Strong Anharmonicity and Lattice Dynamics in LiTaO$_3$ by Raman Spectroscopy

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Abstract. The phonon-dispersion relations of LiTaO$_3$ crystal are calculated using the first-principle calculations approach described earlier [1]. We found that the $TO_1$ (206 cm$^{-1}$) and the $TO_2$ (256 cm$^{-1}$) are the $z$-vibration of Li ions and other ions, respectively, while the $z$-displacements are negligible in the $TO_3$ (357 cm$^{-1}$) and the $TO_4$ (600 cm$^{-1}$) modes using this calculation. The first-order Raman spectra in the LiTaO$_3$ were measured in the temperature range 23-896K for rhombohedral phase. In the experiment the $TO_2$ mode softens more rapidly than the $TO_1$ mode and then pushes it down to lower frequencies. The temperature dependence of linewidth of four $TO$ modes was analyzed using TDOS due to cubic term based on the first-principle calculations. The calculated results reproduce the observed ones in this temperature range. We found that the ionic motions associated with the $TO_1$ and the $TO_2$ modes are transferred to each other, and in the $TO_4$ mode, torsion of individual octahedral take place, giving a strong anharmonic contribution.

1. Introduction

LiTaO$_3$ crystal is ferroelectric at room temperature (RT) and have rich applications in electromagnetic devices, i.e., surface acoustic filters, ultrasonic transducers, and optical device such as electro-optic, nonlinear optic, and photorefractive devices [2-4]. At RT, LiTaO$_3$ possesses rhombohedral (RH) space group $Rar{3}c(C_{3v}^6)$ and above 950K undergoes a structural phase transition to the high-temperature paraelectric RH phase from the low-temperature ferroelectric RH phase. IR absorption and Raman scattering spectra of LO and TO phonons [5-9] have been measured by many researchers. Jayaraman and Ballman [5] have investigated the pressure dependence of Raman spectra of LiTaO$_3$. They concluded that the phase transition is order-disorder type. Penna et al [6], found a Debye-like central peak in Raman spectra of the ferroelectric phase. Tomeno and Matsumura [7] measured the dielectric susceptibilities and conductivity, and reported that a comparison with light-scattering measurements which an intermediate character between the displacive and order-disorder phase transition. Recently, the temperature dependence of Raman spectra of TO modes have been measured in the X(ZZ)Y configuration above room temperature [8]. They reported that the two low-frequency peaks (206 cm$^{-1}$ and 256 cm$^{-1}$) of TO mode show significant changes as the temperature increases above room temperature, and “Mode softening” and
“frequency-repulsion” are observed [8]. However, the temperature dependence of Raman spectra of these modes has not been analyzed with respect to the anharmonicity of the phonon-modes by using the first-principles calculations in detail. Very recently, Hushur et al., [9] have reported that the central peak (CP) (quasielastic and softening) is observed [8]. However, the temperature dependence of Raman spectra of LiTaO$_3$ polarized scattering, CP is observed at the polarized scattering geometry in all the temperatures studied. It is found that the relaxation time determined from the width of CP clearly shows a critical slowing down of an order-disorder phase transition in the vicinity of $T_c$. Recently, we studied the temperature dependence of Raman-active phonon spectra in certain GdFeO$_3$-type crystal (i.e., LaGaO$_3$ [1]) and found that the temperature dependence of the linewidth of the $A_g$ modes in these Raman spectra was well described by the cubic anharmonic term in the expansion series of the crystal potential energy. We found that a large frequency gap in the DOS (phonon density of states) gives the difference between anharmonic effects on each peaks’ channel in the RH phase [1]. In this study, the observed temperature dependence of the Raman spectra for LiTaO$_3$ is examined in terms of phonon-dispersion relations based on the first-principles calculations in RH phase. We also clarify the origin of anharmonic effects on the linewidth of four TO modes using these calculations in viewpoint of “Mode softening” and “frequency-repulsion” including low temperature range.

2. Experimental details
The specimen used in the present study was a single crystal sample (a purity of 99.99%), and was cut perpendicularly on the c axis (7.0×6.0×8.0 (c axis) mm$^3$ in dimension), and its surface was optically polished. The polarized Raman scattering spectra (Fig. 1) of several modes were measured in the range of 23-896K. These results above 77K were similar to the previous works [5-9]. The excitation source was the 514.5-A line of an Ar+-ion laser at a power level of 100-200mW, and it was introduced to the thin side of the sample. 90˚ scattering geometry has been used. The scattered light from the surface was analyzed using a double monochromator (CT-1000D, JASCO Co.) having a spectral resolution of about 2.0cm$^{-1}$ and the accuracy of the wave number was $\pm$ 1 cm$^{-1}$.

