Lattice dynamics of PbTiO$_3$

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Abstract. Inelastic neutron scattering experiments were performed to investigate the phonon dispersion relations along the [1,0,0], [1,1,0] and [1,1,1] directions in cubic PbTiO$_3$. All of the transverse optic (TO) branches soften significantly toward the zone center around $T_c$. The zone-center TO mode stiffens considerably at 1173 K. The [$\xi$, $0$, $0$] TO branch for PbTiO$_3$ measured at 793 K are considerably higher than those for Pb(Zn$_{1/3}$Nb$_{2/3}$)O$_3$ at 423 K in the entire zone. The [$\xi$, $0$, $0$] transverse acoustic (TA) branch is found to soften slightly at 793 K. The [$\xi$, $\xi$, $\xi$] TA branch exhibits two minima at the middle point (1/4,1/4,1/4) and the zone boundary (1/2,1/2,1/2). These two modes are weakly temperature dependent up to 1173 K.

1. Introduction

Lead titanate PbTiO$_3$ undergoes only a single phase transition at $T_c = 763$ K from a cubic paraelectric to tetragonal ferroelectric phase. The covalent nature of Pb 6$s$ and O 2$p$ states plays an important role in the stability of tetragonal PbTiO$_3$ [1]. In the 1970s, Shirane et al. [2] investigated the lattice dynamics of PbTiO$_3$ by inelastic neutron scattering. The [$\xi$, $0$, $0$] TO branch softens significantly around the zone center as the temperature approaches $T_c$. Recently, Kempa et al. [3] determined the phonon dispersion curves along the [1,0,0] and [1,1,0] directions in cubic PbTiO$_3$. However, the results for the [$\xi$, $0$, $0$] TO branch are in disagreement with those reported previously [2]. Tomeno et al. [4] studied systematically the phonon dispersion relations in tetragonal PbTiO$_3$. The experimental results for tetragonal PbTiO$_3$ are generally in agreement with the first-principles calculations for the zone-center and zone boundary phonon energies [5]. Ghosez et al. [6] computed the full phonon dispersion curves in cubic PbTiO$_3$ from first-principles calculations. Unfortunately, until recently, the lack of the experimental phonon data above $T_c$ could neither confirm nor disprove the predicted phonon behavior.

Lead titanate PbTiO$_3$ is also the end member of relaxor ferroelectrics (1-x)Pb(Zn$_{1/3}$Nb$_{2/3}$)O$_3$-xPbTiO$_3$ (PZN-PT) and (1-x)Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-xPbTiO$_3$ (PMN-PT). The donation of approximately 10% Ti atoms to PZN is crucial to piezoelectric-constant enhancement [7]. The low-lying TO phonon branch in these relaxors drops sharply near the zone center [8,9]. The
soft TO mode in Pb-based relaxors has been discussed in connection with the polar nanoregions [8,10], but the origin of the sharp drop remains controversial [11].

2. Experiment
The inelastic neutron scattering experiments were performed on the triple-axis spectrometers TAS-1 and T1-1 at JRR-3M in the Japan Atomic Energy Agency, and HB-3 at the High Flux Isotope Reactor, Oak Ridge National Laboratory. The TAS-1 and T1-1 spectrometers were operated with fixed incident energy, $E_i = 13.7$ or 14.7 meV. Collimation was 40'-40'-40'-40' for TAS-1, and guide-40'-40'-40' for T1-1. The HB-3 spectrometer was operated with fixed final energy, $E_f = 14.7$ meV. Collimation was either 48'-20'-20'-70' or 48'-40'-40'-70'. The energy resolution for TAS-1 and T1-1 was 0.66 meV in full width at half maximum (FWHM) at zero energy transfer, whereas that for HB-3 was 0.91 or 1.07 meV. The single crystals used in this work were grown using the top-seeded growth technique described in detail previously [12]. Most of the measurements were performed at 793 K, but selected phonons were also determined up to 1173 K.

3. Phonon dispersion relations
Figure 1 shows the phonon dispersion relations for cubic PbTiO$_3$ measured at 793 K. The TO $\Delta_5$, $\Sigma_3$, $\Sigma_4$ and $\Lambda_3$ branches soften significantly toward the zone center. A set of TO branches shows the isotropic nature of the soft modes. The softening of these TO modes corresponds to the ferroelectric instability of the $\Gamma_{15}$ TO mode. It is difficult to determine accurately the energies of the $\Gamma_{15}$ TO mode near $T_c$. However, a series of constant-$E$ scans indicates that the energy of the zone center TO mode is lower than 3 meV at 793 K. The present value for the soft mode energy is lower than the value reported by Shirane et al [2] or by Kempa et al [3]. The discrepancy in the soft-mode energy suggests that the phase-transition properties of PbTiO$_3$ are influenced by the crystal growth conditions. Figure 2 shows typical constant-$E$ scans in search of the TO $\Delta_5$ branches. Here the data are taken using the HB-3 spectrometer. The $\Gamma_{15}$ TO mode stiffens considerably with increasing temperature. The energies of the $\Gamma_{15}$ TO mode are approximately 6 meV at 1073 K and 8 meV at 1173 K.

In figure 3, the $\Delta_5$ branches in cubic PbTiO$_3$ are compared with the corresponding $\Delta_2$ branches in tetragonal PbTiO$_3$ measured at 295 K [4]. The significant softening of the TO $\Delta_5$ branch is confined to the region $q \leq 0.2$.

