High-pressure Raman study of two ferroelectric crystals closely related to PbTiO₃

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We report high-pressure Raman measurements of the zone-center phonons in two ferroelectric crystals that closely resemble the ABO_3 perovskite crystal $PbTiO_3$. These crystals are $(Pb_{0.22}Ba_{0.78})TiO_3$, i.e., Ba replacing Pb on the A site, and $Pb(Ti_{0.81}Sn_{0.19})O_3$, i.e., Sn replacing Ti on the B site. In both cases, at room temperature, we follow the modes and determine P_c, the transition pressure from the ferroelectric tetragonal phase to the cubic phase, to be 4.3 and 9.0 GPa, respectively. By observing the coalescence to the same frequency of the appropriate high-energy $A_1(TO)+E(TO)$ pairs of phonons, we determine the second-order character of the phase transitions at P_c. The tendency towards a second-order phase transition seems to be the rule at P_c as long as one makes the measurements at a temperature well below T_c; this is in agreement with theory. Thus, these systems exhibit tricritical points in the (P,T) phase diagram. The soft-$E(TO)$-phonon frequency (ω_0) and damping constant (γ) can be measured to pressures reasonably close to P_c while the mode remains underdamped. These results are discussed in terms of a frequency-independent damping constant for the behavior of ω_0 and γ near P_c. In the $(Pb,Ba)TiO_3$ crystal, the hydrostatic pressure increases the intensity of the soft $A_1(TO)$ mode making it observable. This seems to happen in general in the perovskites. In the $Pb(Ti,Sn)O_3$ crystal we observe the coupling of the soft $E(TO)$ mode with an extra mode at 59 cm^{-1}; this also has been studied as a function of temperature.

I. INTRODUCTION

It is becoming clear that PbTiO₃, from a lattice-dynamical point of view,[1] behaves as a classic ferroelectric material. In the high-temperature paraelectric phase it is cubic (space group $Pm3m$-O_h^1) with the perovskite crystal structure. Below the phase-transition temperature, $T_c = 492\,°C$, it is tetragonal (space group $P4mm$-C_{4v}^1) with the Ti^{4+} ion shifted against its surrounding oxygen octahedra.[2]

Some time ago we reported[3] the temperature dependence of the ($k \approx 0$) Raman spectra of the phonons in PbTiO₃. The measurements were made at atmospheric pressure as a function of temperature T up to T_c. More recently, we have reported[4] the Raman spectra as a function of pressure P at room temperature. By combining several experimental techniques we successfully measured the Raman spectra to above P_c, the transition pressure, to the paraelectric phase.

In this paper we discuss the extension of these earlier results to two mixed-system single crystals closely related to PbTiO₃ and BaTiO₃. These are $(Pb_{0.22}Ba_{0.78})TiO_3$ and $Pb(Ti_{0.81}Sn_{0.19})O_3$. Both are solid solutions having the perovskite crystal structure, but in the first crystal the replacement is on the A site while in the latter it is on the B site. We have measured the pressure dependence of the phonon modes in both of these crystals, and the composi-

tion dependence of the modes in the Pb(Ti,Sn)O₃ system. The temperature dependence of the modes in the (Pb,Ba)TiO₃ sample was reported previously.[5]

II. EXPERIMENTAL DETAILS

The single crystals were grown from a flux of PbO-B₂O₃ as described previously.[5,6] The composition was determined by comparing the ferroelastic transition temperatures of the crystals to those of ceramics of known composition, and by checking these results with the energies of the observed Raman modes.[5,6] The values obtained from the two methods were in close agreement.

The high-pressure measurements were performed on small polished pieces of the crystal (30 μm thick) in a gasketed diamond-anvil cell as described previously.[4] The crystals reported on here were not of as good quality as the PbTiO₃ already discussed.[3,4] This is to be expected since these crystals are mixed systems, small, and not very "nice" looking. Thus, inhomogeneities are to be expected. Experimentally, this shows up as broadened phase transitions and more laser elastic scattering. The latter effect translates into our inability to measure close to the laser line; the former effect, which has been more of a hindrance in the high-pressure work, translates into weak signals and greater difficulty in the determination of P_c for these materials than for PbTiO₃.

III. MODE CLASSIFICATION

In the high-temperature phase the 12 optic modes transform as the $3T_{1u}+T_{2u}$ irreducible representations of the $m3m\text{-}O_h$ point group. The T_{2u} mode is neither infrared nor Raman active, so it is called a silent mode. The T_{1u} modes are infrared active and thus are labeled T_{1u} (TO) and T_{1u} (LO), depending whether the wave vector $\vec{k}$ is perpendicular or parallel to the polarization (mechanical separation of charge) of the mode.

