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Raman study of morphotropic phase boundary in $PbZr_{1-x}Ti_xO_3$ at low temperatures

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The Raman spectra of $PbZr_{1-x}Ti_xO_3$ ceramics with titanium concentration varying between $x=0.40$ and 0.60 were measured at 7 K. By observing the concentration-frequency dependence of the vibrational modes, we identified the boundaries among the rhombohedral, monoclinic, and tetragonal ferroelectric phases. The analysis of the spectra was made in the view of group theory analysis making possible the assignment of some modes for the monoclinic phase.

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I. INTRODUCTION

The $PbZr_{1-x}Ti_xO_3$ (PZT) solid-solution system contains several compositions that are suitable for important technological applications in the electronic field such as piezoelectric transducers, pyroelectric detectors, and nonvolatile ferroelectric memories. The main application of PZT has been as transducers that are fabricated using compositions closely related to the morphotropic phase boundary (MPB).[1] For this reason, the MPB has been widely investigated by means of both experimental techniques[2] and theoretical approaches.[3] In this region, PZT exhibits outstanding electromechanical properties that have been attributed to the phase coexistence produced by compositional fluctuations.[4] Due to this, the nature of the physical properties for compositions close to the MPB has not been well established.

The recent discovery of a new monoclinic ferroelectric phase by Noheda *et al.*[5] has shed a new light on the understanding of the dielectric and piezoelectric enhancement for compositions in the vicinity of the MPB. In fact, the monoclinic distortion was interpreted as either a condensation along one of the (110) directions of the local displacements present in the tetragonal phase,[6] or as a condensation along one of the (100) directions of the local displacements present in the rhombohedral phase.[7] This monoclinic phase exhibited by PZT at low temperatures would be the first example of a ferroelectric material with $P_x^2=P_y^2\neq P_z^2$, where $P_x^2,\ P_y^2,P_z^2\neq 0$.[5] Hence, the monoclinic structure can be considered as a derivative form from both the tetragonal and the rhombohedral phases by representing a link between them. This model provides a microscopic picture in which such a striking electromechanical response close to the MPB region[6] is associated with the monoclinic distortion. A successful explanation for the large piezoelectricity found in PZT ceramics near the MPB was recently obtained by means of first-principles calculations.[8] The piezoelectric coefficients were calculated by considering the rotation of the polarization vector in the monoclinic plane, which is an unique characteristic of the monoclinic phase when compared with other ferroelectric perovskites.[8] Also, the stability of the monoclinic phase was recently described by means of phenomenological thermodynamic studies within the framework of the Landau-Devonshire theory[9] by considering the linear coupling between the polarization and the monoclinic distortion β-90°.

In spite of all investigations of the monoclinic phase in the PZT system, Raman studies performed on this phase[9–11] were limited to few Ti concentration. However, information on the phase transitions for other PZT compositions close to the MPB is strongly desirable and appears as an interesting investigation. In this way, the purpose of this work is to investigate the extension of the monoclinic phase for compositions close to the MPB by means of Raman spectroscopy at low temperatures. A careful analysis of the data allowed us to determine the extension of the monoclinic phase based on the phonon behavior at low temperatures.

II. EXPERIMENT

Samples of $PbZr_{1-x}Ti_xO_3$ (with $0.40\leqslant x\leqslant 0.52$) 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 ceramics disks with 10 mm diameter and 5 mm thickness. Finally, the disks were sintered at a temperature of 1250 °C for 4 h and an excellent homogeneity was obtained. The sintering atmosphere was enriched in PbO vapor by using $PbZrO_3$ powder around the disks inside a covered alumina crucible in order to avoid significant volatilization of PbO.

Micro-Raman measurements were performed using a T64000 Jobin Yvon spectrometer equipped with an Olympus microsocope and a N_2-cooled charge coupled device to detect the scattered light. The spectra were excited with an argon-ion laser ($\lambda=514.5$ nm). The spectrometer slits were set to give a spectral resolution always better than 2 cm^{-1}. A Nikon 20× objective with focal distance 20 mm and numeric aperture 0.35 was used to focus the laser beam on the polished sample surface. Low-temperature measurements were performed using an Air Products closed-cycle refrigerator that provides temperatures ranging from 7 to 300 K. A

