

Electronic structures and phonon modes in wide-bandgap semiconductors investigated by Raman spectroscopy and first-principles calculations

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1. General introduction

1.1 Electron-lattice interaction

The strongly correlated electron system occupies a part of the semiconductor and insulator materials. It is known that substantial materials in the system have an electron-electron interaction via strong electron-lattice interactions. Electron-lattice interaction is a phenomenon in which electrons moving in a material are scattered by the collective vibrations (phonons) of the lattice. The source of this phenomenon is that the charged electrons and the polarization of the collective vibration mode that constitutes lattice vibration, or phonon mode, exert forces on each other through the Coulomb force. Not only for the physical properties during the normal conduction state, but those at superconductivity depend on the phonon properties [1]-[3]. Therefore, it is important to elucidate the electron-lattice interaction of semiconductors. For that purpose, it is necessary to clarify the role of each individual lattice vibration mode.

Each collective vibration mode has its unique combination of atoms in lattice. In general, low-frequency modes have large effective masses and large number of constituent atoms, while high-frequency modes are local and confined. Therefore, each mode has its characteristic value for the polarization, whether it is from cation and anion arrangements or from displacements between cationic cores (nucleus plus core electrons) and conducting electrons. In this way, physical properties such as thermal or thermoelectric properties are naturally strongly dependent on mode. Besides, electronic properties correlated to phonon properties are also strongly mode-dependent.

As for the applications, phonon engineering is the focus of attention [4]-[8]. For this purpose, it is essential to investigate the effect of individual phonon mode one by one.

1.2 Selective lattice vibration excitation

In order to elucidate the electron-lattice interactions, it is necessary to clarify the correlation between individual lattice vibrational modes and electronic states. Solid crystals have phonons determined by the symmetry of their lattice. Each of the phonon mode is assigned

a unique energy corresponding to its vibration frequency. For the clarification of the role of each individual vibrational mode which plays in physical properties, an effective means to select and excite specific lattice vibrational mode is required.

There are four types of phonons: longitudinal wave optics (LO), longitudinal wave acoustics (LA), transverse wave optics (TO), and transverse wave acoustics (TA), and these phonon modes are generally excited by heat. At room temperature, all of these types of phonons are excited, according to the statistics corresponding to the thermal energy at that temperature. At low temperatures, all phonons are suppressed in contrast. Therefore, in thermal excitation of phonon mode, it is difficult to excite only a single lattice vibration mode. In order to perform selective lattice vibration excitation, a method called coherent phonon excitation using stimulated Raman scattering has been widely used [9]-[11]. However, when it is applied to a sample having plural phonons of different frequencies and one vibration mode, especially high-frequency mode, is chosen to be excited, all the modes below the target frequency are excited. Advanced pulse control is required to ensure the selectivity of singular mode excitation [12].

As an alternative to the coherent phonon excitation, a new method of selective lattice vibration excitation can be proposed: to irradiate the sample with coherent mid-infrared free electron laser (MIR-FEL) light that corresponds to the absorption wavelength of the lattice vibrations, namely same frequency of the target mode. This method temporarily stops all lattice vibrations at extremely low temperatures, selectively exciting specific modes with mid-infrared free electron laser light, and observing the anti-Stokes Raman scattered light signal of the successfully excited phonon mode [13]. Raman scattering is a phenomenon in which light incident on a material is inelastically scattered by molecular vibrations or lattice vibrations, producing light with a shift of wavelength different from that of the incident light corresponding to the vibration mode energy. The details of this principle will be explained in the next section. In this study, the authors are conducting joint research with the mid-infrared free-electron laser facility (KU-FEL) of the Institute of Advanced Energy, Kyoto University. At KU-FEL, they are developing a free electron laser that oscillates monochromatic light in the mid-infrared region (wavelength range from 5 to 20 μm) that corresponds to the typical optical phonon absorption region of solid-state materials or

vibration mode of molecules [14]. Since FEL enable a choice of continuously variable wavelength, it is possible to selectively excite various lattice vibrations in solid materials. Instead of the instantaneous excitation as in the conventional coherent phonon excitation method, it can be expected to excite a specific lattice vibration mode stably at the resonant frequency continuously, by irradiating with an FEL light tuned to the absorption wavelength corresponding to the lattice vibration of the sample. In other words, we believe that phonons can be selectively excited by irradiating coherent light of a specific target wavelength. Furthermore, by using FEL for excitation and anti-Stokes Raman scattering for observation, ultrafast spectroscopy is not necessary, as instantaneous excitation of optical phonon needs an order of femto-second ultra-short pulse in general.

1.3 Aim of this study

In this study, I mainly used two approaches to investigate the electronic structures and phonon modes of wide-gap semiconductors. One is Raman spectroscopy, which is a method we have been conducting joint research with the KU-FEL research group targeting on selective excitation of arbitrary single mode. The samples handled in our joint research to date have been SiC and GaN, both of which were selectively excited by one-photon excitation in the infrared-active mode which is Raman-active at the same time, as I adopted anti-Stokes Raman scattering as a probe [13][15]. Here, I plan to extend this method to infrared-inactive or Raman-inactive modes. Also, resonant Raman scattering to probe weak phonon signals are aimed to be included in the method. The other is first-principles calculations to investigate mainly in and around bandgap electronic states in order to design resonant Raman spectroscopy.

In Chapter 2, selective excitation of phonon modes was performed in the infrared-inactive mode of diamond using two-photon free-electron laser excitation.

In Chapter 3, I performed some preliminary researches on yttria-stabilized zirconia, titanium oxide, and gallium phosphide in order to extend selective phonon excitation method to phonon modes in Raman inactive mode or modes of weak signals. Hyper-Raman scattering was adopted to measure Raman inactive modes, and resonance Raman scattering

was selected to measure weak-signal modes.

In Chapter 4, I conducted Stokes Raman spectroscopy for a crystal of chirality in order to extend the method to chiral phonon excitation using dextrorotatory α -quartz.

For the experimental design, predictive calculations were performed for the bandgap state of STO in Chapter 5, and CsAlCl₄ in Chapter 6. I performed density-functional first-principles predictions of the states in and round the gap that become noise sources, or electronic state for resonance in resonant Raman spectroscopy.

I aim to apply Raman scattering spectroscopy adopted in mode-selective phonon excitation method to extend to all vibrational phonon modes in energy-functional wide-bandgap semiconductors.

2. Selective lattice vibration excitation of diamond using FEL

2.1 Introduction

2.1.1 Diamond

Diamond is a material composed only of carbon atoms and has a crystal structure as presented in Figure 2-1 [16]. Additionally, compared to other allotropes of carbon such as graphite, fullerene (C_{60}), and carbon nanotubes (CNT), each covalent bond between carbon atoms in diamond is extremely strong. For this reason, diamond is said to be the hardest substance found in nature.

As shown in Table 2-1, diamond is a semiconductor with a wider band gap than other semiconductors and a typical wide gap semiconductor. It has excellent physical properties such as high electron mobility, high dielectric strength, and high thermal conductivity [17][18]. Therefore, by combining these features, it is expected as semiconductor devices which are dramatically more advanced than the current ones.

Figure 2-2(a) shows the phonon dispersion curve of diamond [19]. Diamond has two atoms in its unit cell, and due to its symmetry, there are a total of six vibrational modes: three optical modes and three acoustic modes. At Γ point, the three optical modes are degenerated, and the resulting Raman scattering spectrum is expected to have a single peak. Actually, pure diamond crystal has a very sharp single peak at 1332 cm^{-1} [20]-[23](Figure 2-2(b)).

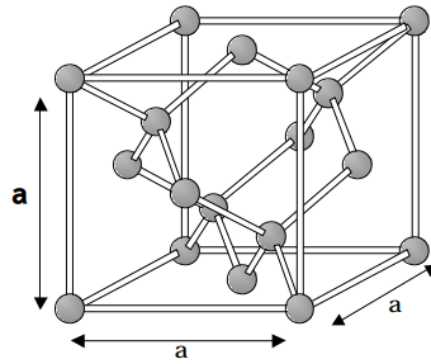
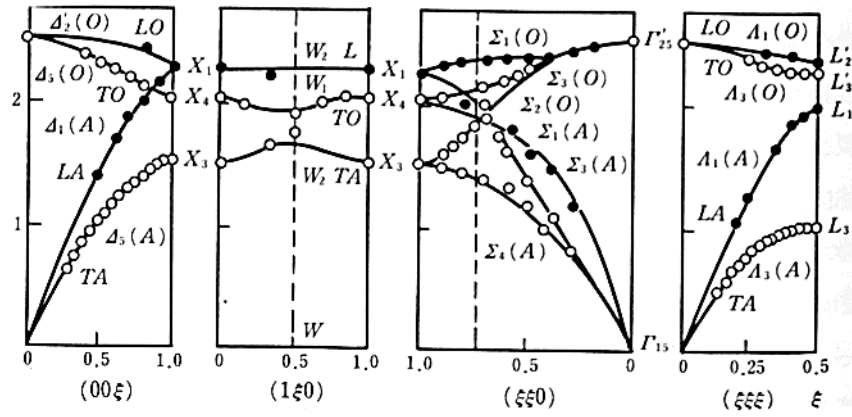


Figure 2-1 A schematic for diamond structure [16].

Table 2-1 Comparison of physical properties of typical semiconductor materials and diamond [17][18].

	Si	4H-SiC	GaN	ZnO	Diamond
Band gap(eV)	1.11	3.26	3.39	3.4	5.47
Electron mobility (cm²/Vs)	1500	1000	1200	300	2200
Hole mobility (cm²/Vs)	600	115	150	-	1600
Breakdown electric field (MV/cm)	0.3	3.5	3.4	-	10
Thermal conductivity (W/cmK)	1.5	4.9	2.0	0.25	21.3
Electron saturation velocity (cm/s)	1.0×10^7	2.2×10^7	2.7×10^7	3.0×10^7	2.71×10^7
Relative permittivity	11.8	9.7	9.0	8.7	5.5

(a)



(b)

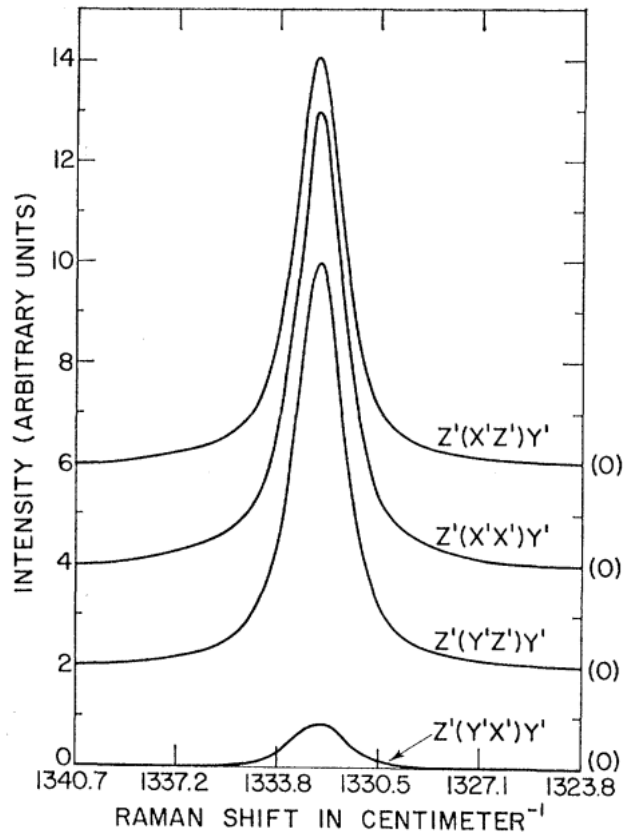


Figure 2-2 (a) Diamond phonon dispersion relationship [19]. The vertical axis unit is phonon frequency ω [10^{14} /s]. (b) Raman spectra of natural diamond crystals [23].