In the ferroelectric phase, each T_{1u} mode splits into two modes transforming as the A_1+E irreducible representations of the $4mm\text{-}C_{4v}$ point group. These modes are infrared and Raman active and thus can have a polarization transverse to the direction of propagation (TO mode) as well as polarization along the direction of propagation (LO mode). In order to label these various modes we use a straightforward scheme,[3,4]

$$A_1(3\text{TO})\quad A_1(3\text{LO})\quad E(3\text{TO})\quad E(3\text{LO})$$
$$A_1(2\text{TO})\quad A_1(2\text{LO})\quad E(2\text{TO})\quad E(2\text{LO})$$
$$A_1(1\text{TO})\quad A_1(1\text{LO})\quad E(1\text{TO})\quad E(1\text{LO})\ ,$$

where the numbers 1, 2, and 3 are used merely as a method for labeling these modes. For each series, 1 refers to the lowest-frequency phonon and 3 refers to the highest-frequency phonon. The very-lowest-frequency modes are $E(1\text{TO})$ and $A_1(1\text{TO})$, which are the "soft modes" in that they tend to zero frequency as T_c or P_c is approached from below. The $A_1(1\text{TO})+E(1\text{TO})$ modes "connect" to the $T_{1u}(1\text{TO})$ modes in the cubic phase, as do the corresponding modes labeled 2 and 3. In fact, for a second-order phase transition these connected modes should have the same frequencies at the phase transition.

In the tetragonal phase the silent T_{2u} mode, in principle, splits and transforms as B_1+E. In practice, the splitting is so small that it is not observed in the Raman spectra, so we still label it the silent mode—even though it is observable easily in the Raman spectra. Note that in either the cubic or tetragonal phase, for any one-crystal orientation, there are only 12 optic modes.

IV. RESULTS FOR $(\text{Pb}_{0.22}\text{Ba}_{0.78})\text{TiO}_3$

A. High-frequency modes

Figure 1(a) shows typical Raman spectra from the sample in the high-pressure cell. The effect of the scattering of the unshifted laser light can be seen clearly (the broad "wing"). This scattering is larger than in our high-pressure work on pure PbTiO$_3$. In Fig. 1(b) we plot the phonon frequencies obtained from the data. (The details associated with soft modes are discussed below.)

The broad bands at ≈ 110 and ≈ 170 cm^{-1} that can be clearly seen in Fig. 1(a) are of unknown origin. In studies of the complete system, $(\text{Pb}_{1-x}\text{Ba}_x)\text{TiO}_3$, mostly with ceramics,[5] we have seen bands in this region. It is clear that these are not the $A_1(1\text{TO})$ mode, which is discussed below. Possibly they are observed due to a breakdown in the selection rules and arise from combinations phonons with large densities of states in the Brillouin zone.

B. P_c determination

P_c was obtained as follows. Note, in Fig. 1(a), the sharp, "silent" mode at 300 cm^{-1}. Since the position of this mode is remarkably independent of the concentration of Ba to Pb,[5] one expects that it should be sharp, as observed. We determined P_c (=4.3±0.5 GPa) by the disappearance of this mode. The error in the value comes from the observation that the mode does not disappear as sharply as in PbTiO$_3$ and because fewer pressure values were used. Note in Fig. 1(b) that in the same pressure range the appropriate $A_1(2\text{TO})+E(2\text{TO})$ pair of modes coalesce to approximately the same frequency; in the cubic phase this pair of modes originates from the $T_{1u}(2\text{TO})$ mode.

For pure PbTiO$_3$ one finds that $P_c=12.1$ GPa (Ref. 4) and for pure BaTiO$_3$ one finds $P_c=1.9$ GPa (Ref. 7). Thus, for our crystal composition a linear extrapolation yields 4.1 GPa; this is in good agreement with our value, $P_c=4.3±0.5$ GPa.

From the high-pressure Raman measurements[4] for PbTiO$_3$, the second-order nature of the phase transition at P_c is rather clear. From the coalescence of the appropriate pair of modes, as noted above, this crystal appears to have a second-order phase transition. Also, for the other end member of this series, namely BaTiO$_3$, dielectric data indicate that the phase transition at P_c is nearly second order.[7] Then a second-order phase transition is expected throughout most of the composition range of $(\text{Pb}_{1-x}\text{Ba}_x)\text{TiO}_3$ and there is a tricritical point in the (P,T) phase diagram. Such a point has been found experimentally[8] in SbSI and KH$_2$PO$_4$.

