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Raman scattering from PbTiO_3 of various grain sizes at high hydrostatic pressures

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Abstract. The Raman spectra for PbTiO_3 of various grain sizes at different hydrostatic pressures have revealed that the soft $E(1\text{TO})$ phonon mode appears to undergo a red shift in frequency and increases in linewidth with decreasing grain size, and that the pressure dependences of the soft mode in nanocrystalline PbTiO_3 can be correlated with the diffuse phase transition.

1. Introduction

It is well known that PbTiO_3 has been extensively investigated because of its special features of soft-mode behaviour and the phase transition. The Raman scattering in single-crystal PbTiO_3 showed that the phase transition from the tetragonal phase (space group, $P4mm$ (C_{4v})) to the cubic perovskite structure (space group, $Pm3m$ (O_h^I)), as a function of temperature (pressure), is driven by the soft optical phonon mode [1, 2]. More recently, Ishikawa *et al* [3] have investigated the size effects on the ferroelectric phase transition in PbTiO_3 ultrafine particles. They found that, when the particle size is less than 50 nm, the transition temperature T_c , determined by Raman scattering, decreases abruptly. In this paper we shall study the Raman spectra of PbTiO_3 as a function of hydrostatic pressure and grain size and shall pay particular attention to the soft-mode behaviour and the phase transition.

2. Experimental details

The samples were prepared by the sol-gel method [4], which enables us to obtain small particles of different sizes with fewer mechanical distortions and to study the size effect on the phase transition properties in ferroelectrics. The average grain size was determined from the full width at half-maximum of the x-ray diffraction peak and transmission electron microscopy (TEM). The backscattering Raman spectra at high pressures were measured using a miniature diamond anvil cell, a Spex-1403 Raman spectrometer with a third monochromator and a standard photon-counting technique [5]. A 514.5 nm line from an argon-ion laser was used as the light source at an output power of 80 mW. A 16:3:1 methanol-ethanol-water mixture, which has good hydrostatic pressure properties under 14 GPa, served as the pressure-transmitting medium in our experiments, and the fluorescence of a small ruby chip was used for the pressure calibration.

3. Results and discussion

The Raman spectra for PbTiO_3 of various grain sizes are shown in figure 1. It is found that the soft E(1TO) mode decreases in frequency from 83 cm^{-1} (50.5 nm) to 72 cm^{-1} (20.2 nm) and increases in linewidth from 12 to 31 cm^{-1} . The relationship between the change in the frequency and the width of the soft E(1TO) mode in figure 2 is very similar to that of microcrystalline silicon [6].

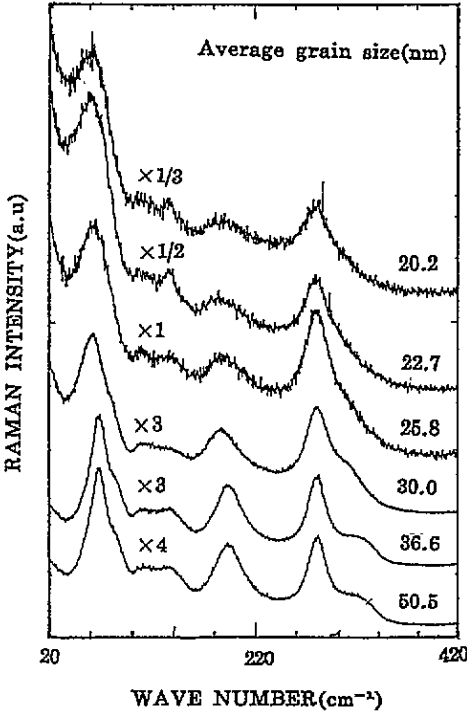


Figure 1. Typical Raman spectra for PbTiO_3 of several grain sizes (a.u., arbitrary units).

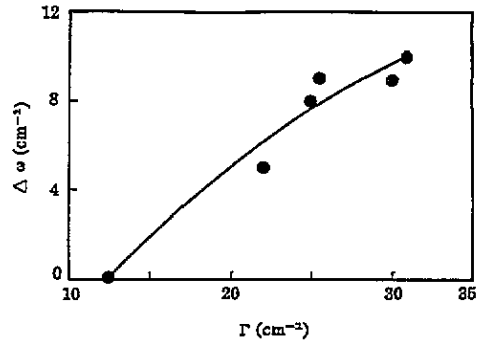


Figure 2. Relationship between the shift and the linewidth of the soft E(1TO) mode for PbTiO_3 of various grain sizes.

