Raman scattering study of the $PbZr_{1-x}Ti_xO_3$ system: Rhombohedral-monoclinic-tetragonal phase transitions

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In this paper we present a Raman-scattering study of the phase transitions in the $PbZr_{1-x}Ti_xO_3$ systems around the morphotropic phase boundary over a wide temperature range. The boundary between rhombohedral and monoclinic phases was found to be a quasivertical line between $x=0.46$ and $x=0.47$. We also studied the monoclinic-tetragonal phase boundary and our spectroscopic results agree very well with those reported by using x-ray diffraction.

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I. INTRODUCTION

The $PbZr_{1-x}Ti_xO_3$ (PZT) solid solution is a ferroelectric system presenting unusual ferroelectric properties close to the morphotropic phase boundary (MPB) related to the giant electromechanical coupling due to a polarization rotation mechanism.[1] This new concept in the origin of outstanding ferroelectric properties was recently confirmed in PZT with the discovery of a new ferroelectric phase with monoclinic symmetry,[2] where the polarization vector is no longer constrained to lie along a symmetry axis, but instead the polarization vector can rotate within the monoclinic plane.[3–6] This property is now associated with a universal characteristic of ferroelectric systems with MPB and huge electromechanical coupling.[7] This phenomenon has already been experimentally observed in PZT, $Pb(Mg_{1/3}Nb_{1/3})O_3$-$PbTiO_3$ (PMN-PT),[8] and $Pb(Zn_{1/3}Nb_{1/3})O_3$-$PbTiO_3$ (PZN-PT).[7,9,10]

The main technique used to study these new structural properties has been x-ray scattering that has indeed provided a very detailed structural characterization including the observation of phase transitions. Raman spectroscopy has also been widely used for studying structural phase transitions in ferroelectric systems. In particular, Raman spectroscopy has been applied for studying these novel structural features in PZT ceramics.[11–14] Raman scattering is a simple, nondestructive, and readily available characterization technique allowing one to study the material already incorporated in a device. The understanding of the Raman spectra is useful in the characterization of PZT-based devices.

Recently, we have successfully determined through Raman-scattering studies the rhombohedral-monoclinic-tetragonal phase-transition sequence at low temperatures (7 K).[12] In this paper we present the phase-transitions studies in PZT system near the MPB over a wide range of temperatures ($7 \leqslant T \leqslant 750$ K). We determined both phase boundaries between the rhombohedral and the monoclinic phase and between the monoclinic and the tetragonal phase. The boundary between the rhombohedral and the monoclinic phase was found as a quasivertical line and the boundary between the monoclinic and the tetragonal phases agrees well with the x-ray-diffraction results.

II. EXPERIMENT

The details of the sample preparation are reported elsewhere.[12] The spectral excitation was provided by an Ar-ion laser, using the 514.5-nm line (2.41 eV) and with a power density of ~ 1 MW/cm^2 on the sample surface (this laser power density was found to optimize the signal-to-noise ratio without overheating the sample). The scattered light was analyzed with a Jobin Yvon T64000 spectrometer, equipped with a N_2-cooled charge-coupled device detector. The low-temperature measurements were performed using an air products closed-cycle He cryostat that provides temperatures ranging from 7 to 300 K. A Lakeshore controller was used to control the temperature with precision of ± 0.1 K. The high-temperature studies ($T \geqslant 300$ K) were performed by using a resistive homemade furnace.

III. RESULTS AND DISCUSSION

The extension of the monoclinic phase around the MPB in the x-T phase diagram was first studied by Noheda *et al.*[8] through x-ray-diffraction measurements. Recently, Lima *et al.*[12] confirmed those results by studying the extension of the monoclinic phase at 7 K through Raman-scattering measurements and group theory analysis based on the point group C_s for the monoclinic phase. It should be pointed out that the recent studies performed on the composition $PbZr_{0.52}Ti_{0.48}O_3$ have suggested that there are two monoclinic phases.[15,16] One of them is the C_s^2 (M_{HT}) phase discovered by Noheda *et al.*,[2] which is stable in the temperature range $210 \leqslant T \leqslant 280$ K. For $T \leqslant 210$ K, Ranjan *et al.*[16] have proposed a monoclinic phase with C_s^3 (M_{LT}) space group. This new phase arises from an antiferrodistortive mechanism driven by instabilities at the R point of the cubic Brillouin zone. Since our Raman analysis is based on the point group (C_s), our previous analysis[12] remains valid independent of whether the space group is C_s^2 or C_s^3. Due to the doubling of the unit cell, it is expected to observe new Raman modes in the Raman spectra. However, these changes are expected to appear for the external modes (low-frequencies modes). This phase transition proposed by Ranjan *et al.*[16] occurs at rela-