2.1.2 Selective lattice vibration excitation

This chapter summarizes the results of selective lattice vibrational excitation of single crystal diamond using FEL through two-photon excitation for infrared inactive mode in the mid-infrared region. Below, I will explain the principle of two-photon excitation, transition probability, and selection measurement [24]-[29].

Light absorption and emission depend on the interaction of light and matter. When light is irradiated to a molecule, the probability of the light absorption is directly proportional to the intensity of the incident light. This phenomenon of linear relationship is called one-photon absorption. In excitation process by one-photon absorption, one molecule absorbs one photon corresponding to energy difference between ground and excited state, and the excitation transition occurs. On the other hand, two-photon excitation is a phenomenon in which one molecule simultaneously absorbs two photons with half the energy of the transition energy and is excited. Figure 2-3 shows a simple energy level diagram for one-photon excitation and two-photon excitation [30].

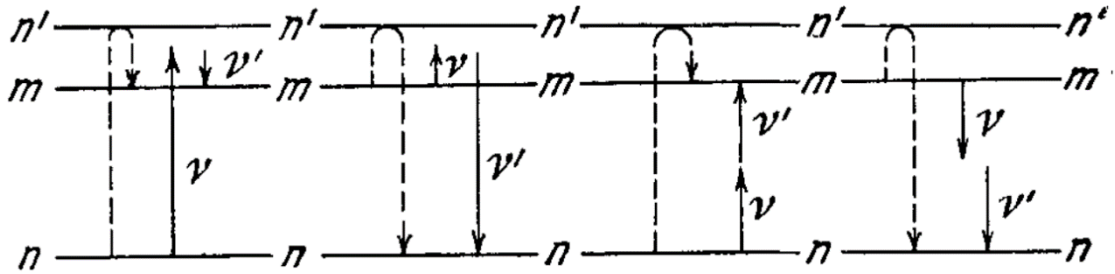


Figure 2-3 Schematics for the Stokes Raman, anti-Stokes Raman, two-photon absorption, and two-photon emission processes (from left to right) [30]. n and m are ground and excited states. n' is intermediated state.

In describing the transition probability of a two-photon absorption process, I will first explain the case of a one-photon absorption process. For simplicity, consider an atom with only two levels (two-level system), where the energy of the ground level is $E_1 = \hbar\omega_1$ and the energy of the excited level is $E_2 = \hbar\omega_2$ ($\hbar$: Planck's constant, ω : frequency). The level

1 and 2 correspond to n and m state in Figure 2-3 for orbitals in molecule or crystal, respectively. Also, write the two-level spacing as follows.

$$E_2 - E_1 = \hbar\omega_2 - \hbar\omega_1 \equiv \hbar\omega_0 \quad (1)$$

Next, consider the interaction between the atom and the electromagnetic field when a single mode of light ω is projected close to the interval of energy between the ground state $|a\rangle$ and the excited state $|b\rangle$ of the atom, as shown in Figure 2-4. If the state of the atom (A) and field (F) is written as $|A, F\rangle$, the absorption process corresponds to the transition $|a, n\rangle \rightarrow |b, n-1\rangle$. (n : number of photons). Assuming that the atom represented by equation (1) is placed in a multimode radiation field, the transition probability per unit time in this absorption process (level $|a\rangle \rightarrow |b\rangle$) is given by the following equation.

$$W_{ab} = \frac{\pi |\mu_{ab}|^2}{\varepsilon \hbar^2} u(\omega_0) \quad (2)$$

(μ_{ab} : the electric dipole efficiency, ε : the dielectric constant of the medium, $u(\omega_0)$: the density of states of the incident light)

It can be seen from equation (2) that the transition probability of one-photon absorption is linearly proportional to the irradiation density of states of the incident light $u(\omega_0)$. Moreover, one-photon absorption is dominated by the matrix element $\mu_{ab} = \langle b | \mu | a \rangle = \int \psi_b \mu \psi_a dv$ of the electric dipole efficiency of the atom (initial state is indicated in right and final state is indicated in left). When μ_{ab} has a large value, the transition probability from a to b becomes large, and the absorption process is easily observed. This case is called as allowed transition. Conversely, when μ_{ab} is very small or zero, it becomes difficult to observe the absorption process, and this case is called as forbidden transition.

In general, state functions include an even function that becomes $\varphi(\mathbf{r}) = \varphi(-\mathbf{r})$ and an odd function that becomes $\varphi(\mathbf{r}) = -\varphi(-\mathbf{r})$ when its spatial coordinate $\mathbf{r}$ is reversed to $-\mathbf{r}$. Such a state function is said to have even or odd parity.

Whether absorption transitions are allowed or prohibited depends on μ_{ab} . However, in a molecule with central symmetry, the electric dipole which can be formulated as $\sum_i e \mathbf{r}_i$ is contained in it, and it changes sign when $\mathbf{r} \rightarrow -\mathbf{r}$. Namely, its parity is odd. In this case, if the two wave functions $|a\rangle$ and $|b\rangle$ that the operator μ_{ab} act have the same parity, the

product of two wave function and the operator is odd function. Then, the matrix element of the transition probability, which is calculated as the integration of the product over all space, is zero and no absorption is observed (forbidden transition). On the other hand, if they have different parities, the product is even function, and absorption will be observed (allowed transition). That is, in order to make the electric dipole transition to be allowed, it is necessary that the wave functions of the ground state and the excited state have different parities. The laws that define whether optical absorption of a certain system is allowed or prohibited are generally referred to as selection rules.

Next, consider the case of a two-photon absorption process. In two-photon absorption, two photons are annihilated from the field. However, this is done in a way that compensates for energy changes in elementary excitations of atoms, molecules, crystal lattices, etc. that interact with the field. The two-photon absorption described here is a secondary process in which two photons are absorbed simultaneously, and is a single nonlinear phenomenon in which only the beginning and end of the event are observed in experiment in general. To portrait the theory, I introduce an intermediate state $|T\rangle$ which is denoted as m in Figure 2-3 for convenience. As described above, only the initial state $|I\rangle$ and the final state $|F\rangle$ are observed experimentally. In the two-photon process, if the ground state is $|g\rangle$ and the excited state is $|e\rangle$, $|I\rangle$ and $|F\rangle$ are expressed as follows.

$$|I\rangle = |g, n_1, n_2\rangle, \quad |F\rangle = |e, n_1 - 1, n_2 - 1\rangle \quad (3)$$

The notations for the field, n_1 and n_2 , are the number of photons whose energies are $\hbar\omega_1$ and $\hbar\omega_2$, respectively. The energy corresponding to each state is as follows.

$$E_I = E_g + n_1\hbar\omega_1 + n_2\hbar\omega_2, \quad E_F = E_e + (n_1 - 1)\hbar\omega_1 + (n_2 - 1)\hbar\omega_2 \quad (4)$$

(n_1, n_2 : numbers of photons)

For the energy conservation, $E_I = E_F$ is required. Therefore, the following relationship holds.

$$E_e - E_g = \hbar\omega_1 + \hbar\omega_2 \quad (5)$$

Also, for the two-photon absorption, consider the following two intermediate states $|t_1\rangle$ and $|t_2\rangle$.

$$|T\rangle = \begin{cases} |T_1\rangle = |t_1, n_1 - 1, n_2\rangle \\ |T_2\rangle = |t_2, n_1, n_2 - 1\rangle \end{cases} \quad (6)$$

$|T_1\rangle$: the state of the system after one photon of frequency ω_1 is absorbed

$|T_2\rangle$: the state of the system after one photon of frequency ω_2 is absorbed.

The two processes for absorption $|I\rangle \rightarrow |T_1\rangle \rightarrow |F\rangle$ and $|I\rangle \rightarrow |T_2\rangle \rightarrow |F\rangle$ are shown in Figure 2-5. The energy of the intermediate state is expressed as follows.

$$E_{T_1} = E_{t_1} + (n_1 - 1)\hbar\omega_1 + n_2\hbar\omega_2, \quad E_{T_2} = E_{t_2} + n_1\hbar\omega_1 + (n_2 - 1)\hbar\omega_2 \quad (7)$$

Using equation (4), I get the following equations.

$$E_I - E_{T_1} = E_g - E_{t_1} + \hbar\omega_1, \quad E_I - E_{T_2} = E_g - E_{t_2} + \hbar\omega_2 \quad (8)$$

Therefore, the transition probability per unit time for two-photon absorption W_{TPA} when the energy of two photons is identical, $\hbar\omega_0$ ($E_e - E_g = 2\hbar\omega_0$), is given by the following equation [31].

$$W_{TPA} = \frac{\pi}{2\varepsilon^2\hbar^2} \left| \sum_t \frac{\langle e|\boldsymbol{\mu}|t\rangle\langle t|\boldsymbol{\mu}|g\rangle}{E_{tg} - E + i\Gamma_t} \right|^2 u^2(\omega_0) \quad (9)$$

$$\hbar\omega_{tg} \equiv E_{t_1} - E_g \equiv E_{t_2} - E_g \quad (10)$$

$i\Gamma_t$ is a relaxation term introduced phenomenologically to avoid divergence under resonance conditions.

It can be seen from equation (9) that the transition probability of two-photon absorption is proportional to the square of the incident light energy $u(\omega_0)$. For a two-photon absorption transition to be permissible in a system with inversion symmetry, the states associated with each other must have inverse parity. That is, the parity of $|T_1\rangle$ and $|T_2\rangle$ must be opposite to the parity of both $|g\rangle$ and $|e\rangle$. This means that $|g\rangle$ and $|e\rangle$ must have the same parity, and this selection rule is the same as the selection rule for the Raman scattering, which is to be explained in the next section.

In single-crystal diamond, the center of symmetry is at the midpoint of the bond between neighboring atoms (Figure 2-1). In optical modes in which two atoms in the unit cell vibrate in opposite directions, the symmetry coordinates do not change sign for inversion symmetry

operations. Therefore, the parity is even. In diamond single crystal, one-photon absorption is a forbidden transition, and two-photon absorption is an allowed transition.

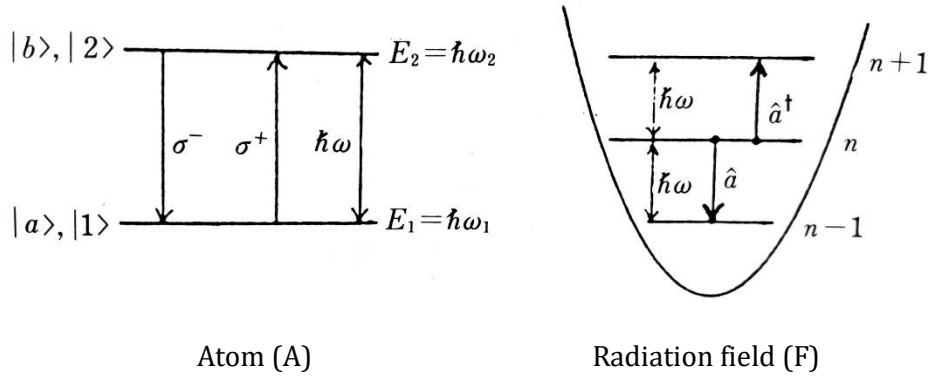


Figure 2-4 Schematic diagram for handling interactions between atoms and radiation fields (reproduced and modified from the reference [28]).