C. Soft-mode frequencies

The lowest-frequency, "soft" mode is of $E(1\text{TO})$ character and can be seen in Fig. 1(a). As the pressure is increased, its frequency decreases. In PbTiO$_3$ at $P=0$ the other member of this pair of soft modes, the $A_1(1\text{TO})$ mode, could not be observed directly.[3] However, its frequency was determined from quasimode spectra. For reasons that we do not understand, in PbTiO$_3$ at high pressures the $A_1(1\text{TO})$ becomes observable and we have been able to follow its pressure dependence.[4] In our $(\text{Pb}_{0.22}\text{Ba}_{0.78})\text{TiO}_3$ crystal we can see the $A_1(1\text{TO})$ mode at pressures between 2 and 3 GPa, but see hints of it at lower and higher pressures. Some of these data are shown in Fig. 1(c).

The damping γ of the $E(1\text{TO})$ and $A_1(1\text{TO})$ modes is comparable to the frequencies ω_0. Thus, in order to obtain these quantities properly we fit the data to the usual damped harmonic-oscillator function,

$$I(\omega)=[n(\omega)+1]\sum_{i=1}^{2}\frac{F\omega_{0i}^2(\gamma\omega)}{(\omega_{0i}^2-\omega^2)^2+\gamma_i^2\omega^2}\ ,\qquad(1)$$

where I is the experimentally observed intensity and $n(\omega)$ is the Bose-Einstein function; F, ω_0, and γ are the scale factor, the soft-mode frequency, and its damping constant for the $E(1\text{TO})$ and $A_1(1\text{TO})$ soft modes, respectively. Figure 1(c) shows examples of a few of the fits when the weak $A_1(1\text{TO})$ is seen clearly. The fitting is fairly insensi-
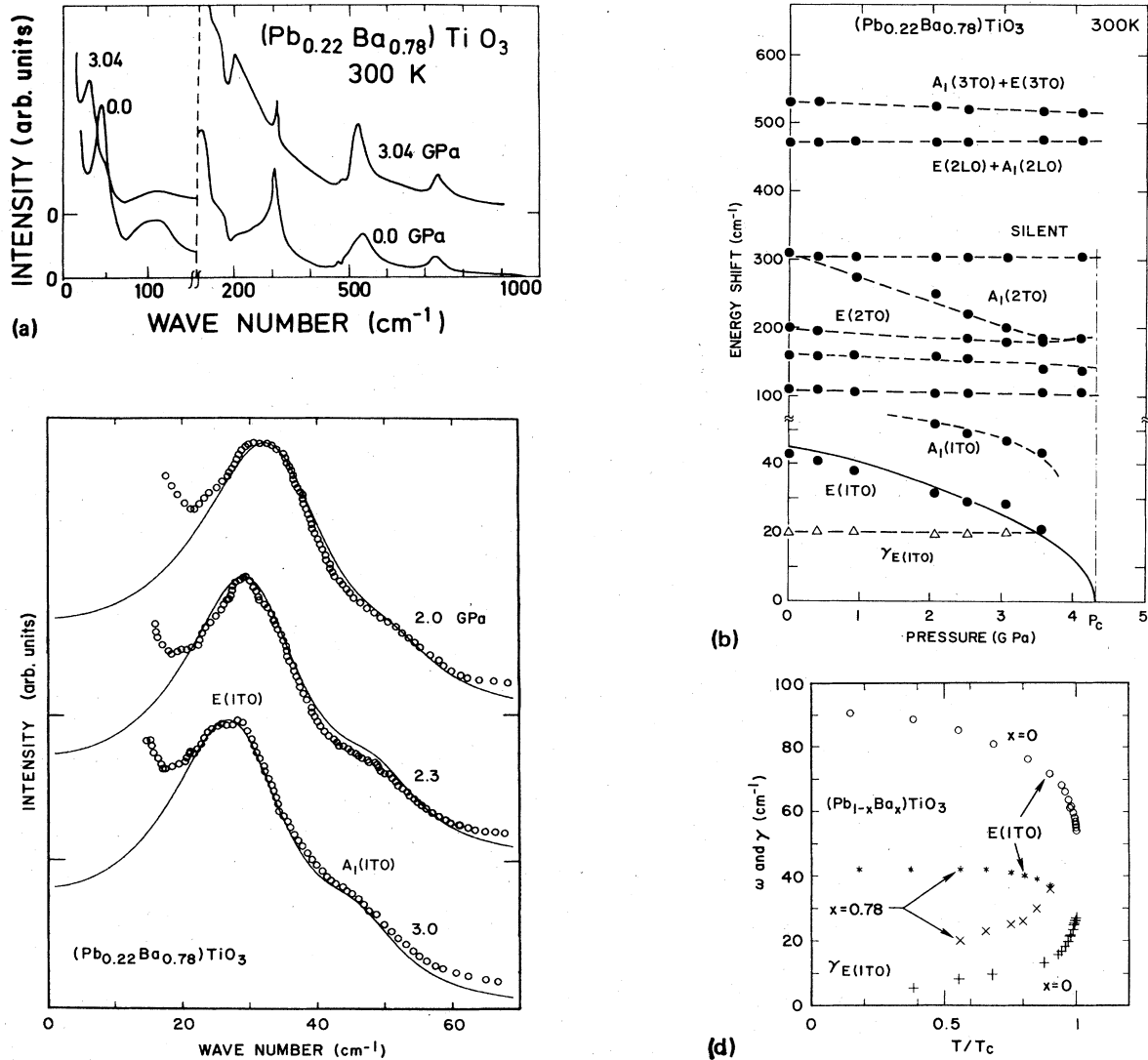
FIG. 1. Various Raman results from the crystal $(Pb_{0.22}Ba_{0.78})TiO_3$. (a) Typical Raman spectra in the high-pressure cell. (b) Phonon energies vs pressure. (c) Typical fits of the soft $E(1TO)$ mode. (d) Temperature dependence (on a reduced scale) of the frequency and damping of the soft $E(1TO)$ mode; the corresponding results for $PbTiO_3$ also are shown.