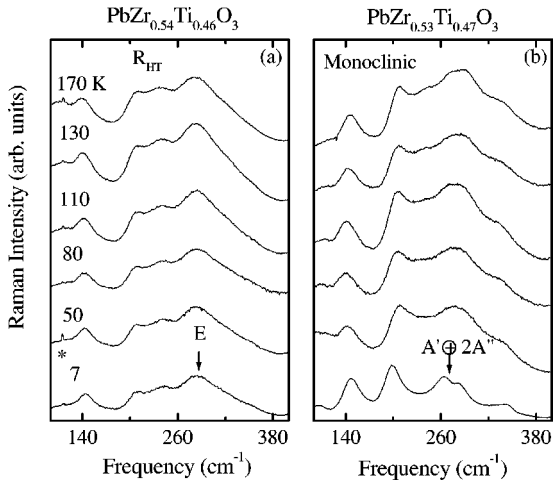

FIG. 1. Raman spectra for (a) $x=0.46$ rhombohedral and (b) $x=0.47$ (monoclinic), respectively, taken at several temperatures. The narrow mode marked with an "*" stands for a plasma from the laser source.

tively high temperatures where the elastic scattering is strong and some extra modes due to the zone folding should be underneath this elastic scattering. Since we were not able to observe the transitions between M_{HT} and M_{LT}, we hereafter refer to these phases only as the monoclinic phase.[17]

Both studies by Noheda *et al.*[4] and Lima *et al.*[12] suggested that the boundary separating the rhombohedral from the monoclinic phase is more vertical than the well-known tetragonal-monoclinic line boundary for which the slope is ~ 90 K/1% concentration.[18] While the monoclinic-tetragonal phase boundary is well determined, few reports has been published to study the rhombohedral-monoclinic phases so far.[4,12] We have performed a detailed study of the rhombohedral-monoclinic boundary by analyzing the data keeping the temperature fixed and changing the concentration. This approach is, in particular, very important for determining the line boundary by using Raman scattering as the experimental technique to probe phase transitions in the x-T phase diagram. The PZT system exhibits a considerable amount of anharmonicity and is somewhat hard to distinguish whether the small changes induced by the temperature in the phonon spectra are associated with the anharmonic effects or with the structural changes. By keeping the temperature constant, the anharmonic effects are surpassed and the effects of the structural changes induced by the concentration become accessible in the phonon spectra. With this, we were able to determine by using Raman spectroscopy, with a precision better than 1% in concentration, the rhombohedral-monoclinic and monoclinic-tetragonal phase boundaries.

A. Monoclinic phase at low temperatures

Raman spectra taken at several temperatures for compositions $x=0.46$ and $x=0.47$ are presented in Figs. 1(a) and 1(b), respectively. The spectra shown in Fig. 1(a), from the bottom to the top, exhibit slight changes in the relative intensity thus suggesting that the material does not undergo a

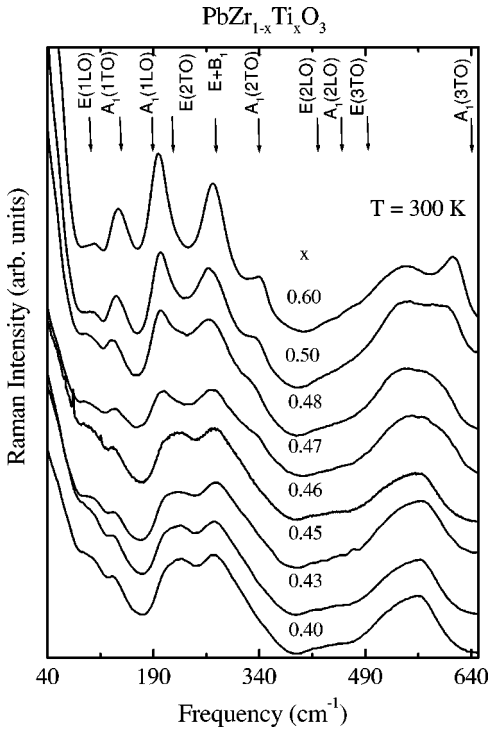

FIG. 2. Raman spectra for $PbZr_{1-x}Ti_xO_3$ around the morphotropic phase boundary taken at 300 K. The mode symmetry labeling stand for the tetragonal phase (Ref. 19).

phase transition in the temperature range from 7 to 170 K, remaining in the starting rhombohedral phase at 7 K. The same behavior is observed for the composition $x=0.47$ [Fig. 1(b)] for which the monoclinic phase remains stable in the temperature range 7 K$\leqslant T \leqslant$200 K. By comparing the spectra presented in Figs. 1(a) and 1(b), one can clearly observe that they present different spectral signatures thereby indicating that the compositions $x=0.46$ and $x=0.47$ exhibit different structural phases.[4,12] The main difference in the Raman spectra lies in the doublet mode indicated by down arrows in Fig. 1. In the rhombohedral phase, the three modes with symmetry $A_2 \oplus E$ come from the T_{2u} representation of the cubic phase. The mode belonging to the A_2 irreducible representation has no Raman activity in the point group C_{3v} of the rhombohedral phase. When the rhombohedral-monoclinic phase transition takes place, the A_2 mode transforms into the A'' modes and the E mode into the $A' \oplus A''$ modes thus giving rise the observed splitting.[12] Both A' and A'' are Raman-active modes in the monoclinic phase.