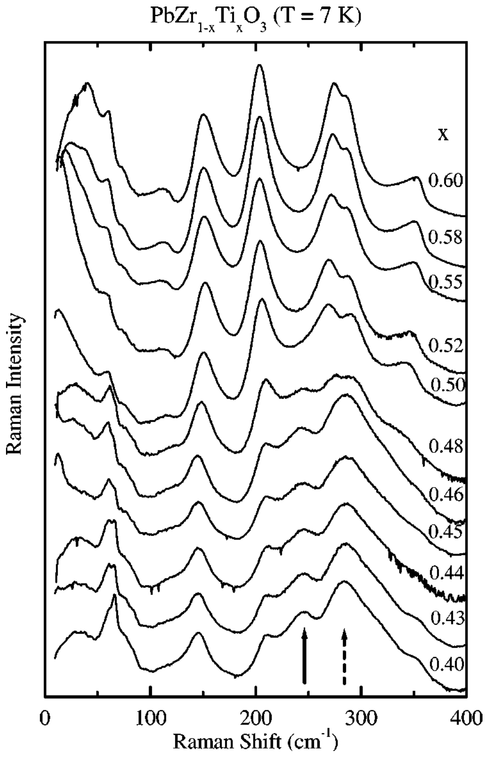


FIG. 1. Raman spectra of $PbZr_{1-x}Ti_xO_3$ ceramics recorded at 7 K. The numbers stand for the Ti concentration.

Lakeshore controller was used to control the temperature with precision of the order of ± 0.1 K.

We have made a systematic study of the laser-induced heating of the samples in order to improve the signal-to-noise ratio minimizing, and at the same time estimate the increment of the local temperature. On the other hand, the samples close to the MPB display strong elastic scattering, which leads to an unreliable determination of temperature from the Stokes/anti-Stokes ratio. A $PbZr_{0.98}Ti_{0.02}O_3$ sample, whose spectra can be easily fitted, was therefore used to calibrate the temperature. According to our observations, a laser power of 0.1 mW can be used without inducing sample overheating.

III. RESULT AND DISCUSSION

In Fig. 1, Raman spectra for several PZT compositions varying from $x=0.40$ to 0.60 are displayed. From $x=0.40$ to $x=0.46$, the spectra remain exactly the same or change slightly, not only in frequency but also in relative intensity for all modes. For this concentration range and at 7 K, a phase transition from the rhombohedral low-temperature phase (R_{LT}) to the rhombohedral high-temperature (R_{HT}) phase is expected. The boundary between the R_{LT} and R_{HT} phases has been established by Jaffe *et al.*[1] for temperatures higher than 300 K. An extension of this boundary to low temperatures was made by Amin *et al.*[14] for $x=0.40$ and more recently by Noheda *et al.*[13] for $x=0.42$.

The R_{LT} phase, whose space group is C_{3v}^6, is characterized by opposite rotations of adjacent oxygen octahedra around the [111] polar axis. Due to this fact, the unit cell of the R_{LT} phase has a volume that is twice that of the unit cell of the R_{HT} phase, whose space group is C_{3v}^5. From the diffraction point of view, this transition is detected through the appearance of very weak superlattice peaks that originate just from the doubling of the unit cell.[14] Concerning the vibrational properties, the dispersion relation for the R_{LT} phase is obtained by folding the dispersion curves of the R_{HT} phase. Thus, the observation of additional Raman modes is expected since wave vectors belonging to the zone boundary have, after the zone folding, pseudomomenta equivalent to $q=0$. For Zr-rich PZT, this phase transition was observed from Raman spectroscopy by analyzing the low-frequency modes located at about 62 and 68 cm^{-1} that are, according to El-Harrad *et al.*,[15] exclusive features of the R_{LT} and R_{HT} phases, respectively. The mode at 62 cm^{-1} is initially a zone-boundary mode that becomes a zone-center active mode due to the doubling of the unit cell. In the vicinity of the MPB, this kind of analysis is somewhat complicated due to the overlapping of the bands, which complicates the fitting procedure and, as a consequence, the identification of the phase transition. In the intermediate-frequency region ($120 \leqslant \omega \leqslant 400$ cm^{-1}, shown in Fig. 1) significant changes are not expected in the vibrational modes since they are closely related to the intrinsic modes of octahedral units such as stretching, torsion, and bending.