3. Computational details
The phonon-dispersion relations [Fig. 2(a)] of LiTaO$_3$ are calculated using the first-principle calculations approach described earlier [1]. The phonon modes (Fig. 2(b)) are also obtained as usual by the diagonalization of the dynamical matrix.

Fig. 1 Polarized Raman spectra at RT [(a)] and temperature dependence of polarized Raman spectra in a X(ZZ)Y configuration[(b)].
Fig. 2 The (a) phonon dispersion relations in LiTaO$_3$. The (b) calculated vibrational patterns of the $TO_1$ (206 cm$^{-1}$), the $TO_2$ (256 cm$^{-1}$), the $TO_3$ (357 cm$^{-1}$), and the $TO_4$ (600 cm$^{-1}$) in a top of view along z-axis.

Fig. 3 Temperature dependence of the (a) linewidth and the (b) line shift of the 206 cm$^{-1}$ and 256 cm$^{-1}$ peaks. The observed values were denoted by closed and open circles, respectively. The calculated values are denoted by the solid lines.

Fig. 4 Temperature dependence of the (a) linewidth and the (b) line shift of the 357 cm$^{-1}$ and 600 cm$^{-1}$ peaks. The observed values were denoted by closed and open circles, respectively. The calculated values are denoted by the solid lines.
4. Results and discussion

The temperature dependence of linewidth of the four TO modes was analyzed using TDOS due to cubic term based on the first-principle calculations. The calculated results reproduce the observed ones in this temperature range. In Fig. 2(b), we found that the $TO_1$ and the $TO_2$ are the z-vibration of Li ions and other ions, respectively. In Figs. 1(b), 3(a), and 3(b), we found that the $TO_2$ mode softens more rapidly than the $TO_1$ mode and then pushes it down to lower frequencies above 350K (“Mode softening” and “frequency-repulsion”). We found that the ionic motions associated with the $TO_1$ and the $TO_2$ modes are transferred to each other. This may be originated that $TO_1$ and the $TO_2$ are almost similar z-vibration of Li ions [Fig. 2(b)] and the difference between frequencies of two peaks is small. In Fig. 2(b), the z-displacements are negligible in the $TO_3$ and the $TO_4$ modes, and practically only oxygen ions are participating them. In Fig. 4(a), we found that the variation of linewidth of the 600cm$^{-1}$ peak is almost equal to those for the 357cm$^{-1}$ peak, because the vibration pattern of $TO_3$ is almost similar to that of $TO_4$. The difference between these two modes is following: in $TO_4$, the whole oxygen octahedra are tilted essentially rigid objects, that is, relatively soft and smaller anharmonic vibration. In the $TO_3$ mode, the torsion of individual octahedral take place, that costs much higher energy and has a strong anharmonic contribution including low temperature range. Therefore, the variation of linewidth of the 600cm$^{-1}$ peak is a little greater than those for the 357cm$^{-1}$ peak [Fig. 4(a)].

5. Conclusion

The phonon-dispersion relations of LiTaO$_3$ crystal are calculated using the first-principle calculations approach described earlier [1]. We found that the $TO_1$ (206 cm$^{-1}$) and the $TO_2$ (256 cm$^{-1}$) are the z-vibration of Li ions and other ions, respectively, while the z-displacements are negligible in the $TO_3$ (357 cm$^{-1}$) and the $TO_4$ (600 cm$^{-1}$) modes using this calculation. The first-order Raman spectra in the LiTaO$_3$ were measured in the temperature range 23-896K for rhombohedral phase. In the experiment the $TO_4$ mode softens more rapidly than the $TO_1$ mode and then pushes it down to lower frequencies. The temperature dependence of linewidth of the four TO modes was analyzed using TDOS due to cubic term based on the first-principle calculations. The calculated results reproduce the observed ones in this temperature range. We found that the ionic motions associated with the $TO_1$ and the $TO_2$ modes are transferred to each other, and in the $TO_4$ mode, torsion of individual octahedral take place, giving a strong anharmonic contribution.

Acknowledgement

This work was supported in part of a Grant-in-Aid for Scientific Research (C) from the Ministry of Education, Science and Culture of Japan (Grant No. 20540322).

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