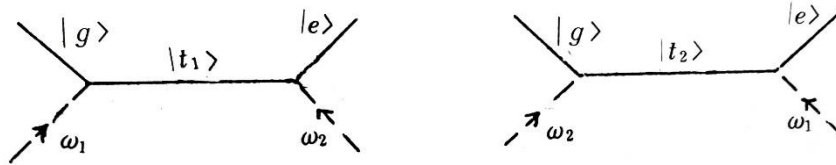


Figure 2-5 How to create an intermediate state for two-photon absorption [28].

2.1.3 Raman scattering

In this study, I use anti-Stokes Raman scattering spectroscopy to demonstrate the selective lattice vibration excitation by FEL described in the previous chapter.

When incident light is irradiated on a material, (Stokes or anti-Stokes) Raman scattering is a phenomenon that, the incident photons and lattice vibrations exchange energy, producing light with a wavelength different from that of the incident light. When a material is irradiated with monochromatic light of angular frequency ω_0 , Rayleigh scattering occurs with a component whose frequency is equal to that of the incident light. In addition, Stokes Raman scattering occurs with a component of frequency $\omega_0 - \omega_r$, where the angular frequency is shifted by lattice vibration frequency ω_r in the negative direction. Anti-Stokes Raman scattering has a component of $\omega_0 + \omega_r$, where the angular frequency is shifted by ω_r in the positive direction. The frequency ω_r is called as the Raman shift and is equal to the angular frequency corresponding to the transition energy of the material. At room temperature, multiple vibrational modes are excited by thermal energy, and their multiple anti-Stokes scattering light bands are observed. On the other hand, no anti-Stokes scattering light is observed at extremely low temperatures because thermal excitation is totally suppressed. Therefore, if anti-Stokes Raman scattering light is observed at extremely low temperatures under a certain light irradiation condition, this should prove the lattice vibration whose frequency corresponds to the frequency of the irradiation light is excited. In other words, if specific anti-Stokes scattering light is successfully observed only during FEL irradiation at an extremely low temperatures, selective lattice vibration excitation of a single mode can be demonstrated. Energy diagrams for this process are shown in Figure 2-6 (a) to (c) [13].

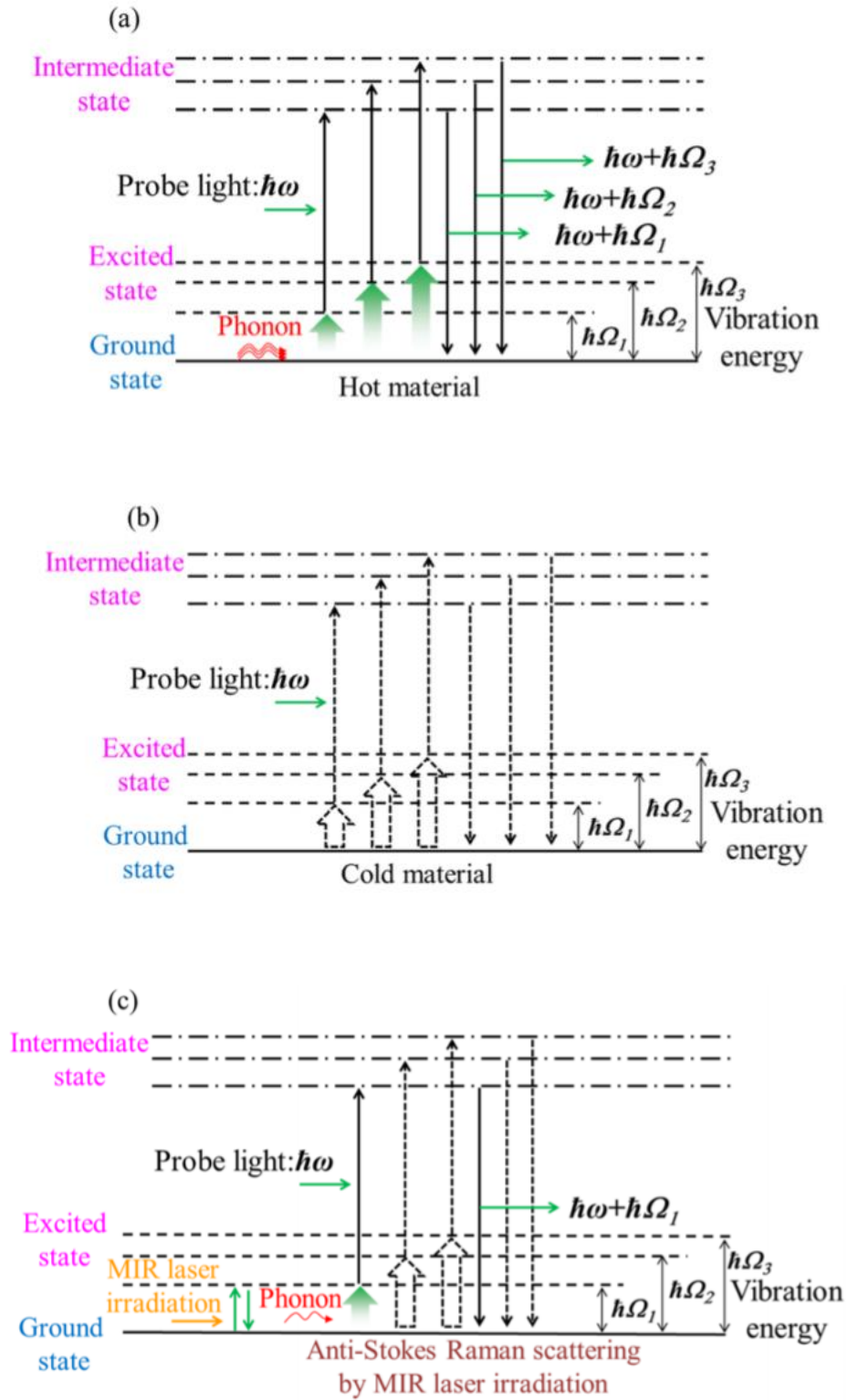


Figure 2-6 Energy diagrams of anti-Stokes Raman scattering: (a) hot material (b) cold material, and (c) cold material with MIR laser irradiation[13].

2.2 Experiment

I describe selective lattice vibration excitation and a measurement system for its demonstration of the mode-selective phonon excitation. Figure 2-7 shows a schematic diagram of the measurement system. The FEL, which is an excitation light source for the selective lattice vibration mode excitation, and a probe laser for anti-Stokes Raman scattering are used for measurements. I constructed an equipment system for the purpose of irradiating them temporally and spatially synchronously and measured the anti-Stokes Raman scattered light. Both the pump FEL and probe lasers are pulse lasers, and a trigger, function generator, and delay generator were used to synchronize the time they irradiate the sample and the time they measure the scattered light. An optical delay stage was also used for synchronization with the picosecond probe laser.

The flow of actual measurement is explained in detail. First, the fundamental wave of 1064 nm from the probe laser is incident on the second harmonic crystal to generate the light of 532 nm. A short-pass filter (SPF) is then used to cut the 1064 nm fundamental wave, and a quartz lens is used to focus the laser onto the sample surface. A parabolic mirror is used to irradiate the FEL to the focused probe laser from the same axis, and the beams are adjusted so that they overlap. The sample is kept in vacuum in a cryostat (1005 337; TAIYO NIPPON SANSO CORPORATION) and cooled to 5 K using a helium compressor (CKW-21A; Sumitomo Heavy Industries). A film heater installed in the cryostat is used to adjust the temperature. For the window material, KBr, which has high transmittance to infrared light, is used on the incident light side, and quartz glass is used on the scattered light side. The scattered light is made parallel by a collimator lens and propagated. In general, the intensity of Rayleigh scattering light is about six orders of magnitude stronger than that of Raman scattered light [32], leading to a decrease in the S/N ratio. Therefore, the Rayleigh scattering light generated from the sample is removed through a notch filter (NF533-17; Thorlabs). The light is then focused by a lens and incident on a spectrometer (Triax 190; Horiba Scientific). The generated scattering light is output as an electrical signal regarding wavelength and intensity using a spectrometer and a cooled CCD with an image intensifier (PI-MAX2; Princeton Instruments), which is analyzed using a digital oscilloscope and computer.

In addition, to improve the S/N ratio, I used a sample stage in the cryostat with a hole on the back of the sample. This hole is thought to suppress stray light generated inside the cryostat and reduce noise. When using a picosecond probe laser, I measure the sum frequency generation using ZnS Cleartran (Pier Optics), which does not have inversion symmetry and supports multiple wavelength spectra. The size is 5.0 mm × 5.0 mm × 0.3 mm. As the measurement sample, a single crystal diamond (100) surface polished sample (145-500-0253; Element six) is used. The sample size is 3.0 mm × 3.0 mm × 0.3 mm. Coaxial with the laser beam, I placed ZnS and single-crystal diamond next to each other (Figure 2-8).

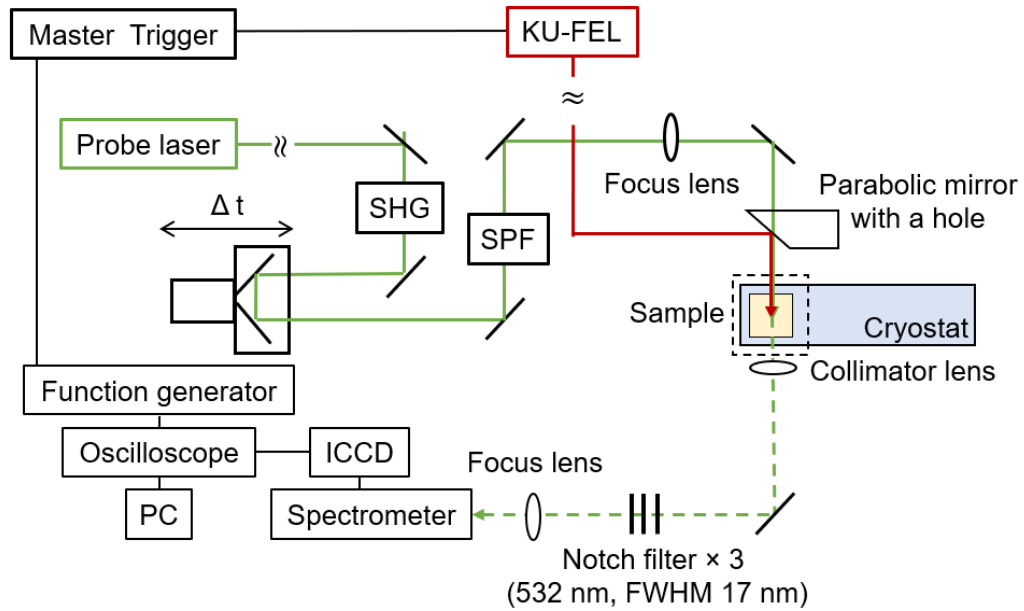
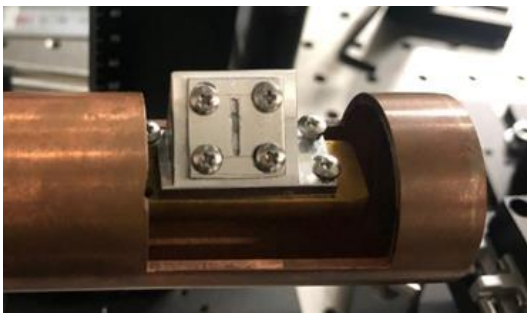


Figure 2-7 Schematic diagram of measurement system.