tive to the parameters for the $A_1(1TO)$ because it is so weak. Thus, in Fig. 1(b) we plot ω_0 and γ of the strong $E(1TO)$ soft mode, but only ω_0 of the weak $A_1(1TO)$, γ of this latter mode being much less certain. Examples of the data and fits are given in Fig. 1(c). As can be seen, the fits are good, with a constant (frequency-independent) value for γ. The solid line in Fig. 1(b) is a fit to the soft-mode $E(1TO)$ frequency of the form

$$\omega_0^2 = \Omega_0^2 \left[1 - \frac{P}{P_c} \right] , \qquad (2)$$

where $P_c = 4.3$ GPa and $\Omega_0 = 46.0$ cm^{-1}. Of course, this form is chosen since we believe that the phase transition is a second-order one, and hence should have Curie-Weiss behavior near P_c. As can be seen, the agreement with the experimental results is reasonable.

Figure 1(d) shows the temperature dependence of the

same $E(1TO)$ mode (at $P=0$) measured up to T_c; the data are from Ref. 5. For reference, the results for pure $PbTiO_3$ also are plotted. At zero pressure, as a function of temperature, the phase transition is first order. Thus, the soft $E(1TO)$ mode never really softens very much. At room temperature, as a function of pressure, the phase transition at P_c appears to be second order. As discussed above, this is why we have used Eq. (2) to fit the soft-mode data as shown in Fig. 1(b). Thus, because of the different order of the phase transitions as a function of pressure and temperature, the soft-mode behavior upon approaching the phase transition is quite different. This affects our understanding of the damping behavior discussed below.

D. Soft-mode damping

The soft-mode damping in ferroelectric perovskite crystals is an intriguing, often discussed, and not understood problem.

PbTiO$_3$. In PbTiO$_3$, as a function of temperature, the soft E(1TO) mode remains underdamped[3] right up to the first-order phase transition at $T_c = 492$ °C, i.e., $\gamma/\omega_0 < 1$, and it never exceeds $\frac{1}{2}$. [This is apparently true for the soft A_1(1TO) mode as well, although it was not measured directly, but via the quasimode spectra.[3]] The temperature dependence of γ for PbTiO$_3$ is shown in Fig. 1(d). It is important to realize that, especially near T_c, the soft mode is very broad, extending over 100 cm^{-1}, yet the entire detectable Raman response can be fitted extremely well by a single, frequency-independent γ.[3,9]

In PbTiO$_3$, as a function of pressure, a slightly different effect is seen.[4] The phase transition is second order, so ω_0 goes to zero and, at least near P_c, one must have $\gamma/\omega_0 \gg 1$, even if γ is approximately independent of pressure. However, the experiments show that while γ depends approximately linearly on temperature or pressure well away from T_c or P_c, near the phase transition singular behavior is observed.[3,4] For example, see Fig. 1(d), where the temperature behavior is shown.

In addition to the above approach to try to detect a frequency dependence of γ, i.e., $\gamma(\omega)$, by fitting the E(1TO) mode at one temperature or one pressure, we can take another point of view. We can consider varying the pressure to be equivalent to tuning the soft E(1TO) mode in PbTiO$_3$ from 88 cm^{-1} ($P = 0$) to 0 cm^{-1} ($P = P_c$) and observe the frequency dependence of the damping at room temperature. We have examined this[10] and find that $\gamma(\omega)$ is independent of ω from 88 to ≈ 30 cm^{-1}. These results are in disagreement with some earlier polariton measurements.[11] We have discussed why the polariton results may be in error.[10]

BaTiO$_3$. In BaTiO$_3$ the situation is much less clear. Both the soft A_1(1TO) and the soft E(1TO) modes can be observed. However, the A_1(1TO) mode, which has $\gamma/\omega_0 \ll 1$, is very weak and tends to be obscured by a much stronger, higher-energy feature. In order to see it clearly, even at room temperature, forward Raman (polariton) scattering must be used.[12] Doing this as a function of temperature has not revealed any anomalies in the damping of this A_1(1TO) mode.[13] Since this mode is so weak, its pressure dependence has not yet been observed.