B. Monoclinic phase at high temperatures

At high temperatures (300$\leqslant T \leqslant$450 K), Noheda *et al.*[4] has proposed based on x-ray-diffraction measurements a coexistence of monoclinic and tetragonal phases. The Raman spectra in this temperature range exhibit very broad peaks. Hence it is not possible to clearly identify exclusive features of each phase thus not allowing to precisely determine the amount of each phase present in the such a phase coexistence (see Fig. 2). However, there is some experimental evidence for this coexistence in the Raman spectrum of composition

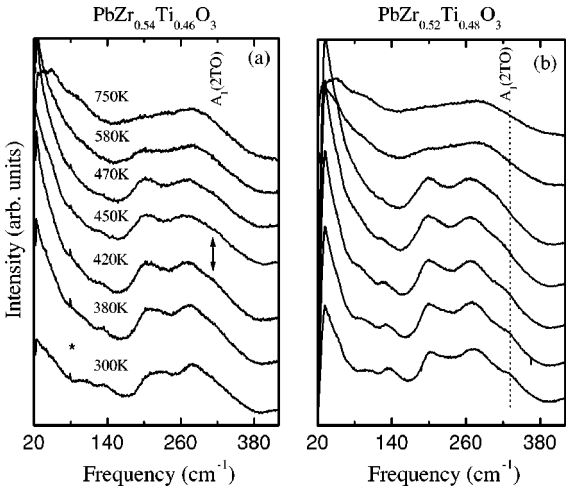

FIG. 3. Raman spectra for (a) $x=0.46$ and (b) $x=0.48$, respectively, taken at several temperatures. The narrow mode marked with an "*" stands for a plasma from the laser source.

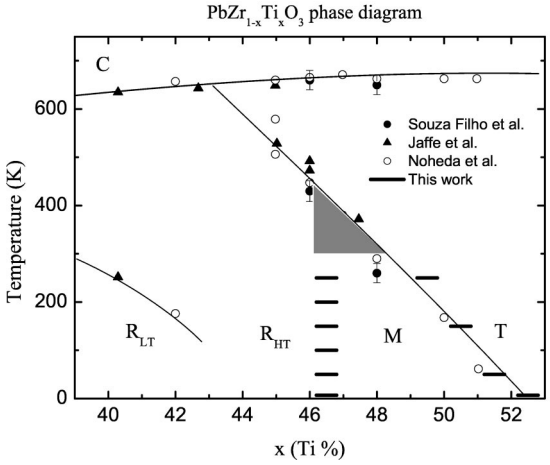

FIG. 4. Phase diagram for $PbZr_{1-x}Ti_xO_3$ around the MPB. *C*, *T*, *M*, R_{LT}, and R_{HT} stand for cubic, tetragonal, monoclinic, rhombohedral at low temperature, and rhombohedral at high temperature, respectively. The gray area denotes the region where $M+T$ phases possibly coexist. The thick horizontal bars separate two probed samples with different structural phases. The boundary between the phases is placed somewhere in the thick horizontal bars.

$x=0.47$. This result in connection with the transitions between the different phases is discussed in the following.

In Fig. 2, we show the Raman spectra for several compositions ($0.40\leqslant x\leqslant 0.60$) around the MPB taken at 300 K. The labeling in the top of the Fig. 2 denotes the mode symmetry based on the polarization studies performed in $PbTiO_3$ single crystals.[19] By analyzing the Raman spectra, from the bottom to the top, the main changes observed are, namely:

(i) From $x=0.40$ to $x=0.46$, the spectra remains exactly the same, there are no changes either in frequency or in relative intensities of the different modes. This indicates the stability of the rhombohedral phase from $x=0.40$ to $x=0.46$ at 300 K.

(ii) For $x=0.47$, the relative intensity of some modes seems to exhibit some changes, mainly the relative intensity of the bands $A_1(1\mathrm{LO})$ and $E(2\mathrm{TO})$ where the spectra for composition $x=0.47$ has intermediate properties from those of $x=0.46$ (rhombohedral) and $x=0.48$ (tetragonal). The changes in line shape for the broadband that appears between 490 and 640 cm^{-1} is also observed. These changes might be due to the coexistence of monoclinic and tetragonal phases at $x=0.47$ as reported by Noheda *et al.*[4]

(iii) For $x\geqslant 0.48$ the Raman spectra clearly exhibit new features. The bands composed of $E(1\mathrm{LO})\oplus A_1(1\mathrm{TO})$, $A_1(1\mathrm{LO})\oplus E(2\mathrm{LO})$, and $E\oplus B_1$ modes have an abrupt increase in intensity and the mode $A_1(2\mathrm{TO})$ appears.