(a)



(b)

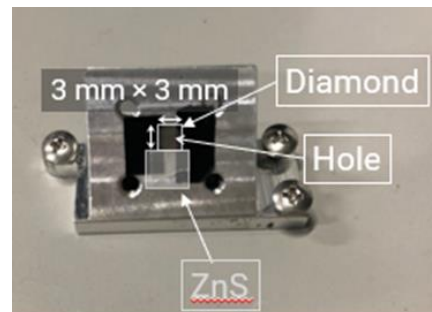


Figure 2-8 (a) Sample stage inside the cryostat (b) Sample installation diagram.

2.3 Results and discussions

2.3.1 Sample properties

First, in order to confirm thermal lattice vibration excitation at ambient temperature, I irradiated only the probe light without irradiating the FEL and observed the Raman scattering spectrum of single-crystal diamond. A nanosecond laser was used as the probe laser.

Figure 2-9 shows the Stokes Raman scattering spectrum. Various parameters of this measurement are listed in Table 2-2. When fitting the scattering band in Figure 2-9 using a Gaussian function, the peak position was found to be 1333 cm^{-1} (FWHM: 18 cm^{-1}).

Table 2-2 Experimental parameters for Stokes Raman scattering spectrum observation.

Temperature / K	297	Measurement average / times	3611
Nd:YAG laser pulse energy / μJ	85	Spectrometer slit width / mm	0.1

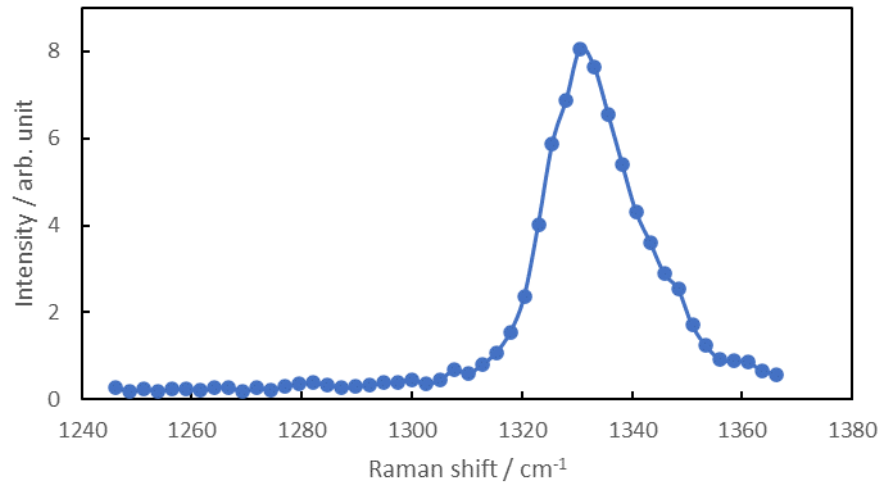


Figure 2-9 Stokes Raman scattering spectrum of single crystal diamond at room temperature.

Next, the anti-Stokes Raman scattering light of the diamond at ambient temperature was measured. When I measured the energy intensity of the probe laser at 90 μJ , the peak intensity was small, so I increased the energy intensity of the probe laser to 150 and 200 μJ . As a result, as the energy intensity of the probe laser increased, the peak intensity also increased, making it possible to obtain a sharper waveform. The anti-Stokes Raman scattering spectra obtained from the experiments are shown in Figure 2-10 to Figure 2-12, and the various parameters of each experiment are shown in Table 2-3 to Table 2-5. Figure 2-13 shows the change in peak intensity at that time. Using a Gaussian function to fit the scattering band at a probe laser intensity of 200 μJ , where the strongest peak intensity was obtained, the peak position was -1336 cm^{-1} (FWHM: 43 cm^{-1}).

Table 2-3 Experimental parameters for Anti-Stokes Raman scattering spectrum observation.

Temperature / K	297	Measurement average / times	3042
Nd:YAG laser pulse energy / μJ	90	Spectrometer slit width / mm	0.3

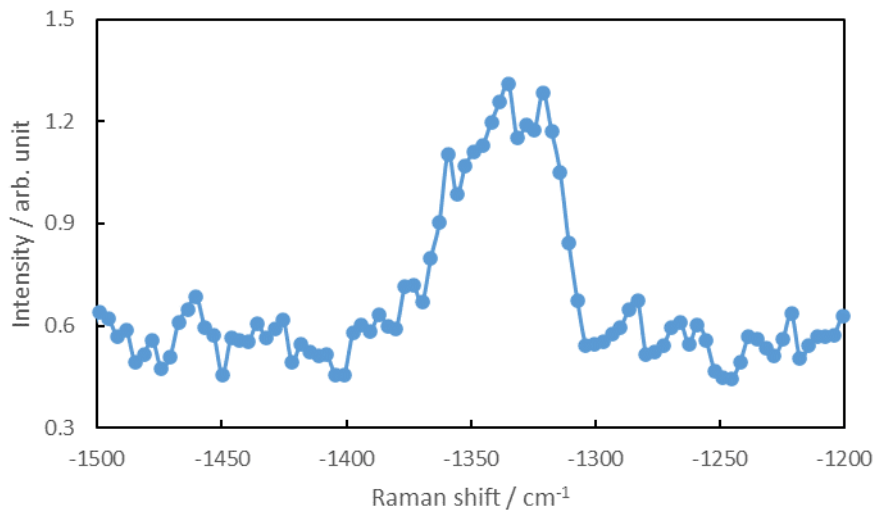


Figure 2-10 Anti-Stokes Raman scattering spectrum of single crystal diamond at room temperature.

Table 2-4 Experimental parameters for Anti-Stokes Raman scattering spectrum observation.

Temperature / K	297	Measurement average / times	3017
Nd:YAG laser pulse energy / μJ	150	Spectrometer slit width / mm	0.3

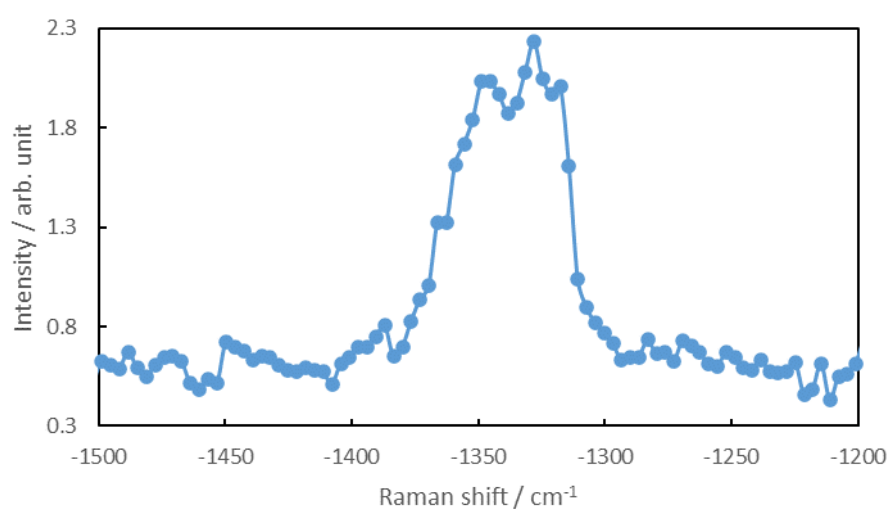


Figure 2-11 Anti-Stokes Raman scattering spectrum of single crystal diamond at room temperature.

Table 2-5 Experimental parameters for Anti-Stokes Raman scattering spectrum observation.

Temperature / K	297	Measurement average / times	3129
Nd:YAG laser pulse energy / μJ	200	Spectrometer slit width / mm	0.3

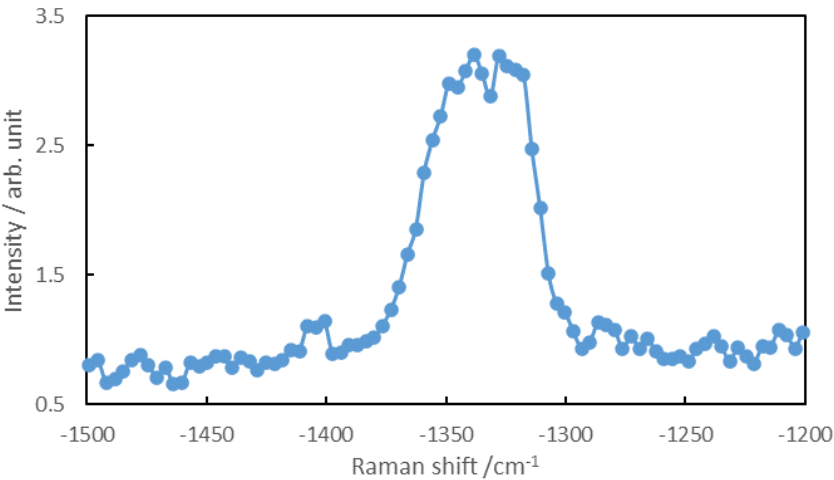


Figure 2-12 Anti-Stokes Raman scattering spectrum of single crystal diamond at room temperature.

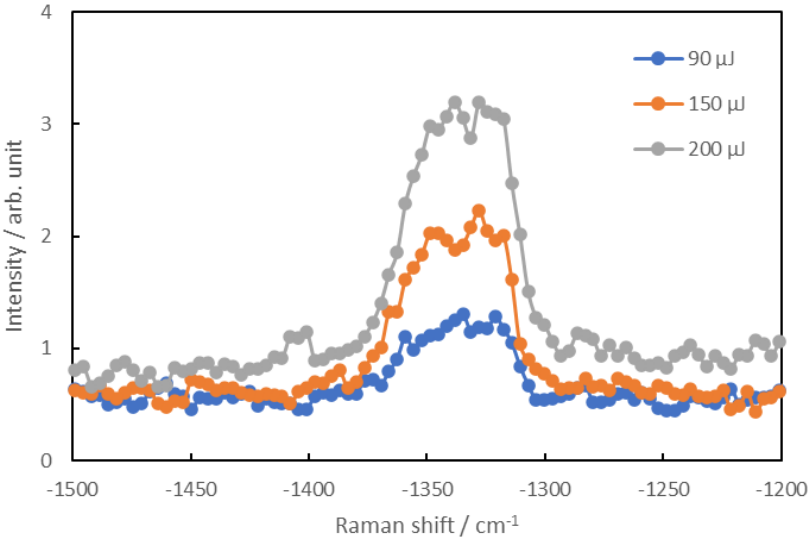


Figure 2-13 Peak intensity change when changing probe laser energy intensity.

2.3.2 Selective lattice vibration excitation

Selective lattice vibration excitation experiments of single-crystal diamond were performed at 5 K using a picosecond laser as a probe laser. Only when irradiated with FEL light (666 cm^{-1}), which corresponds to half the energy of the diamond T_{2g} mode, a signal with a peak around -1,340 cm^{-1} could be observed. The anti-Stokes Raman scattering spectra obtained from the experiment are shown in Figure 2-14 and Figure 2-15, and experimental parameters are shown in Table 2-6.

When fitting the scattering band in Figure 2-16 with a Gaussian function, the peak position was -1339 cm^{-1} (FWHM: 26 cm^{-1}). This value is 7 cm^{-1} off from the typical diamond T_{2g} mode peak value of -1332 cm^{-1} . A more detailed analysis of the peaks is required to discuss this shift. To this end, I next performed selective lattice vibration excitation experiments by varying the width of the spectrometer slit.

