Ultrafast zone-center coherent lattice dynamics in ferroelectric lithium tantalate

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Abstract

Femtosecond time-resolved pump–probe experiments were carried out to study ultrafast lattice dynamics of ferroelectric lithium tantalate. Both the fully symmetric ($A_1$ mode) and doubly degenerate (E mode) coherent phonons at the center of the Brillouin zone were excited via impulsive stimulated Raman scattering, as confirmed by the excitation intensity dependence.

Keywords: lithium tantalate, ISRS, coherent phonon

1. Introduction

The progress in laser technologies has allowed generating laser pulses shorter than the vibrational period of a crystal lattice \cite{1}. With such an ultrafast probe the lattice dynamics can be studied in real time, providing a new insight into the vibrational properties and related phenomena of materials. As compared to the frequency-domain measurement, the time-domain measurement provides the unique information on dynamic processes of phonon decay and coupling with other quasi-particles \cite{2}.

Lithium tantalate ($\text{LiTaO}_3$) is a functional material, which is widely used for various room-temperature piezoelectric, electro-optical and nonlinear optical applications. The lattice dynamics of $\text{LiTaO}_3$ has been the object of numerous investigations in the time domain. Especially, the phonon–polariton dispersion at nonzero wavevectors studied with ultrashort laser pulses attracts much attention \cite{3,4}. Such efforts remarkably improved our understanding of the low-frequency ($<6\text{THz}$) dielectric response of $\text{LiTaO}_3$. In contrast, the importance of studying the transient phonon characteristics at the center of the Brillouin zone (BZ) has been underappreciated. On the one hand, it is now well accepted that the relaxation of transverse optical modes at the BZ center is directly responsible for the ferroelectric–paraelectric phase transition, although the exact transformation mechanism is still under debate \cite{5-10}. As far as other modes are concerned, one can expect them to contribute significantly at temperatures much lower or higher than the Curie point $T_C$. On the other hand, the zone-center lattice dynamics of ferroelectric materials irradiated by ultrashort laser pulses is a prerequisite for understanding the ultrafast polarization switching \cite{11-13}, which is essential for ultrafast reading and writing of data in a ferroelectric memory. Therefore, it is important to study ultrafast lattice dynamics at the BZ center of ferroelectric materials, using $\text{LiTaO}_3$ as a prototype.

In this work, we report observation of coherent optical phonons at the BZ center in a ferroelectric $\text{LiTaO}_3(0001)$ crystal using femtosecond laser pulses, which provides complementary information on lattice dynamics of materials subjected to ultrashort laser irradiation.

2. Experimental details

The sample of $\text{LiTaO}_3(0001)$ used for this study was a commercially available (Superconix, USA) congruent single crystal plate of the size $10 \times 10 \times 0.5 \text{mm}^3$, grown
from a melt by the Czochralski pulling technique. The orientation accuracy of the sample is better than 0.5°. The femtosecond time-resolved pump–probe technique was employed to measure the transient transmission change ($\Delta T / T_0$) of LiTaO$_3$ irradiated by ultrashort laser pulses at room temperature. Figure 1 depicts schematically the experimental setup. A mode-locked Ti:sapphire laser delivered the ultrashort pulses centered at 800 nm with a full-width at half-maximum (FWHM) of 45 fs at a repetition rate of 86 MHz. The pulse was divided with a beam splitter into an intense pump beam and a weak probe beam. The time delay between the two beams was periodically controlled by a fast scan delay (APE, Germany) at a frequency of 20 Hz. A reference signal was further split off the probe beam by a fast scan delay, oscillating at 20 Hz. Two mirrors, M1 and M2, are mounted on a fast scan delay, oscillating at 20 Hz. A photodetector. In the scan delay, two mirrors, M1 and M2, are used in isotropic transient transmission measurements. M denotes a mirror, BS a beam splitter, P a polarizer, L a lens and PD a photodetector. In the scan delay, two mirrors, M1 and M2, are mounted on a fast scan delay, oscillating at 20 Hz. In the scan delay, two mirrors, M1 and M2, are mounted on a fast scan delay, oscillating at 20 Hz.

The Raman spectrum was measured with a 541 nm laser (Jobin Yvon Co.).