The energies of the TA $\Delta_2$ branch at 295 K are higher than those of the TA $\Delta_5$ branch at 793 K. In the cubic phase, the long-wavelength TA $\Delta_5$ and $\Lambda_3$ modes soften gradually with decreasing temperature. Constant-$Q$ scans in figure 4 demonstrate that the TA $\Delta_5$ mode softens simultaneously in cubic PbTiO$_3$. A similar tendency has been observed for the TA $\Delta_5$ branch in KTaO$_3$ [13]. The significant softening of the zone-center TO mode in $ABO_3$ appears to lower the relevant TA phonon branch.

Moreover, the TA $\Lambda_3$ branch exhibits two minima around the middle point (1/4,1/4,1/4) and the zone boundary (1/2,1/2,1/2). Constant-$E$ and constant-$Q$ scans in figure 5 indicate the existence of the energy minimum around (1/4,1/4,1/4). The broad minimum of the TA $\Lambda_3$ mode around (1/4,1/4,1/4) suggests the tendency toward forming a fourfold periodicity along the [1,1,1] direction. Note in figure 1 that the other TA branches show the normal phonon dispersion. A possible interpretation is that the octahedron rotation of successive oxygen layers follows the sequence of same, same, opposite, and opposite senses. To our knowledge, our findings on the middle-point softening are the first report on the phonon dispersion in perovskite oxides $ABO_3$. One possibility is that the covalent nature of Pb and O atoms gives rise to the middle-point softening. The present results for the TA $\Lambda_3$ branch support the predictions of the unstable mode at (1/4,1/4,1/4) and the flat $[\xi, \xi, \xi]$ TO dispersion from first-principles calculations [6,14]. Figure 1 clearly shows the coexistence of the $\Gamma_{15}$ and $R_{25}$ mode softening. The lowering of
Figure 1. Phonon-dispersion curves for PbTiO$_3$ measured at 793 K. Each solid circle and the attached bar refer to the phonon peak and its FWHM, respectively. Solid lines are guides for the eye.

the $R_{25}$ phonon energy represents the softening of the oxygen octahedron rotation. The zone-boundary instability in PbTiO$_3$ has been predicted from first-principles calculations [15]. In $ABO_3$, the tendency toward the $R_{25}$ mode softening generally depends on the tolerance factor, $t = (r_O + r_A)/\sqrt{2}(r_O + r_B)$, where $r_O$, $r_A$, $r_B$ are the ionic radii of the O, A, and B ions, respectively. The $R_{25}$ mode softening has been observed for SrTiO$_3$ [16], and NaNbO$_3$ [17]. Lead titanate PbTiO$_3$ has the tolerance factor $t = 1.03$, slightly larger than 1.01 for SrTiO$_3$ and 0.97 for NaNbO$_3$. Theoretically PbTiO$_3$ shows a weak instability at the $(1/2,1/2,1/2)$ point [6,14,15]. In this experiment, we found that the TA phonon energies around $(1/4,1/4,1/4)$ and $(1/2,1/2,1/2)$ are weakly temperature dependent up to 1173 K. Consequently, the softening of the zone-center TO mode dominates the single phase transition in PbTiO$_3$.

In figure 3(b), the TA $\Delta_5$ and TO $\Delta_5$ branches for PbTiO$_3$ at 793 K are compared with those
Figure 2. Constant-\(E\) scans in \(\text{PbTiO}_3\) for the \(\Delta_5\) mode measured at \(T = 793, 1073\) and 1173 K. Solid lines indicate the best fits to a double Gaussian.

Figure 3. Transverse phonon dispersion curves along [1,0,0] in cubic \(\text{PbTiO}_3\), tetragonal \(\text{PbTiO}_3\), and PZN. The \(\Delta_5\) modes in cubic \(\text{PbTiO}_3\) at 793 K are compared with the \(\Delta_2\) modes in tetragonal \(\text{PbTiO}_3\) at 295 K [4], and the \(\Delta_5\) modes PZN at 423 K [9].

for PZN at 423 K [9]. The energies of the TO \(\Delta_5\) branch for \(\text{PbTiO}_3\) are considerably higher than those for PZN in the entire range. On the other hand, there is a slight difference in the TA \(\Delta_5\) branch between \(\text{PbTiO}_3\) and PZN. The replacement of the B site atom has a strong influence on the TO phonon dispersion. The average mass of the B atom in PZN is 1.75 times that of Ti in \(\text{PbTiO}_3\). Therefore, the reduction of the X point TO energy is roughly explained by the square root of the B atom mass. The force constants for \(\text{PbTiO}_3\) appear to be comparable to those for the Pb-based relaxors. The randomness at the B site in PZN broadens the long-wavelength TO phonon spectra. The important role of Pb atom can account for the similarity in the TA phonon dispersion between \(\text{PbTiO}_3\) and PZN.
Figure 4. Constant-$Q$ scans in PbTiO$_3$ for the TA $\Delta_3$ mode measured at $T = 793$ and 1173 K.

Figure 5. (a) Constant-$E$ scans in PbTiO$_3$ for the $\Lambda_3$ mode through (1.25,1.25,0.75) measured at 793 K. (b) Constant-$Q$ scans at $Q=(h,h,2-h)$.

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