Upon increasing Ti concentration, the spectra for $x > 0.47$ exhibits new features. Two of them are remarkable: First, the intensity of the mode located at about 240 cm^{-1} (marked with a solid arrow) in the rhombohedral phase decreases with x, entering into the background for concentrations higher than $x=0.48$. Second, the mode at about 280 cm^{-1} (marked with a dashed arrow) for $x=0.40$ presents a splitting for $x \geqslant 0.46$, resulting in a doublet mode. These spectral changes were interpreted as due to the rhombohedral-monoclinic phase transition. Thus, the boundary between the R_{HT} and the monoclinic structure is closely related to the composition $x=0.46$. Noheda *et al.*[13] observed that PZT with $x=0.46$ has the monoclinic symmetry down to 20 K. Our results show that this composition is just in the rhombohedral-monoclinic transition region. Since the boundary between the R_{HT} and the monoclinic structure is almost vertical, we believe that a small deviation in composition can account for the observed disagreement between our results and those reported in Ref. 13.

In a first analysis, there are no clear changes in the Raman spectra from $x=0.48$ to $x=0.60$. However, the monoclinic-tetragonal phase transition is expected around $x=0.52$.[13] In order to study the effects of the phase transition in the phonon spectra we constructed the frequency versus x (ω vs x) plot where the transitions can be observed in detail. The frequencies were obtained by deconvoluting the spectra using a set of Lorentzian peak shapes. The number of peaks used to fit the spectra and their assignment were determined by means of group theory analysis that will be discussed later. In Fig. 2, we show the deconvoluted spectrum for both monoclinic $PbZr_{0.50}Ti_{0.50}O_3$ [Fig. 2(a)] and tetragonal $PbZr_{0.60}Ti_{0.40}O_3$ [Fig. 2(b)]. For the tetragonal phase we used the assignment earlier reported[10] and the observed frequen-

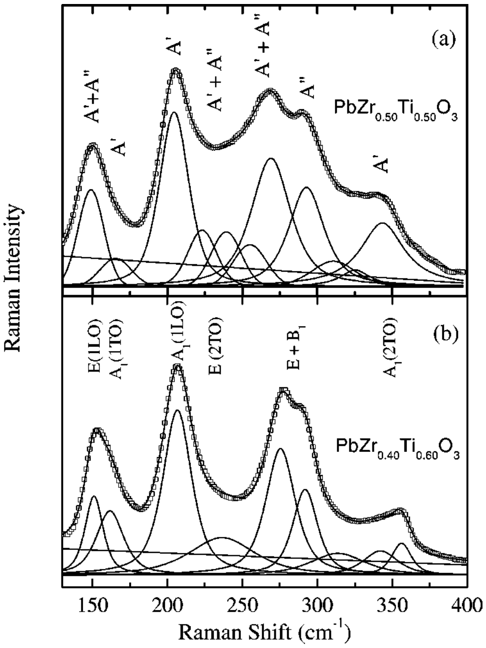


FIG. 2. Raman spectra of monoclinic $PbZr_{0.50}Ti_{0.50}O_3$ (a) and tetragonal $PbZr_{0.40}Ti_{0.60}O_3$ (b) recorded at 7 K illustrating the fitting procedure used to deconvolute them into a set of Lorentzian curves.

cies are in good agreement with those found there.

In order to understand the tetragonal-monoclinic transition, let us first discuss the mode symmetry related to tetragonal phase in $PbTiO_3$. When the cubic phase transforms into tetragonal, the T_{2u} silent mode transforms into the $B_1 \oplus E$ irreducible representation of the C_{4v} and a degeneracy breaking of this mode is expected.[12] Despite its Raman activity in C_{4v} symmetry, this mode has been called a *silent* mode because its splitting was not observed for $PbTiO_3$ at room temperature.[12] However, when Ti is replaced by Zr, the splitting is observed at low temperatures.[10] The member of the doublet with higher frequency is assigned as the B_1 mode[10] and the value $\omega_{B_1} - \omega_E$ increases in the vicinity of the MPB. This observation was made by Frantti *et al.*[10] who studied this feature in compositions with $x = 0.49$, 0.50, 0.60, 0.70, 0.80, and 0.90. Here, we can extend this study to intermediate compositions making possible a detailed description of the B_1 mode when the monoclinic-tetragonal transition takes place. To describe the phase transition in detail we have constructed, based on group-theory analysis, the ω vs x plot shown in Fig. 3. The point group of the monoclinic phase is C_s, where all the irreducible representations (A' and A'') are Raman active. The C_s group is a subgroup of both C_{3v} and C_{4v} and the correlation between them and O_h can be summarized in the scheme shown in Table I. Following that scheme, we observe that the B_1 and E modes, belonging to the tetragonal phase, transform into A'' and $A' \oplus A''$, respectively. Therefore, we have used three modes in the monoclinic phase to fit the region around 280 cm^{-1}. It is interesting to note that the highest frequency member of the doublet $A' \oplus A''$ presents the same behavior earlier reported by Frantti *et al.*[10]