In BaTiO$_3$ the situation for the E(1TO) mode is the opposite. The mode is very intense, however, that is, $\gamma/\omega_0 \gg 1$; this causes very small differences in experimental results to yield different values for γ and ω_0. The latest results from two different groups agree[13(b),14] and show that this mode probably increases in frequency as T_c is approached (rather than decreases) and that γ increases as T_c is approached. High-pressure studies of this mode have not been made because it is very difficult to get very close to the laser line in a high-pressure cell.

A proposal to explain the very large value of γ found for the E(1TO) mode in BaTiO$_3$ has been put forth.[11] These authors propose, in light of the polariton results[11] in PbTiO$_3$, that when $\omega_0 \approx 30$–50 cm^{-1} in a perovskite crystal, γ will be very large. This would be caused by a resonance with zone-boundary phonon-difference frequencies. Above and previously[10] we have already discussed our disagreement with this idea. Our point of view also is supported by recent hyper-Raman work.[15] The authors of

Ref. 15 find that at their highest temperature studied, 430 °C, $\omega_0 = 92$ cm^{-1}, yet the damping is still very large ($\gamma = 247$ cm^{-1}). Thus, the very large damping found in BaTiO$_3$ for the E(1TO) soft mode seems to be independent of the frequency of the mode. Instead, it seems to be intrinsic to BaTiO$_3$ itself. As we shall see, the results in Pb$_{0.22}$Ba$_{0.78}$)TiO$_3$ support this conclusion.

(Pb$_{0.22}$Ba$_{0.78}$)TiO$_3$. Because the A_1(1TO) mode is very weak, resulting in large uncertainties in its γ and ω_0 values, we discuss principally the E(1TO) results. For PbTiO$_3$ [Fig. 1(d)], γ is approximately linear with temperature up to a reduced temperature of $T/T_c \approx 0.9$. For our crystal this is true to $T/T_c \approx 0.8$. Thus the results are consistent with each other.

For PbTiO$_3$, measurements of γ as a function of pressure show that it is independent of pressure up to[4] $P/P_c \approx 0.8$. It is only above this value that a very steep rise in the pressure dependence of γ is observed. As can be seen in Fig. 1(b), for our crystal we obtain a pressure-independent γ but only up to 3 GPa. At higher pressures, although we can see this line as a shoulder, we cannot fit the data with any certainty. Unfortunately, 3 GPa only corresponds to $P/P_c \approx 0.69$. Thus, the fact that we do not see any singular behavior in γ is to be expected. It should occur closer to P_c.

Also note from the pressure data for the soft mode in Fig. 1(b) that while the frequency sweeps from 42 to 28 cm^{-1}, γ is approximately constant. Just like our pressure-dependent data in PbTiO$_3$, this result is in sharp disagreement with the proposed explanation[11] for the broad line in BaTiO$_3$.

V. RESULTS FOR Pb(Ti$_{0.81}$Sn$_{0.19}$)O$_3$

The end members of the solid solution under discussion in Sec. IV are ferroelectric. For the crystal discussed here this is not the case; only PbTiO$_3$ is ferroelectric.
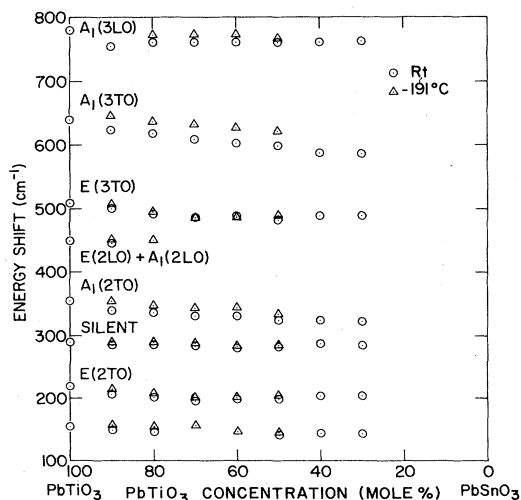

FIG. 2. High-frequency modes measured from ceramic samples in the system Pb(Ti$_{1-x}$Sn$_x$)O$_3$. The powder Raman technique was used (Ref. 16) to determine the values.