In the previous study of our research group, a signal with a peak at around -1306 cm^{-1} was observed when the same sample was irradiated by the MIR-FEL (the macropulse energy: 6.5 mJ) and the picosecond probe laser of 70 μJ with the spectrometer slit width of 1.0 mm [29]. This peak shows a redshift from the typical T_{2g} phonon peak which is 1332 cm^{-1} . Not only the redshift but also the broadening of the band width up to 120 cm^{-1} was observed. However, in the current study, the redshift was eliminated and a sharp line shape of the band was obtained by lowering the probe laser intensity as shown in Figure 2-14.

Table 2-6 Experimental parameters for selective lattice vibration excitation in single crystal diamond.

Temperature / K	5	FEL wavelength / μm	15.0
Nd:YVO ₄ laser pulse energy / μJ	30	FEL macropulse energy / mJ	4.9
Measurement average / times	807	FEL wavenumber (two-photon) / cm^{-1}	1332
Spectrometer slit width / mm	0.3		

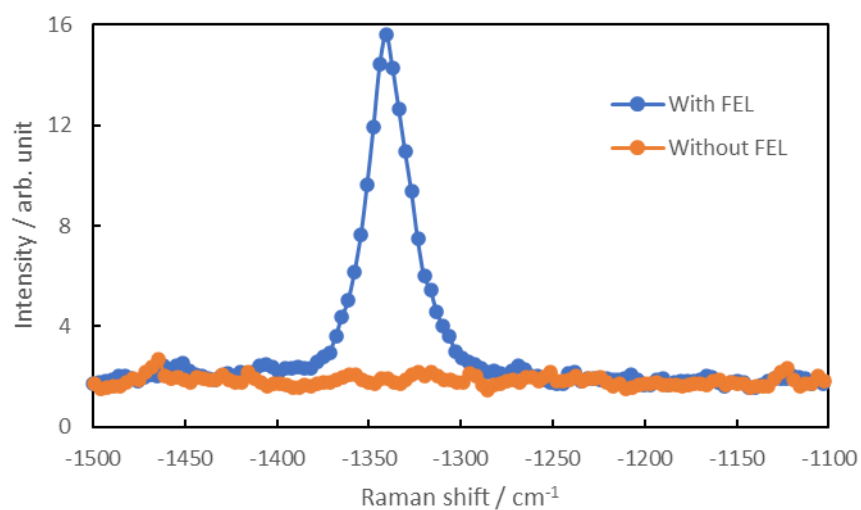


Figure 2-14 Anti-Stokes Raman scattering spectra of selective lattice vibrational excitation of diamond T_{2g} mode.

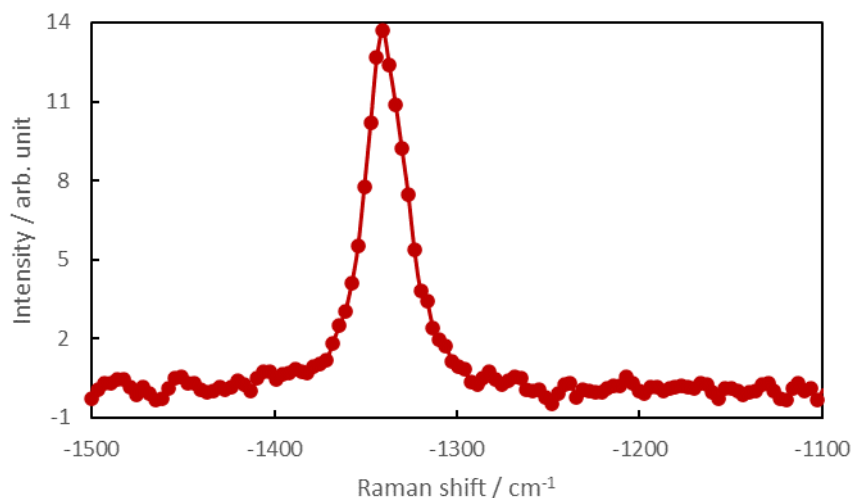


Figure 2-15 Spectrum obtained by subtracting the intensity when FEL is not irradiated from the intensity when FEL is irradiated.

In order to analyze the peaks of the scattering bands in more detail, I adjusted the slit width of the spectrometer. At the sample installation point, I also visually narrowed down the FEL beam diameter as much as possible. The beam diameter of the picosecond laser was also narrowed down to bring the focus of the pump light as close to the surface as possible.

The slit width was narrowed to 0.3 mm, 0.1 mm, 0.05 mm, and 0.01 mm, and the change in peak intensity at that time was investigated. The peak intensity changes are summarized in Figure 2-16, experimental parameters are shown in Table 2-7 and the fitting results for each spectrum are summarized in Table 2-8. The peak position (-1336 cm^{-1}) when the slit width was 0.05 mm was close to the typical diamond T_{2g} mode peak position (-1332 cm^{-1}). From Figure 2-16, the narrower the spectrometer slit width, the lower the peak intensity. Nevertheless, the peak width for the slit width of 0.05 mm compared with 0.3 mm is about one half, and the resolution is improved. However, when comparing the slit widths of 0.05 mm and 0.01 mm, neither the peak intensity nor the peak width changed much. When the slit width was narrowed, the peak position became affected by minute changes in the background. Based on this, I thought that it would be difficult to narrow the slit width any further.

Table 2-7 Experimental parameters for selective lattice vibration excitation in single crystal diamond.

Temperature / K	5	FEL wavelength / μm	15.0
Nd:YVO ₄ laser pulse energy / μJ	30	FEL macropulse energy / mJ	4.6
Spectrometer slit width / mm	0.01, 0.05 0.1, 0.3	FEL wavenumber (two-photon) / cm^{-1}	1332
Measurement average / times	About 800		

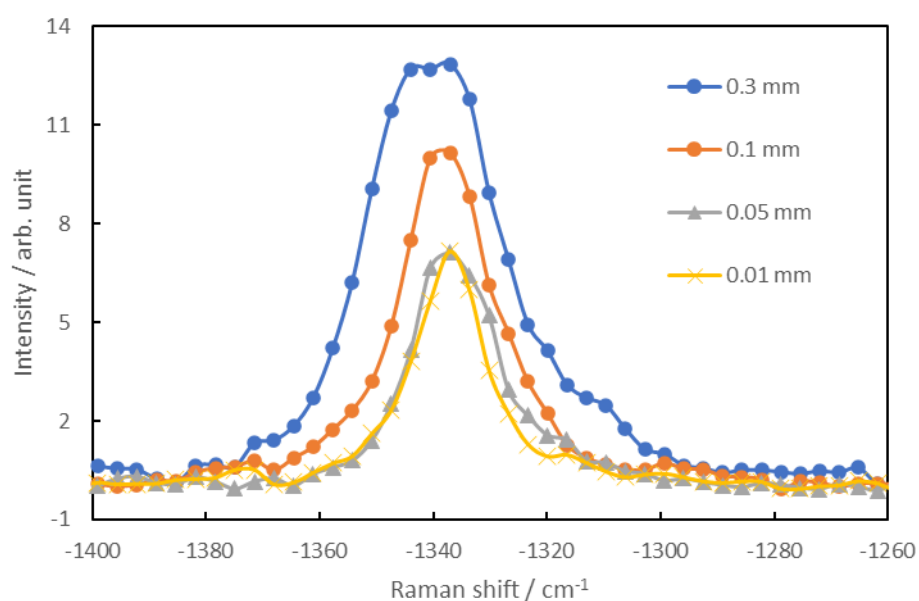


Figure 2-16 Change in peak intensity when changing the slit width (spectrum obtained by subtracting the intensity when FEL is not irradiated from the intensity when FEL is irradiated).

Table 2-8 Fitting results for the data in Figure 2-16.

Spectrometer slit width / mm	0.3	0.1	0.05	0.01
Peak intensity / arb. unit	12.75	9.58	6.86	6.44
Peak position / cm^{-1}	-1339.72	-1337.67	-1336.27	-1337.18
FWHM / cm^{-1}	26.09	19.19	16.93	16.05

2.3.3 KU-FEL energy dependence

The transition probability of two-photon absorption shows a second-order nonlinear optical response to the ‘energy’ of incident light. Note that the term ‘energy’ In this subsection means irradiation intensity indicated with the unit J (joule), not photon energy (eV) proportional to the inverse of the light wavelength. Based on this, as a demonstration experiment of selective lattice vibration excitation in diamond, I conducted an experiment to investigate the FEL energy intensity dependence of the peak. If the signal peak around -1340 cm^{-1} observed in the previous section is actually anti-Stokes Raman scattering light of the diamond T_{2g} mode, its intensity should be proportional to the square of the FEL energy, as it is excited by two-photon absorption of the pump laser. The energy intensity of the FEL was adjusted to 4.9 mJ, 3.2 mJ, 2.1 mJ, and 1.1 mJ by manipulating the aperture system. Various experimental parameters are shown in Table 2-9. And Figure 2-17 shows the spectrum obtained by subtracting the intensity during non-irradiation from the intensity during FEL irradiation. The signal intensity at -1340 cm^{-1} and their fitting to $y = ax$, $y = bx^2$ are shown in Figure 2-18 (a), and the logarithm of (a) is summarized in (b).

In Figure 2-17, the intensity is maximum at -1340 cm^{-1} , so the peak intensity at -1340 cm^{-1} is plotted against FEL energy (Figure 2-18 (a)). Figure 2-18 (b) shows this on a logarithmic scale. As a result of fitting the peak intensity with respect to FEL energy to a linear function and a quadratic function, it is closer to a quadratic function than a linear function. However, it did not show a perfect second-order nonlinear optical response. The reason is that the signal strength is low and the background has a large influence on the peak when measuring

FEL energy intensity of 2.1 mJ and 1.1 mJ.

Table 2-9 Experimental parameters of FEL energy intensity change.

Temperature / K	5	FEL wavelength / μm	15.0
Nd:YVO ₄ laser pulse energy / μJ	30	FEL macropulse energy / mJ	1.1, 2.1, 3.2, 4.9
Measurement average / times	807	FEL wavenumber (two-photon) / cm^{-1}	1332
Spectrometer slit width / mm	0.3		

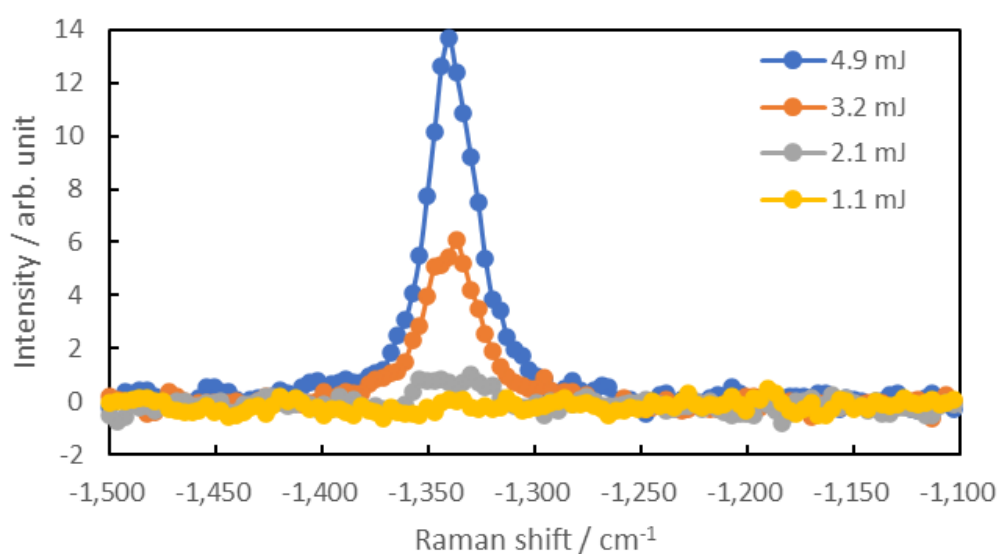
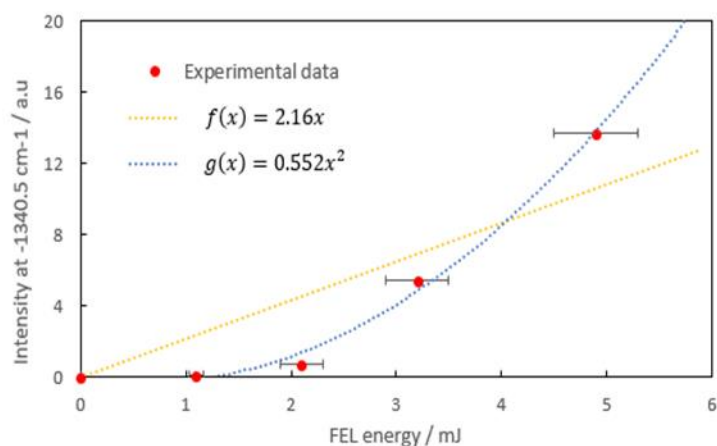


Figure 2-17 Anti-Stokes Raman scattering spectra when changing FEL energy (spectrum obtained by subtracting the intensity when FEL is not irradiated from the intensity when FEL is irradiated).