In the case of bulk PbTiO_3 materials it was shown that the damping anomaly of the soft mode near T_c is a frequency-dependent effect because of the tuning of a difference combination of zone-boundary acoustic phonons [2]:

$$\Gamma(\omega) \approx 18\pi(n_1 + n_2 + 1)|W_{av}|^2 \rho_2^+(\omega) + 18\pi(n_1 - n_2)|W'_{av}|^2 \rho_2^-(\omega) \quad (1)$$

where W_{av} and W'_{av} are effective third-order interaction strengths. $\rho_2^+(\omega)$ and $\rho_2^-(\omega)$ are sum and difference combinations (two-phonon density of states). n_1 and n_2 are Bose-Einstein thermal factors and Γ is the linewidth. Normally, the strongest decay channel for the zone-centre TO phonon is by a combination of zone-boundary acoustic phonons. However, in nanocrystalline PbTiO_3 , the frequency-dependent effect of Γ may be correlated with the relaxation of the phonon wavevector selection rules or the confinement of phonons even if there are no external effects, for instance pressure or temperature. In this model the phonons with $q \neq 0$ will add contributions to the Raman spectra at energies $\omega(0)$ so that the phonon

transition matrix elements $|\langle q_0 | Q | q \rangle|^2$ have non-vanishing values also for $q \neq q_0$ according to [6]

$$|\langle q_0 | Q | q \rangle|^2 = |\langle q_0 | Q | q_0 \rangle|^2 C(q, q_0)^2 \quad (2)$$

where Q is the photon-phonon interaction operator and $C(q, q_0)$ is the Fourier coefficient obtained from a confinement function. Evidently the additional transitions with $q \neq 0$ will contribute to broadening of the Raman line and its peak has a concomitant red shift $\Delta\omega$ of its mean position. In fact, the lineshape of the first-order Raman spectra can be written as [7]

$$I(\omega) \approx \int d^3q \frac{|C(0, q)|^2}{(\omega - \omega(q))^2 + (\Gamma/2)^2} \quad (3)$$

where $\omega(q)$ is the phonon dispersion. Hence for a material with standard phonon dispersion, in which $\omega(q)$ decreases as the phonon wavevector q increases from zero, equation (3) predicts a downward shift and a broadening of a Raman peak with decreasing size. This is in qualitative agreement with our experimental results. Once one determines $\omega(q)$, quantitative calculations can be completed.

The Raman spectra of bulk PbTiO_3 material at room temperature and hydrostatic pressures up to 11.63 GPa are shown in figure 3(a). The result reveals that the soft E(1TO) phonon linewidth is nearly pressure independent over a wide frequency range (88–30 cm^{-1}) and appears to diverge near the phase transition. Figures 3(b)–(f) describe the hydrostatic pressure Raman spectra for PbTiO_3 of grain sizes 200 nm, 50.5 nm, 36.6 nm, 30.0 nm and 25.8 nm, respectively. These results show that for larger grain sizes (e.g. 50.5 nm) the E(1TO) mode and $A_1(1TO)$ mode are well separated at low pressures. Note that the $A_1(1TO)$ mode is fairly broad even at low pressures, whereas the E(1TO) mode is much narrower so that we can take the frequencies from the peak in the spectra. However, at high pressures the two modes begin to damp and overlap each other (see figure 3(b)) so that a computer-fitting procedure must be used by a least-squares fit with two Lorentzian functions [2]. The pressure dependence of the frequency squared and the linewidth of the E(1TO) mode are given later in figures 5 and 6, respectively (ignoring the soft $A_1(1TO)$ mode).

Figure 4 shows the pressure dependence of each phonon mode of PbTiO_3 with a grain size of 50.5 nm. The results demonstrate that with increasing pressure up to 6.7 GPa the 'silent' mode at 286 cm^{-1} is still pressure independent as in bulk PbTiO_3 material; the E(2TO) mode starts to disappear; the $A_1(1TO)$ and E(1TO) modes first soften with increasing pressure and then appear to be pressure independent as the pressure increases beyond 6.7 GPa. Thus it is probable that the structure of PbTiO_3 with a grain size of 50.5 nm begins to be changed at 6.7 GPa. However, it should be pointed out that, the smaller the grain size, the more difficult it is to measure the E(1TO) mode frequency exactly. In fact, when the grain size is sufficiently small, the softening of the E(1TO) mode can no longer be observed (see figures 3(e) and 3(f)).