A. High-frequency modes

In order to positively identify the modes of our crystal, the safest method is to make ceramics of the $Pb(Ti_{1-x}Sn_x)O_3$ system. Using the powder Raman technique[16,5] the modes can be identified rather easily, especially if the end member ($PbTiO_3$ in this case) is known. Figure 2 shows the results for the high-frequency modes with the appropriate labeling.

Using the above results as a guide, it is rather easy to label the features observed in our crystal. Some typical

Raman spectra in the high-pressure cell are shown in Fig. 3(a). The positions of these modes are shown in Fig. 3(b). As shown in Fig. 3(a), the silent mode is strong and sharp; it serves as an excellent fiducial marker for high-pressure studies.

Also interesting to note is the $A_1(2TO)$ mode. At low pressures it is at higher energies than the silent mode, appearing somewhat as a shoulder in Fig. 3(a). With increasing pressure it clearly crosses the silent mode, and at higher pressures it appears below the silent mode as indicated in Fig. 3(b). Also notice that it approaches the $E(2TO)$ mode.
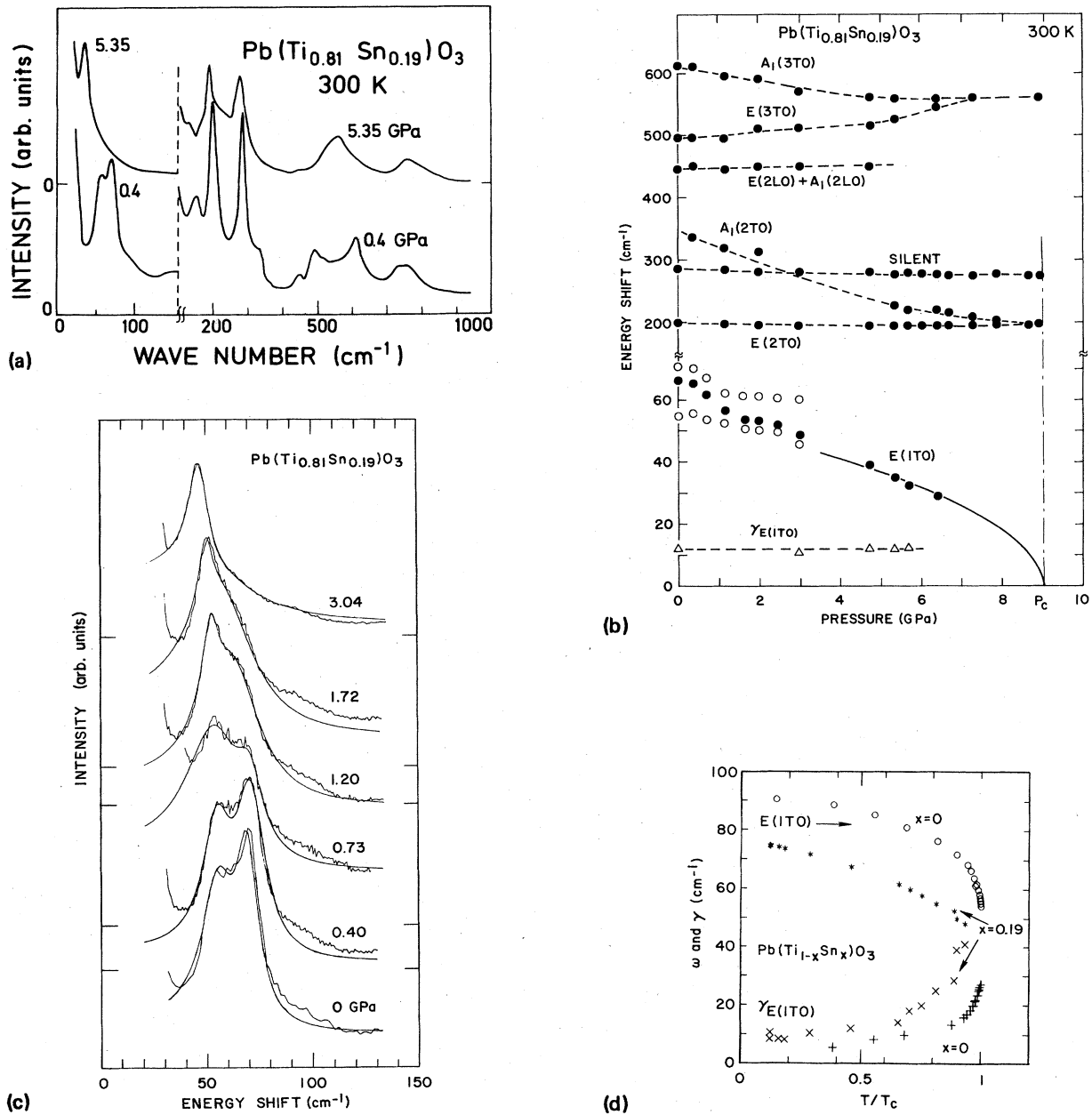