We also plotted in Fig. 3, together with our results, those earlier reported[10,12] for several compositions. We can observe that the B_1 mode presents a single maximum in frequency at about $x = 0.50$. The tetragonal-monoclinic phase transition can be observed by analyzing the splitting $\Delta\omega$ ($\omega_{B_1} - \omega_E$ in the tetragonal phase and $\omega_{A''}$—the highest frequency member of $A' \oplus A''$ in the monoclinic phase). This splitting in the tetragonal phase ($x \geqslant 0.52$) decreases when the Ti content increases, while it presents the same behavior exhibited by the B_1 mode in the monoclinic region (see inset in Fig. 3). Both changes in B_1 and in $\Delta\omega$ indicate the transition between the monoclinic and the tetragonal symmetry. Noheda *et al.*[13] reported that the composition $x = 0.52$ presents a tetragonal symmetry at 20 K. Our results at 7 K indicate that this composition is in the monoclinic phase. In principle, our results do not differ from those of Ref. 13 and we believe that a small deviation in x can account for the minor disagreement between their and our results. The other possibility for such disagreement is the extension of the

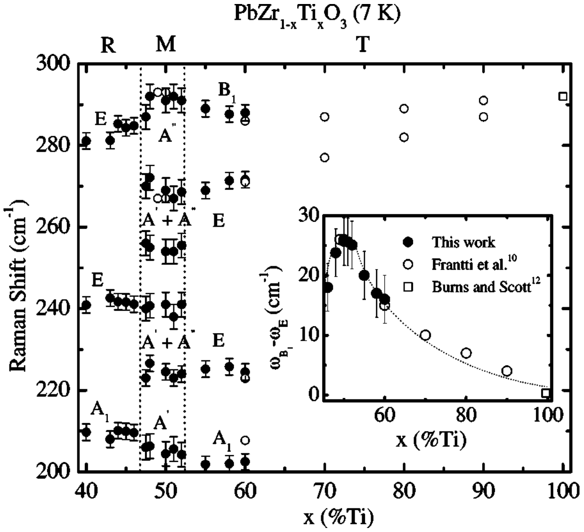
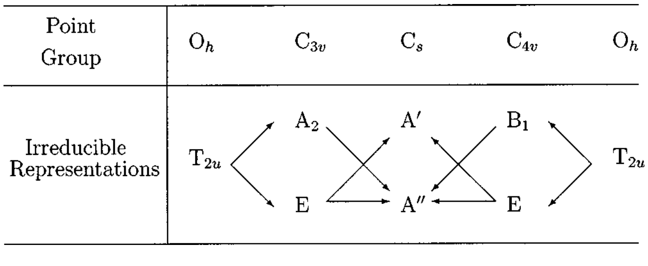


FIG. 3. Variation of the frequency of some of the Raman modes as a function of Ti concentration recorded at 7 K. The vertical dotted lines represent the transitions among the rhombohedral (R), monoclinic (M), and tetragonal (T) phases. The labels stand for the symmetry modes of the different phases. The inset depicts the splitting ($B_1 - E$) in the tetragonal phase and A''—the highest frequency member of $A' \oplus A''$ in the monoclinic phase. The dotted lines through the points are a guide to the eye. The open circles, open squares, and solid circles are data from Refs. 10, 12, and the present work, respectively.

TABLE I. Correlation table for some modes belonging to the monoclinic (C_s), tetragonal (C_{4v}), and rhombohedral (C_{3v}) phases originated from the in cubic (O_h) phase.



monoclinic-tetragonal boundary. Such a boundary line presents, in the T vs x plot, a negative slope that leads to an increment in the concentration range at which the monoclinic phase is stable at lower temperatures.