In figure 5 we plot the pressure dependence of the square of the soft E(1TO) mode frequency (50.5 nm). The data show a non-straight-line dependence of ω^2 against P , or non-Curie-Weiss behaviour obviously at high pressures. This means that the phase transition is not in agreement with that of bulk PbTiO_3 materials, where, as a function of pressure the soft E(1TO) mode softens to zero and all other modes disappear at 11.63 GPa (see figure 3(a)).

The pressure dependence of the linewidth of the E(1TO) mode is shown in figure 6 (50.5 nm). It should be noted that the linewidth does not diverge at high pressures. This

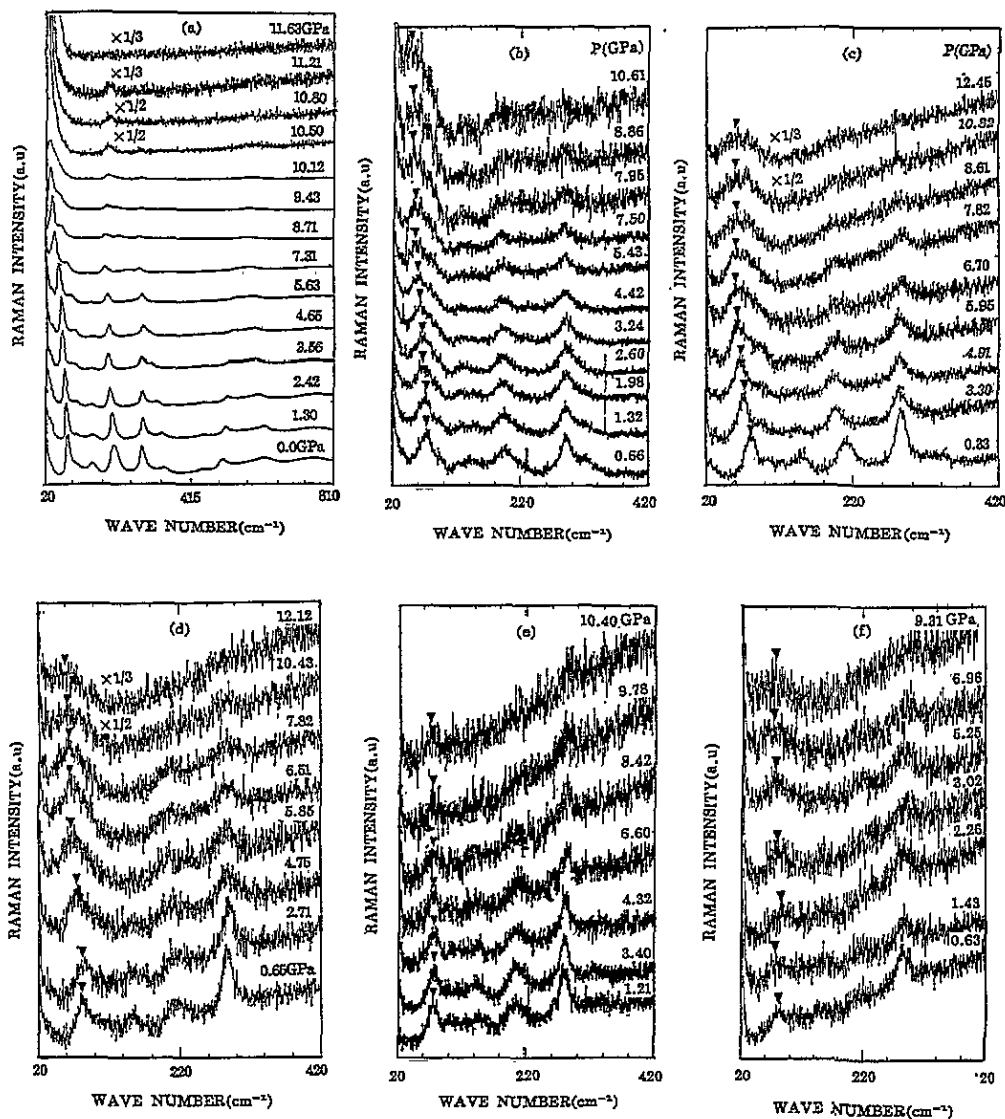


Figure 3. Typical high-pressure Raman spectra for PbTiO_3 of various grain sizes (a.u., arbitrary units); (a) the bulk material; (b) 200 nm; (c) 50.5 nm; (d) 36.6 nm; (e) 30.0 nm; (f) 25.8 nm.

is also different from that of bulk materials, where as a function of temperature or pressure the linewidth follows $t^{-1/2}$ ($t = (T_c - T)/T_c$ is the reduced temperature, $t = (P_c - P)/P_c$ is the reduced pressure) respectively or appears to be singularly damped at T_c or P_c [8]. So, according to the above experimental facts, it is reasonable to suggest that the phase transition occurring in nanocrystalline PbTiO_3 may be a diffuse phase transition.