(a)



(b)

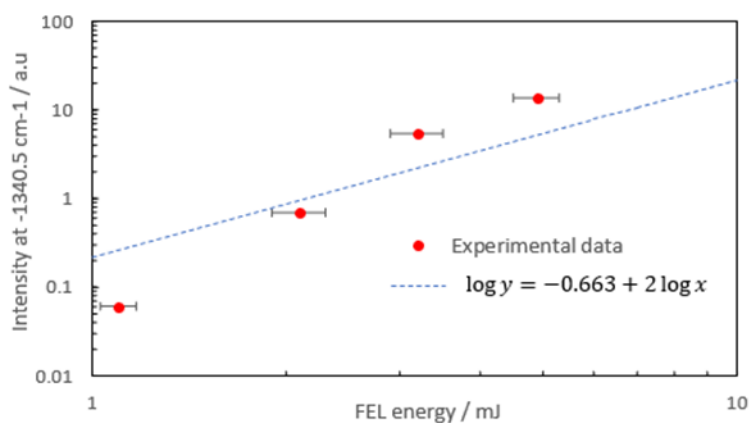


Figure 2-18 (a) FEL energy dependence at -1340.5 cm^{-1} (b) A graph plotting the graph in (a) on a logarithmic scale.

2.3.4 Time change of peak intensity

Finally, I varied the delay time of the probe laser (picosecond laser) with respect to the pump laser (FEL) and measured the change in peak intensity around -1340 cm^{-1} . The results are presented in Figure 2-19. Experimental parameters are shown in Table 2-10. Signals were observed in the range of 3 to 25 ps. The time width of the micropulse of FEL, which is the pump laser, is 0.6 ps, and the pulse width of the picosecond laser, which is the probe laser, is 7.5 ps. The half-width of the observed 22 ps wide time spectrum is approximately 12 ps.

This is thought to be because the excitation phonon signal, which has a lifetime of several ps, is broadened by the probe laser, which has a wider time width of 7.5 ps. This suggests a phonon relaxation time of several ps, which is consistent with the T_{2g} mode phonon relaxation time.

Table 2-10 Experimental parameters of FEL energy intensity change.

Temperature / K	5	FEL wavelength / μm	15.0
Measurement average / times	About 800	FEL macropulse energy / mJ	1.1
Nd:YVO ₄ laser pulse energy / μJ	30	FEL wavenumber (two-photon) / cm^{-1}	1332
Spectrometer slit width / mm	0.3		

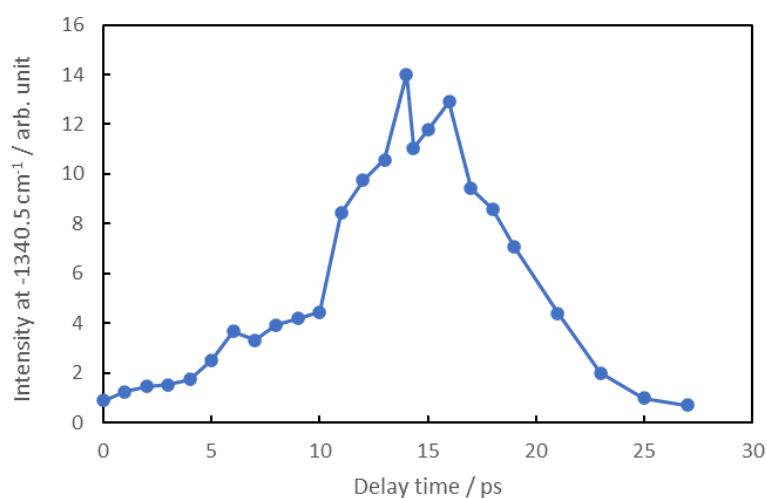


Figure 2-19 Peak intensity change at -1340.5 cm^{-1} when changing the delay time of picosecond laser relative to FEL.

2.3.5 Electron microscopy observation of sample surface

The samples used in this study were observed using a scanning electron microscope (FE-SEM) (SU6600; Hitachi High-Technologies). A photograph and SEM image of the sample are shown in Figure 2-20. There were no irradiation marks found in the samples used in this study, and it is thought that no damage was caused by the laser.

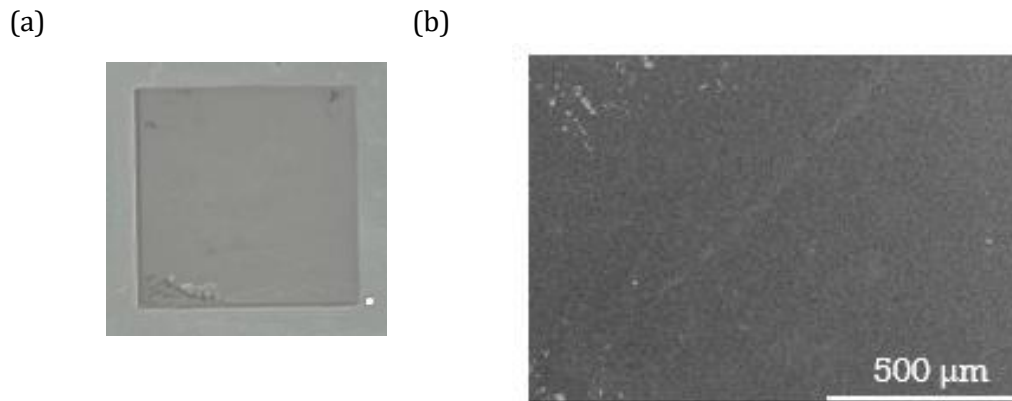


Figure 2-20 (a) Sample photo (b) SEM image.

2.4 Conclusion

I attempted selective lattice vibrational excitation of the Raman-active but infrared-inactive diamond T_{2g} mode (1332 cm^{-1}) using a mid-infrared free electron laser (MIR-FEL). Since the diamond T_{2g} mode is an allowable transition in the two-photon absorption process, the oscillation wavelength of the KU-FEL was adjusted to $15\text{ }\mu\text{m}$ (666 cm^{-1}) and single-crystal diamond was irradiated.

In the previous research of our research group, a laser fracture surface was generated in the sample, and the Raman shift value was red-shifted. However, in this study, both the destruction and the red shift were resolved by lowering the probe light intensity and reviewing the measurement system. By adjusting the slit width and improving the resolution, a signal with a peak around 1339 cm^{-1} was obtained only during FEL irradiation under two-photon excitation conditions. This peak was consistent even if I assumed a dependence close to a second-order nonlinear optical response on the FEL energy.

Furthermore, when changing the delay time of the picosecond laser pulse, which has a time width of 7.5 ps, compared to the FEL micropulse, which has a time width of 0.6 ps, a peak was observed over 22 ps. The excitation phonon lifetime is thought to correspond to a signal pulse width of 10.5 to 25 ps, subtracted from the probe laser. This suggests a phonon relaxation time of several picoseconds, which is consistent with results reported by other research groups. Furthermore, when the sample used in the experiment was observed with an SEM, no traces of irradiation were found, suggesting that no damage was caused by the laser.

Based on the above results, he believes that he has actually demonstrated selective lattice vibrational excitation of the diamond T_{2g} mode by two-photon excitation in the FEL. As a result, selective excitation of the so-called infrared inactive mode using FEL was achieved, and it was suggested that selective excitation of other infrared inactive modes is also possible.

3. Stokes Raman Spectroscopy for mode-selective phonon excitation in widegap semiconductors

3.1 Introduction

3.1.1 Widegap semiconductor samples

In the previous chapter, I succeeded in the selective excitation of the infrared inactive mode. In this chapter I attempted to selectively excite the lattice vibration of the Raman inactive mode and detect a weak signal. $\text{Y}_2\text{O}_3\text{-ZrO}_2$ (YSZ), TiO_2 (rutile), and GaP were used as samples. YSZ has a fluorite-type crystal structure. It is characterized by high hardness and high ionic conductivity, and it is often used in solid-oxide fuel cell materials and oxygen sensors [33]. Rutile is the most stable crystal structure of TiO_2 , and is used in many applications such as white pigments and capacitor insulators [34]. GaP single crystal is an indirect transition type compound semiconductor. Since it emits light when doped with ZnO or S, it is often used as a light-emitting diode [35][36]. Table 3-1 summarizes the target vibration modes and their wavelengths for each sample.

Table 3-1 The target vibration modes and Peak positions of target signal for each sample.

	YSZ [33]	Rutile [34]	GaP [35][36]
Target vibration modes	T_{1u}	E_u	2LO
Peak positions of target signal / cm^{-1}	680	850~900	780~800

3.1.2 Hyper-Raman scattering

Hyper-Raman scattering (HRS) is a three-photon process in which a system is excited with two photons of frequency ω_i and emits one photon at the frequency $2\omega_i \pm \omega$ (ω : the frequency of vibrational excitation of the medium)[37]. Thus the HRS spectrum must be located in the spectral region of the doubled frequency of the ω_i exciting radiation.

The Raman scattering spectroscopy used in the previous chapter was a phenomenon in which the one-photon excited state is the intermediate state of Raman scattering. However, HRS is a nonlinear phenomenon with a two-photon excited state as an intermediate state. Similar to the linear Raman scattering, two types of light are generated: Stokes scattering light, which has an energy lower than the energy of the incident photon, and an anti-Stokes scattering light, which has an energy higher than the energy of the incident photon. In addition, the selection rules for the HRS are almost opposite to those for the linear Raman scattering. If a particular mode is infrared active, it is hyper-Raman active, and even a part of the silent modes which are both Raman-inactive and infrared-inactive turn hyper-Raman active. The law of energy conservation in the HRS process couple the frequency of the excitation light and the frequency of the scattering radiations as displayed in Figure 3-1 [37]. Namely, for ω_i of excitation, $2\omega_i - \omega$ is expected to be observed for the Stokes scattering, and $2\omega_i + \omega$ is expected for the anti-Stokes scattering.