From the above analysis we conclude that the composition $x=0.46$ [Fig. 1(a)] does not undergo any phase transition from 7 to 300 K. For $x=0.46$, a phase transition from rhombohedral to tetragonal phase is expected to occur at about 450 K.[4,18] We show in Fig. 3(a) the temperature dependence of Raman spectra for $x=0.46$. The changes in the Raman spectra can be observed in the temperature range 420–450 K. The main change is the appearance of the mode $A_1(2\mathrm{TO})$ [indicated with a double arrow in Fig. 3(a)]. We attributed the appearance of the $A_1(2\mathrm{TO})$ mode as being due to the tetragonal phase. This mode is indeed a clear signature of the tetragonal phase at high temperatures for $x\geqslant 0.48$ (see Fig. 2). Further evidences that corroborate our analysis can be obtained by analyzing the temperature dependence of the spectra obtained for composition $x=0.48$ [Fig. 3(b)]. This composition is reported to exhibit a tetragonal phase for $T\geqslant 300$ K.[4,11,15] This is actually confirmed by analyzing the Raman spectra shown in Fig. 3(b), where no evidence of a phase transition is observed from $300\leqslant T\leqslant 470$ K and the $A_1(2\mathrm{TO})$ mode is present in all spectra. By comparing the Raman spectra of composition $x=0.46$ [Fig. 3(a)] with that of composition $x=0.48$ [Fig. 3(b)] (both taken at 450 K), it is clear that the structural phase for these compositions is the same, i.e., the tetragonal phase.

For the sake of completeness, we further investigated the tetragonal-cubic phase transition for compositions $x=0.46$ and $x=0.48$ for which the spectra are shown below [second trace from the top in Figs. 3(a) and 3(b)] and above [first trace from the top in Fig. 3(a) and 3(b)] the cubic phase-transition temperature. In this case the phase transitions are clearly observed in the Raman spectra owing to the strong suppression of both the first-order Raman spectrum and the elastic scattering intensity, typical of perovskite cubic phases. The presence of Raman modes in the cubic phase implies that the structure is not a perfectly cubic perovskite but has some disorder that breaks the symmetry thereby allowing Raman activity. The phase-transition temperatures agree well with those reported earlier.[18]

Our results can be summarized in the x-T phase diagram shown in Fig. 4 along with results from other groups (open circles and squares, solid diamonds).[4,15,18] The boundary between the tetragonal and monoclinic phase is consistent with the line determined either by Jaffe *et al.*[18] or by Noheda *et al.*[4] In the present study, the boundary between the rhombohedral and monoclinic regions appears as a quasivertical line between $0.46\leqslant x\leqslant 0.47$. To precisely determine the exact position of the boundary, it would be necessary to carry

out experiments in samples with intermediate compositions between 0.46 and 0.47. It should be pointed out that Noheda *et al.*[4] reported that the composition $x=0.46$ is monoclinic, and we attributed this to a small deviation (0.5%) in concentration as a consequence of the sample preparation procedure. Finally, the verticality of the rhombohedral-monoclinic boundary suggest that the devices taking profit of the huge electromechanical coupling, peculiar of the monoclinic phase, can operate in a large temperature range (from 7 to 300 K).

IV. CONCLUSION

In summary, we have determined a quasivertical boundary separating the rhombohedral from the monoclinic phase in $PbZr_{1-x}Ti_xO_3$ system by using Raman-scattering techniques. The monoclinic-tetragonal boundary was also studied and our results agree well with x-ray-scattering results thus suggesting that our approach in analyzing the Raman-scattering data for PZT can be used to investigate these novel phase transitions in other ferroelectric systems with similar MPB that are currently the subject of intense investigations.

Note added in proof. Recently, we became aware of a work by Frantti *et al.*[20] on phase transitions by using neutron powder diffraction techniques. These authors have verified the symmetry determined by Noheda *et al.*[2] for the monoclinic phase at low temperatures. In addition, they reported that this phase coexists with the rhombohedral low-temperature (R_{LT}) phase, but the former appears dominant thereby not affecting our analysis. Another concern is related whether the phase transition is either from R_{LT} to monoclinic or from rhombohedral high temperature (R_{HT}) to monoclinic. Since these two phases have the same point group C_{3v}, our Raman analysis does apply independently of the kind of rhombohedral phase.

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