3. Results and discussion

LiTaO$_3$ is ferroelectric at room temperature, belonging to the trigonal crystal system with the symmetry of space group R3c [14]. Each primitive cell consists of two formula units having 18 vibrational modes (4A$_1$ + 5A$_2$ + 9E), of which the A$_1$ and E modes are Raman and infrared active and the A$_2$ modes are silent. The Raman tensors associated with the optical modes of LiTaO$_3$ are

$$A_1(Z) = \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{pmatrix}, \quad E(X) = \begin{pmatrix} 0 & c & d \\ c & 0 & 0 \\ d & 0 & 0 \end{pmatrix}. \quad (1)$$

where $X$, $Y$ and $Z$ reflect the polarization of the modes, respectively, to the crystallographic axes. The $Z$-axis is parallel to the unique $c$-axis (the threefold axis). The X-axis coincides with one of the crystallographic axes in the hexagonal base. The $Y$-axis, based on the selection of the $X$ and $Z$ axes, is chosen to make the coordinate system right handed.

Figure 2(a) shows a typical signal observed in the transient transmission measurements, with oscillations following a sharp change in the transmission around zero time-delay. The precursor change arises from the electronic response to the photons, and has the response duration (~53 fs) slightly longer than the excitation pulse. Usually, the electronic response exponentially decays to zero and thus can be decoupled from the subsequent oscillations. The derived pure coherent oscillation is shown in the inset of figure 2(a). The Fourier spectrum of the oscillatory time-domain signal (figure 2(b)) demonstrates that the observed oscillation mainly consists of six modes at 6.06, 7.55, 8.33, 10.6, 12.0 and 13.7 THz. To assign these modes, we measured the Raman spectrum on the same sample in the backward scattering geometry and plotted it in figure 2(c). The Raman shift is expressed in THz instead of cm$^{-1}$ to facilitate the comparison with the coherent phonon spectrum. The excitation of coherent phonons basically obeys the Raman selection rule, that is, all excited coherent phonons are Raman active. There is a disagreement in the literature on the assignment of the long-wavelength optical phonons in LiTaO$_3$ [5–10], [15–19]. Our assignment is mainly based on the Raman results by Kaminow and Johnston [15], which are further supported by the first-principle calculations [20]. According to the Raman tensors and the measurement geometry, only the $A_1$(LO) and E(TO) modes can be excited. The appearance of the forbidden E(LO) mode at 8.37 THz (279 cm$^{-1}$) can be attributed to the large amount of lattice defects in the congruent crystal [14, 16]. The defect-induced forbidden Raman modes have been observed previously [21]. Comparing the Fourier spectrum with the Raman spectrum, we assigned the observed coherent phonons to the E(TO), $A_1$(LO) and E(LO) modes, as indicated in figure 2(b).

To extract the properties of each coherent phonon, we fitted the coherent oscillation signal as follows:

$$\Delta T / T_0 = \sum_{i=1}^{6} A_i \exp(-t/t_i) \sin(2\pi \nu_i t + \phi_i), \quad (2)$$

where $i$ counts over six coherent phonons; $\tau$, $\nu$ and $\phi$ are the relaxation time, frequency and initial phase, respectively.
Figure 2. Transient transmission change measured by the femtosecond time-resolved pump–probe technique at the pump power of 55 mW (a) and the correspondent Fourier transform (b) of the time-domain signal. (c) Shows the Raman spectrum measured for the same sample. The inset in the upper panel illustrates the experimentally observed pure coherent oscillations (dashed line) obtained by removing the electronic response and the fit (solid line) with equation (2).

The fitting results are listed in table 1. The fitted frequencies are slightly different from those in the Fourier-transformed spectrum due to the uncertainties of both methods.

To confirm the excitation mechanism of coherent phonons, a series of experiments was carried out to measure the excitation intensity dependence of the amplitudes of coherent oscillations. The Fourier-transformed results are presented in figure 3. The frequencies of coherent phonons are nearly independent of the pump power, indicating small anharmonicity in the used excitation intensity range. Furthermore, the amplitude of the $A_1(LO_1)$ mode determined by fitting the time-domain signal with equation (2), as shown in the inset of figure 3, increases almost linearly with the excitation intensity. Such dependence can be explained by the impulsive stimulated Raman scattering mechanism, because the driving force of the lattice motion is proportional to the electric field intensity in stimulated Raman processes [22]. Note that the photon energy used (1.55 eV) is much lower than the band gap (3.93 eV) of LiTaO₃ at room temperature [23].

4. Conclusions

In summary, we have measured ultrafast lattice dynamics of ferroelectric LiTaO₃(0001) under irradiation by ultrashort laser pulses. Coherent excitation of six optical phonons ($E(\text{TO}_1)$, $E(\text{TO}_2)$, $E(\text{LO})$, $A_1(\text{LO}_1)$, $A_1(\text{LO}_2)$ and $E(\text{TO}_3)$) at the BZ center, driven by impulsive stimulated Raman scattering, has been observed and the relaxation times of each coherent phonon were estimated.

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