A similar analysis based on group theory can be performed to describe the R_{HT}-monoclinic phase transition observed around $x=0.46$. When the cubic (O_h) phase transforms into the rhombohedral C_{3v} phase, the T_{2u} silent mode transforms into the $A_2 \oplus E$ irreducible representation, A_2 having no Raman activity. For this reason, there is a single peak at about 280 cm^{-1} for compositions in the rhombohedral phase. By observing the correlation between C_{3v} and C_s depicted in Table I, we can observe the splitting of this mode into three new modes, i.e., $A' \oplus 2A''$, as also found in the tetragonal-monoclinic transition.

Let us now try to discuss the monoclinic phase based on the assumption of distortion of the unit cell by strain. The polar axis in the monoclinic phase has a particular feature if it is compared with that of the tetragonal and rhombohedral phase. In fact, it cannot be determined only by symmetry and can be along any direction within the monoclinic plane. This consideration was introduced in the first-principles calculations made by Bellaiche *et al.*[8] where the striking piezoelectric properties for the monoclinic compositions were successfully obtained. To the best of our knowledge, there is no systematic theoretical study concerned with what happens with the optical phonons when the PZT transitions occur. In fact, there are only two studies that report the calculation of vibrational frequency for $\mathrm{PbTiO_3}$. Freire and Katiyar[17] carried out such a calculation by adjusting the parameters of a rigid-ion model, while Garcia and Vanderbilt[16] performed it by using first-principles calculations. Following the results of these latter authors, the tetragonal phase could change either to an orthorhombic or to a monoclinic phase by means of the linear coupling between strain and atomic displacements.

We recall this result because the tetragonal phase in PZT is very similar to that in $\mathrm{PbTiO_3}$ and the monoclinic-tetragonal phase transition is marked by changes in the B_1 symmetry mode. This is very interesting because this mode involves only oxygen motion ($O_{1z}-O_{2z}$) where both oxygen atoms move in opposite directions leading to the tetragonal symmetry breaking. However, this mode appears to be dependent of the Zr/Ti ratio as demonstrated by Frantti *et al.*[10] whose results are partially reproduced in Fig. 3 (open circles). When the temperature is kept constant, the variable responsible for the transition is the Zr/Ti ratio. It is well known that the tetragonal strain, c_t/a_t, decreases when the Zr content increases. This decreasing is mainly due to a_t increasing since the observed c_t decreasing is very small when x varies from 0.52 to 1.0.[13] Taking into account this fact, the unit cell can only be distorted by an in-plane strain. The strain can transform according to the irreducible representation of the C_{4v}^1 space group, where the E distortion leads to a monoclinic symmetry and the B_1 and B_2 ones to an orthorhombic symmetry with axes parallel (B_1) or rotated about 45°(B_2), respectively, with respect to the tetragonal base. In this way, a B_2 distortion could be the transition mechanism since the actual monoclinic phase is characterized by a rotation of 45° in tetragonal plane. Also, the monoclinic phase can be seen as a pseudo-orthorhombic one due to the very small monoclinic angle $90° - \beta$,[13] whose origin could be in the delicate balance between the temperature- and concentration-induced strain. It should be pointed out that the lattice dynamical study made by Garcia and Vanderbilt[16] is limited to the edge of the PZT phase diagram where the doubling of the unit cell was not considered. It is clear that it cannot account for the PZT phase transition because Zr/Ti ratio was not considered. Finally, first-principles calculations of optical phonons as a function of concentration considering the effects of the Zr/Ti ratio would provide a better understanding of the phonon-related phase transitions in PZT as well as in other perovskite systems with a similar MPB.

IV. CONCLUSIONS

In summary, the behavior of the optical modes for $\mathrm{PbZr_{1-x}Ti_xO_3}$ with x varying from 0.40 to 0.60 are reported and discussed. The observed changes at 7 K have been associated with the previously reported phase transition among rhombohedral, monoclinic, and tetragonal phases.[13,10] Both transitions are studied within the framework of group theory where some optical phonons in the monoclinic phase have been assigned. The behavior of the B_1 mode, which has an unusual concentration dependence in the vicinity of tetragonal-monoclinic phase transition,[10] was pointed out. Further studies in PZT single crystals within the monoclinic phase will be needed in order to assign each member of the $A' \oplus A''$ doublet.

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