By using the HRS for the probe system in pump-probe selective phonon-mode excitation spectroscopy, I attempt to demonstrate the selective excitation of the Raman inactive modes.

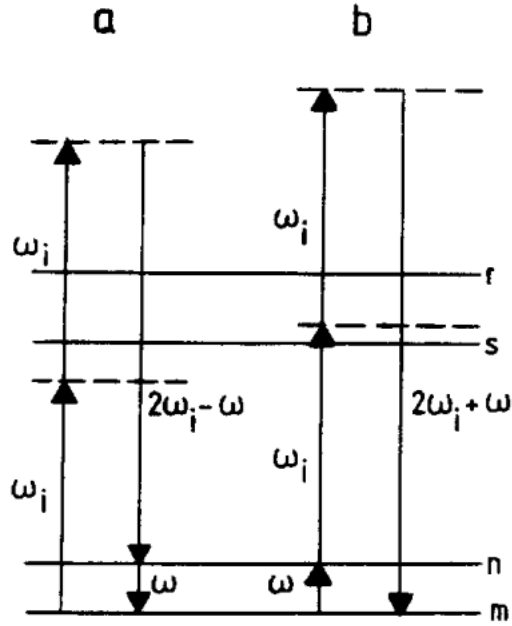


Figure 3-1 (a) Hyper-Raman scattering stokes and (b) anti-stokes vector diagram [37].

3.1.3 Resonant raman scattering

Resonant Raman scattering is a phenomenon in which the wavelength of incident light matches the band gap energy or the energy of a larger interband transition. On such condition, the intensity of Raman scattering light increases significantly due to resonance effects by several orders of magnitude.

By using this resonant Raman scattering spectroscopy for the excitation in probe system, I attempted to detect and measure weak signals with high sensitivity.

3.2 Experiment

The main experimental equipment system is the same as in the previous chapter, but since FEL is not used. (Figure 3-2) All measurements were performed at room temperature. The sample sizes are $3 \times 3 \times 0.5$ mm for YSZ, $5 \times 5 \times 0.5$ mm for Rutile, and $10 \times 10 \times 0.5$ mm for GaP.

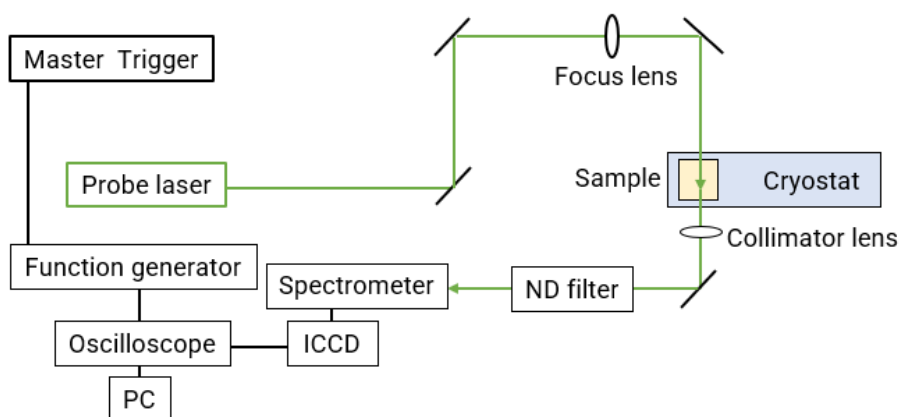


Figure 3-2 Schematic diagram of experimental equipment system.

I also performed electron energy band and phonon band calculations with Quantum ESPRESSO program suite based on the density functional theory (DFT). As for the transition metal elements, DFT+ U , DFT with Hubbard U correction method, along with DFT was used. PBEsol exchange-correlation potentials and Projector Augmented Wave (PAW) pseudopotentials were adopted. Details of the calculation method are described in chapter 5 and in chapter 6. I confirmed the bandgaps and interband transitions at Γ -point. Predicted phonon frequencies at Γ -point were also confirmed.

3.3 Results and discussion

3.3.1 Yttria-stabilized zirconia (YSZ)

Observation of anti-Stokes light is essential for selective lattice vibration excitation of HRS. Since the signal intensity of Stokes light is generally higher than that of anti-Stokes light at finite temperature, I first attempted to observe and confirmed the Stokes scattering light. A picosecond laser (Nd:YVO₄) was used as the probe laser. The measurement conditions are shown in Table 3-2, and the spectrum is shown in Figure 3-3. The target mode was T_{1u} mode located at 690 cm⁻¹, but no distinct signal could be observed. The sample surface was observed with SEM and irradiation marks of fracture were found to be formed. The results are presented in Figure 3-4.

Table 3-2 The measuring conditions.

Probe laser intensity / μJ	2700
Measurement average / times	10155
Slit width / mm	1.0

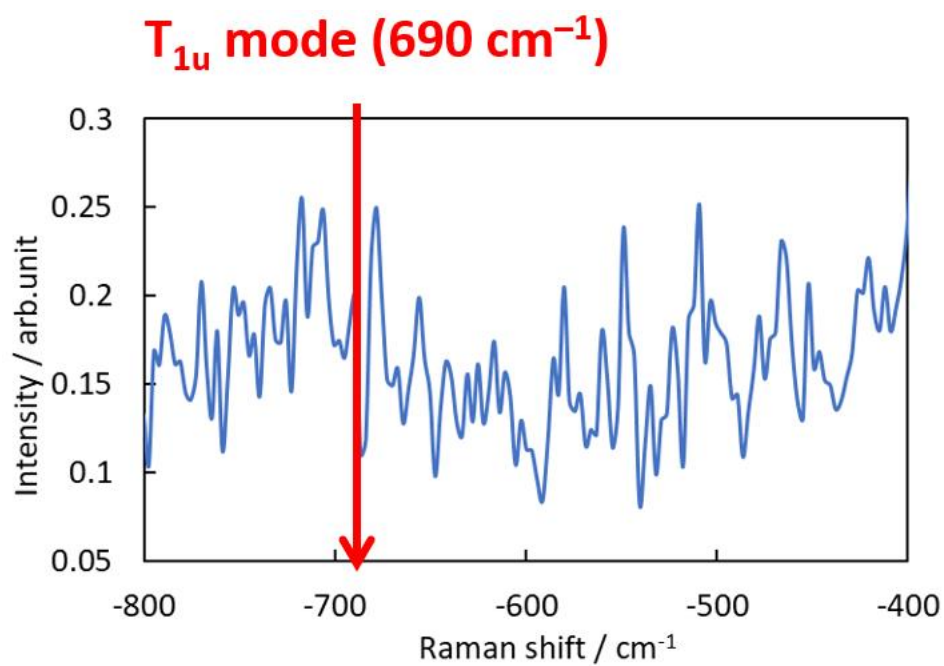


Figure 3-3 Stokes Hyper-Raman spectrum of YSZ.

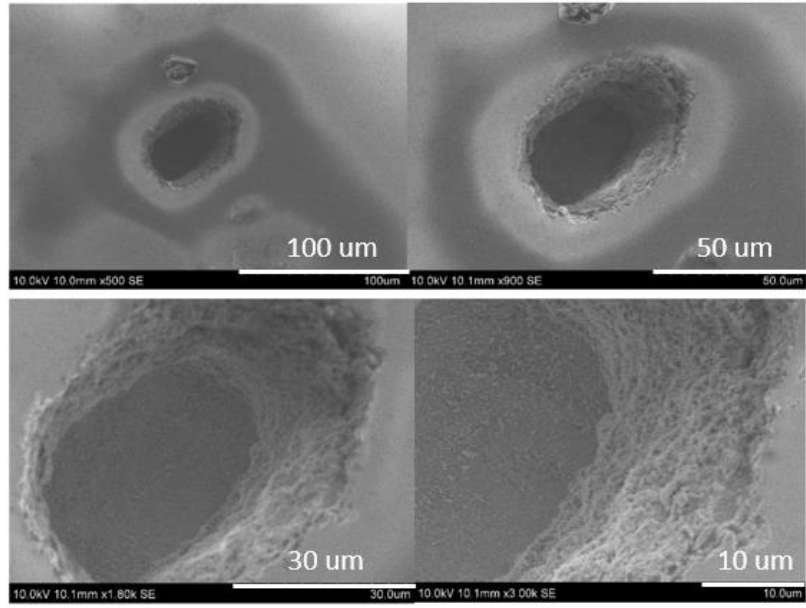


Figure 3-4 SEM image of the fracture surface of the damage induced by laser irradiations.

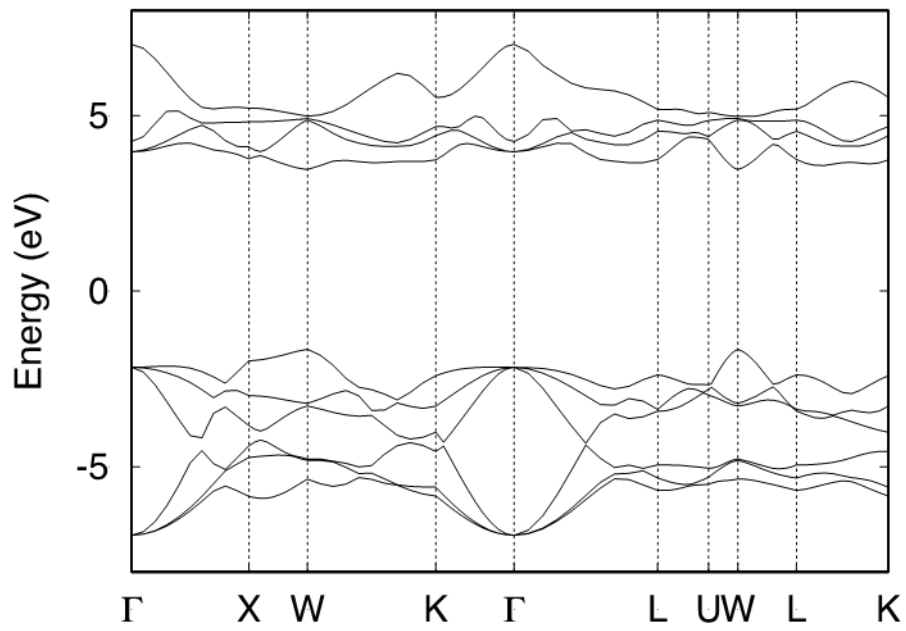


Figure 3-5 Energy band structures for ZrO_2 calculated with DFT+ U method.

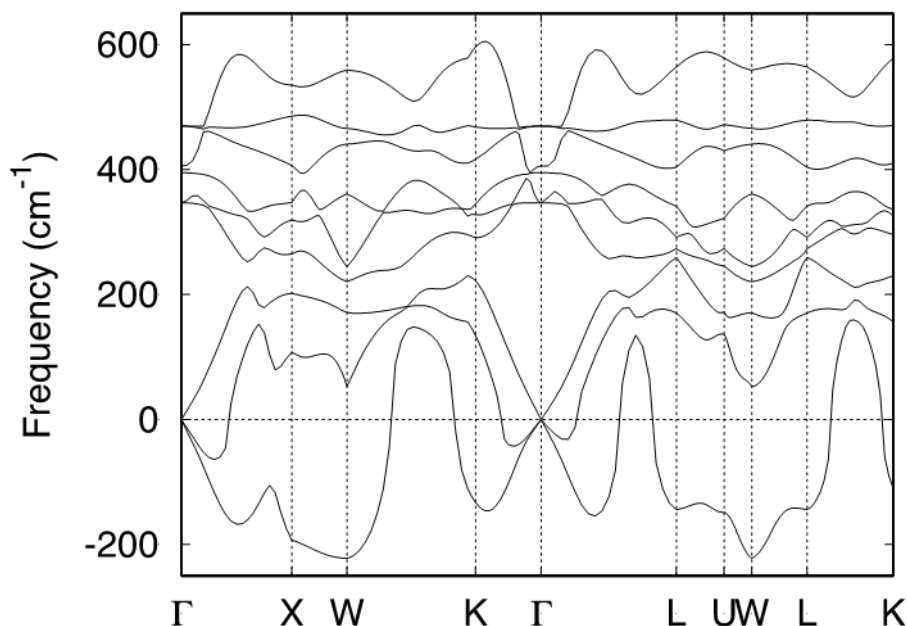


Figure 3-6 Phonon band structures for ZrO₂ calculated with DFT+*U* method.