In nanocrystalline materials, some atoms will be distributed on the interfacial areas and become 'bare' atoms (broken-bond atoms) because of the occurrence of crystal interfacial areas [4, 9]. Each spherical grain (or microregion), whose dimension is as large as one or several unit cells, includes some broken-bond and non-broken-bond atoms. Because the zone-centre ($q = 0$) soft mode responsible for the FE transition in many ABO_3 oxides

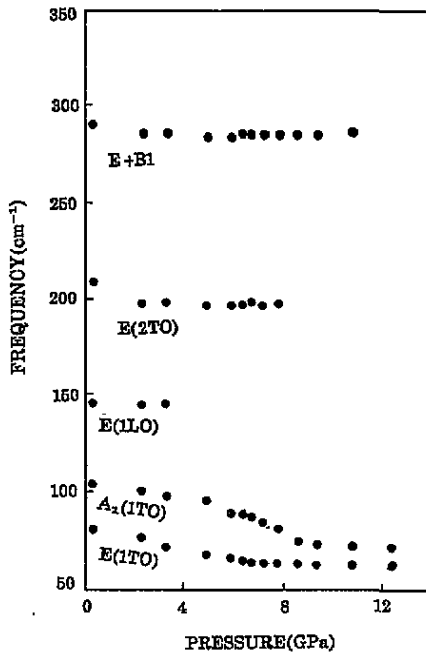


Figure 4. Position of the Raman peaks as a function of pressure in $PbTiO_3$ of grain size 50.5 nm.

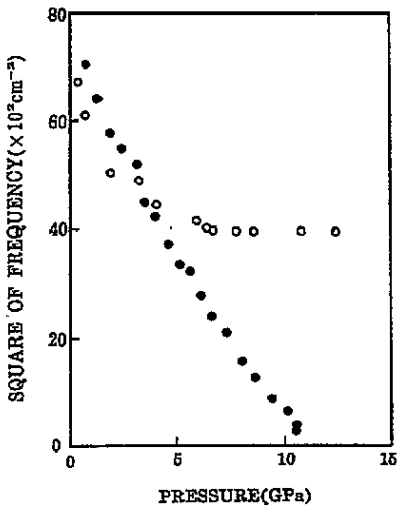


Figure 5. The pressure dependence of the square of the frequency of the soft $E(1TO)$ mode: ○, for $PbTiO_3$ of grain size 50.5 nm; ●, for bulk $PbTiO_3$ material.

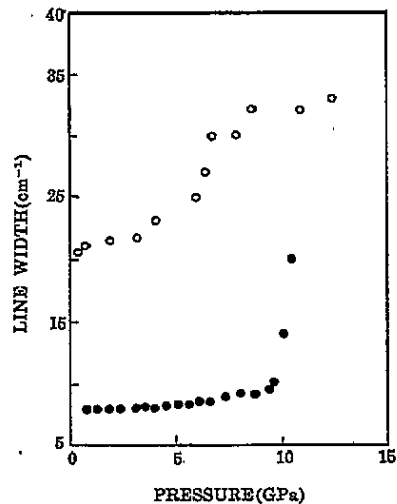


Figure 6. The pressure dependence of the linewidth of the soft $E(1TO)$ mode: ○, for $PbTiO_3$ of grain size 50.5 nm; ●, for bulk $PbTiO_3$ material.

consists of the vibration of the positive A and B ions against the negative oxygen ions [10], the broken-bond atoms no longer contribute to the soft mode with increasing pressure so that each spherical grain has or may have a different transition pressure. The smaller

the grain size, then the more the spherical grains and broken-bond atoms and the less the atoms take part in the soft-mode phase transition. So the phase transition changes from an obvious sharp phase transition for bulk materials (see figure 3(a)) to a large ill defined phase transition region, and from the diffuse phase transition to the disappearance of the ferroelectric phase.

4. Conclusion

The effects of the small grain size on the Raman spectra in PbTiO_3 , where the soft mode appears to undergo a red shift in frequency and increases in linewidth with decreasing grain size, can be correlated with a relaxation in the q -vector selection rule for the excitation of the Raman-active optical phonons. The pressure-induced phase transition occurring in nanocrystalline PbTiO_3 is diffuse and can arise from the occurrences of crystal interfacial areas and the broken-bond atoms.

Acknowledgment

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