FIG. 3. Raman results for the crystal $Pb(Ti_{0.8}Sn_{0.19})O_3$. (a) Typical Raman spectra in the high-pressure cell. (b) Phonon energies vs pressure. (c) Typical fits of the data in the low-frequency region showing the soft mode and the extra mode. (d) Frequency and damping of the soft mode (and that of $PbTiO_3$) on a reduced temperature scale.

B. P_c determination

P_c was determined in the same manner as above. From the disappearance of the silent mode we determined that $P_c = 9.0 \pm 0.8$ GPa. The error is due to the fact that the mode does not disappear as sharply with pressure as was observed[4] in PbTiO$_3$. Further, as an independent determination of P_c we note that the $A_1(2TO) + E(2TO)$ pair of modes coalesce at 9.0 GPa (and also disappear) as does the $A_1(3TO) + E(3TO)$ pair. These pairs of modes arise from the cubic phase $T_{1u}(2TO)$ and $T_{1u}(3TO)$ modes.

Thus, besides determining $P_c = 9.0$ GPa for this crystal, we determine that the phase transition is second order.

C. Soft-mode frequencies

As can be seen in Fig. 3(a), at low pressures the soft mode is a doublet. However, this is not the soft $E(1TO)$ and soft $A_1(1TO)$. In a manner similar to that described in Sec. IV, we have looked for the $A_1(1TO)$ mode with increasing pressure and do not observe it. Instead, the doublet is the soft $E(1TO)$ mode and an impurity mode which is not seen in pure crystals, such as PbTiO$_3$ and BaTiO$_3$, but tends to be seen in mixed crystals. The impurity mode gets its strength from the soft $E(1TO)$ mode, and since they transform as the same irreducible representation of the $4mm$-C_{4v} point group they do not cross (as a function of temperature or pressure). This coupled-mode behavior was also found in the solid solutions Pb(Ti, Zr)O$_3$ and (Pb,La)TiO$_3$.[17] It was proposed that the additional feature might originate from zone-boundary acoustical phonons which become Raman active due to the breakdown of the translational symmetry in the solid solution.[17]

At $P = 0$, at low temperatures, the soft $E(1TO)$ mode is observed at 78 cm^{-1} and the impurity mode is observed at 55 cm^{-1}, and close to $T_c = 370\,°$C the soft mode is considerably below the impurity mode. The temperature dependence of this "no-crossing" has been studied in detail.[6]

At room temperature, as a function of pressure, we see the same no-crossing of the soft $E(1TO)$ mode and the impurity mode. In order to separate the soft-mode behavior from the "extra" mode, we have used the same formalism and experimental approach as before.[6] Figure 3(c) shows typical experimental results at various pressures. In Fig. 3(b) the solid circles are the results for the "decoupled" soft $E(1TO)$ mode. The decoupled impurity mode, not shown, is at 59 cm^{-1} and approximately independent of pressure up to 3 GPa, at which pressure its intensity is very weak. Above 3 GPa only the soft $E(1TO)$ is visible [see Fig. 3(c)]. Consequently, the single-phonon response function, Eq. (1), was used to determine the frequency and damping constant. These results are also plotted in Fig. 3(b).

The pressure dependence of the soft-$E(1TO)$-mode frequency was fitted with Eq. (2). The results are $P_c = 9.0$ GPa (as above) and $\Omega_0 = 55$ cm^{-1}. The solid line in Fig. 3(b) is this fit.

D. Soft-mode damping

In Fig. 3(d) we show the temperature dependence of γ on a reduced scale.[6] Again notice that γ is weakly dependent on temperature until ω gets close to T_c. The results for PbTiO$_3$ are included for comparison, as in Fig. 1(d).

In Fig. 3(b) the pressure dependence of γ is shown over the range that we can measure it. Again, unlike PbTiO$_3$, on a reduced scale, we only can obtain data up to $P/P_c \approx 0.67$. This value is not large enough to begin to see the strongly nonlinear behavior observed[4,10] in PbTiO$_3$. On the other hand, again we notice that while the $E(1TO)$-mode frequency sweeps over a wide spectral region, γ is independent of frequency. This was also discussed in Sec. IV D.

