $x = 0.50$ ).

In our previous study for another PZT composition ( $x = 0.49$  mol% Ti) [13], the predicted monoclinic  $\rightarrow$  tetragonal phase transition was principally observed in the lowest-frequency mode around  $530\text{ cm}^{-1}$ , but all modes were sensitive to this phase transition, as we will show in our next paper. In the present work, this phase transition was observed in the highest-frequency



mode around 780 and 660  $\text{cm}^{-1}$ , while the lower-frequency modes remain unchanged. These differences are possibly associated with the stability of the monoclinic phase at lower temperatures and must be investigated in detail. The reason why the monoclinic  $\rightarrow$  tetragonal phase transition at  $\text{PbZr}_{0.50}\text{Ti}_{0.50}\text{O}_3$  was observed mainly for the higher-frequency  $\nu_1$ -(Ti–O) and  $\nu_1$ -(Zr–O) modes while the other lower-frequency mode remains unchanged, as a function of temperature, is not completely clear at this moment. Complete comprehension of this question will be possible through studies of others PZT compositions in the MPB.

#### 4. Conclusions

In this work, spectroscopic infrared measurements were performed to study the monoclinic  $\rightarrow$  tetragonal phase transition in  $\text{PbZr}_{0.50}\text{Ti}_{0.50}\text{O}_3$  ceramics. With these studies it was possible to track the behaviour, as a function of temperature, of the  $\nu_1$ -stretching modes (Ti–O and Zr–O stretch) in the  $\text{BO}_6$  octahedron of PZT's  $\text{ABO}_3$  structure. The lower-frequency  $\nu_1$ -(Zr–O) mode remains practically unchanged while both intermediate-frequency  $\nu_1$ -(Ti–O) modes decrease linearly as temperature increases from 89 to 263 K. However, the higher-frequency  $\nu_1$ -(Ti–O) and  $\nu_1$ -(Zr–O) modes present anomalous behaviour, with a peak for 193 K and a temperature on-set at 178 K. The singularity observed at these modes was associated with the monoclinic  $\rightarrow$  tetragonal phase transition in  $\text{PbZr}_{0.50}\text{Ti}_{0.50}\text{O}_3$  ceramics.

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