VI. CONCLUSIONS

High-frequency modes. The high-frequency modes, whether measured as a function of pressure (Figs. 1 and 3), composition (Fig. 2), or temperature, behave in a straightforward, continuous manner. The silent mode is relatively sharp and serves as a convenient feature to determine P_c and T_c, as do several pairs of $A_1(TO) + E(TO)$ modes which emanate from the same $T_{1u}(TO)$ cubic mode.

P_c. P_c in both cases was determined by the disappearance of the silent mode. This value was found to be in good agreement with the coalescence of the frequencies of the strong $E(2TO) + A_1(2TO)$ pair of modes. Thus, as in[4] PbTiO$_3$, we conclude that at P_c we have a second-order phase transition. Although we cannot obtain ω_0 and γ of the soft mode near P_c, we can see it as a shoulder on the "central" laser scattering to very close to P_c.

Our experiments show that these types of materials under high pressures have a second-order phase transition at P_c. Thus, in the (P,T) phase diagram there is a tricritical point.[9,8] This fact might be useful in future studies. This second-order phase transition is in agreement with Devonshire's calculations.[18]

Extra modes above P_c. In PbTiO$_3$ above T_c and P_c (Refs. 3 and 4, respectively) we see essentially no Raman spectrum in agreement with the selection rules. However, in BaTiO$_3$, above T_c or P_c, two broad bands are observed. These persist to very high temperatures[19] and pressures.[20] In our crystals we also observe these bands, similar to those in BaTiO$_3$, above the cubic phase. In (Pb$_{0.22}$Ba$_{0.78}$)TiO$_3$ we still see them up to $P = 11.5$ GPa. However, we have no clear idea as to the origin of these bands observed in the cubic phase.

Soft-mode frequencies. As a function of pressure, the soft-mode frequencies fit the expected pressure law, Eq. (2), reasonably well. However, we do not have values of ω_0 close enough to P_c to test this result in a real way.

In PbTiO$_3$ at pressures above atmospheric we experimentally observed the soft weak $A_1(1TO)$ mode as well as the intense $E(1TO)$ mode.[4] The $A_1(1TO)$ mode is also weak in BaTiO$_3$ and only can be observed clearly using the polariton technique.[12,13] In our (Pb,Ba)TiO$_3$ crystal the $A_1(1TO)$ mode can be seen clearly at intermediate pressures, but it is weak. Neither the relatively large difference in intensity between these two soft modes nor the pressure dependence of the intensity is understood.

In the Pb(Ti$_{0.81}$Sn$_{0.19}$)O$_3$ crystal we see an "extra" mode at ≈ 59 cm^{-1}. Just as with temperature,[6] as a function of

pressure we can tune the soft $E(1TO)$ mode through this frequency region and observe the coupled modes (since they both transform as the same E irreducible representation of the $4mm$-C_{4v} point group). The extra mode appears to have little, if any, temperature and pressure dependence, and the origin of this mode is not known. If it existed, this extra mode would not be observed in the (Pb,Ba)TiO$_3$ crystal studied by us because at $P=0$ the $E(1TO)$-mode frequency is too low [Fig. 1(b)].

Soft-mode damping. Previously,[3,4] we have shown experimentally that the damping constant γ is only weakly dependent on temperature or pressure, except near T_c or P_c. (Also, at a given T or P the damping constant is independent of frequency[3,4,9] even though the Raman line can be ≈ 100 cm^{-1} wide.) With our present crystals, as a function of pressure the phase transition is second order (ω_0 goes to zero continuously) so we should be able to obtain data in a very wide range of γ/ω_0. At low pressure, consistent with the previous results, we find the γ is only weakly dependent on pressure. Unfortunately, when $\gamma/\omega_0 \approx 1$ we cannot obtain reliable data in our high-pressure cell. Thus, we are not able to measure the soft mode close enough to P_c to observe a singularity in γ. Therefore, while the experimental results of γ are in agreement with previous results far from the phase transition, we have no information as to what happens near P_c.

Divergent behavior near a structural phase transition also has been observed in other crystals.[21-25] This effect, although rather interesting, is not yet understood.[4,10]

There is another point about γ that is not understood. In BaTiO$_3$ the soft $E(1TO)$ mode is very strongly overdamped, both in the cubic phase[15] and in the tetragonal phase.[13(b),14] For our crystal, (Pb$_{0.22}$Ba$_{0.78}$)TiO$_3$, the mode is underdamped even when the frequency is rather low at $P=0$ (≈ 40 cm^{-1}); yet this crystal is close to being 100% BaTiO$_3$. This has been observed throughout the composition range in[5] (Pb$_{1-x}$Ba$_x$)TiO$_3$. Apparently there is something special about 100% BaTiO$_3$ that even relatively small amounts of Pb^{2+} ion replacing Ba^{2+} destroys. This is not understood.[26]

ACKNOWLEDGMENTS

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