Calculated electron energy band and phonon band for non-doped cubic zirconia are displayed in Figure 3-5 and Figure 3-6. The problem of negative frequencies often observe in metastable crystal structure are discussed in chapter 6. Though calculated bandgap is large, calculated phonon frequencies are shifted toward lower direction and the mode which I tried to observe is not reproduced. It is speculated from the electron band structure that the two-photon excitation with the present probe laser induces rise of noise level especially when the laser excitation intensity is high.

3.3.2 Rutile

As the preliminary measurement for YSZ, I first attempted to observe the Stokes scattering light of rutile. A picosecond laser (Nd:YVO₄) was used as the probe laser. The measurement conditions are shown in Table 3-3, and the spectrum is shown in Figure 3-7. The target mode was E_u mode which was reported to be located at 822 cm⁻¹. Unfortunately, no distinct signal could be observed. Irradiation marks were formed on the sample surface, so it was observed using a SEM. The results are shown in the Figure 3-6.

Next, I calculated the electronic energy band and phonon band of rutile. The calculation results are shown in Figure 3-9 and Figure 3-10. Not only the electron energy band, but frequency dispersion of phonon band are reasonable, while it is estimated to be a little lower. The negative frequency problem did not take place for this system, possibly because rutile is the most stable phase.

Table 3-3 The measuring conditions.

Probe laser intensity / μJ	2000
Measurement average / times	3000
Slit width / mm	0.3

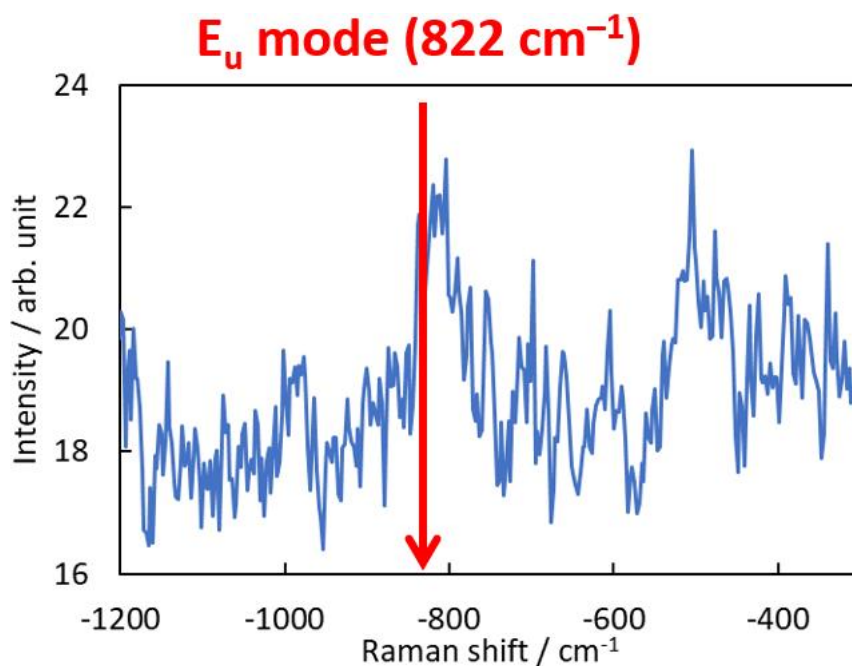


Figure 3-7 Stokes Hyper-Raman spectrum of rutile.

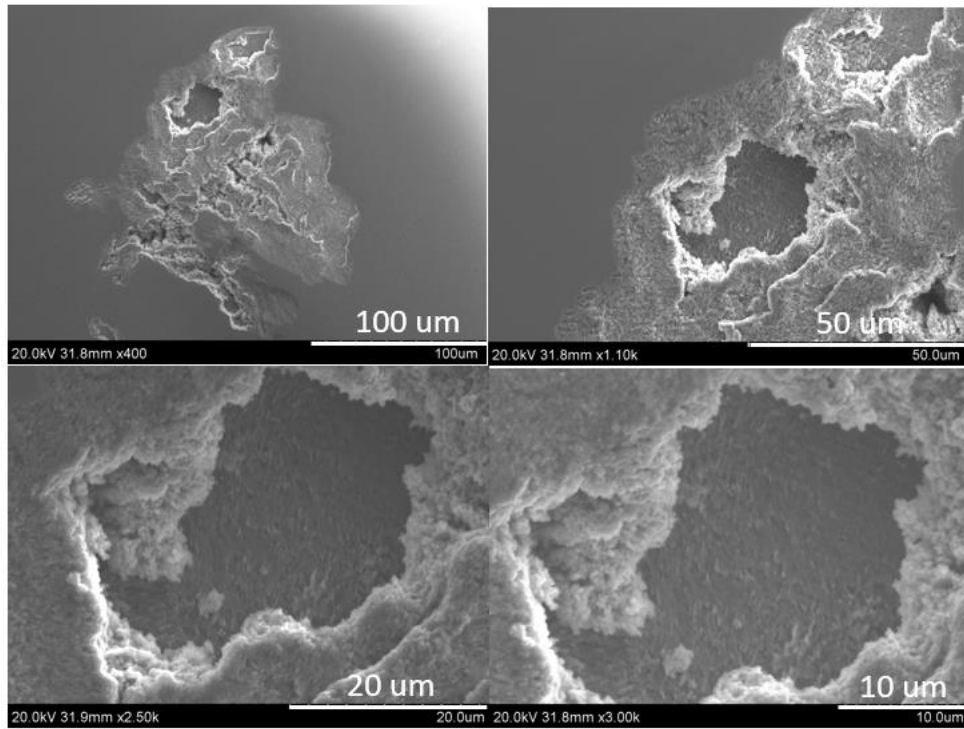


Figure 3-8 SEM images of the fracture surface of the damage induced by laser irradiations.

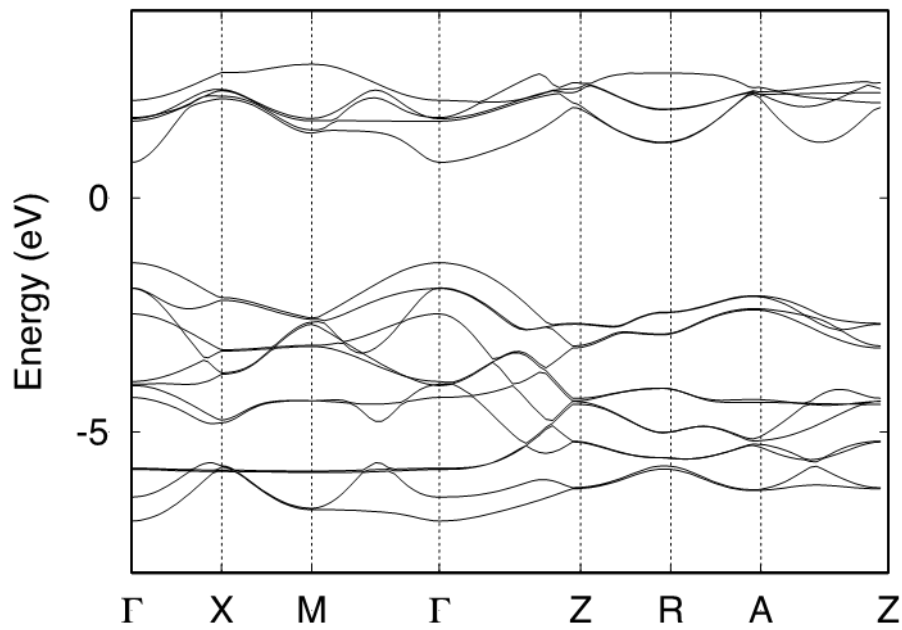


Figure 3-9 Energy band structures for rutile calculated with DFT+*U* method.

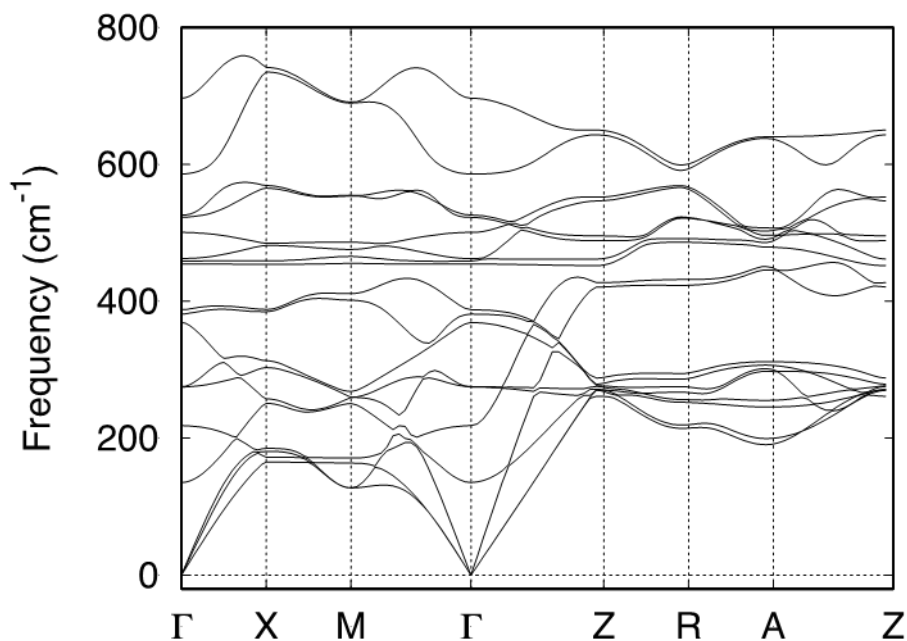


Figure 3-10 Phonon band structures for rutile calculated with DFT+*U* method.

As in the YSZ case, it is speculated from the electron band structure that the two-photon excitation with the present probe laser induces rise of noise level especially when the laser excitation intensity is high.

3.3.3 GaP

As YSZ and rutile measurement, I made preliminary research to observe the Stokes scattering light of gallium phosphide (GaP). OPOLETTE 355 (Tunable from 410 to 710 nm) was used as the probe laser. A long pass filter (LPF : 475 nm) was installed in front of the spectrometer to remove stray light from the excitation light. Furthermore, the tail of Rayleigh light was removed by installing a short pass filter (SPF: 450 nm) in front of the condenser lens. The measurement conditions are shown in Table 3-4, and the spectrum is shown in Figure 3-11. The target mode was 2LO mode located at 810 cm⁻¹. The Stokes

Raman scattering light signal could be observed. However, no anti-Stokes light signal could be observed.

I calculated the electronic energy band and phonon band of GaP. The calculation method will be explained in Chapter 5. The calculation results are shown in Figure 3-12 and Figure 3-13.

Table 3-4 The measuring conditions.

Probe laser intensity / μJ	50
Probe light wavelength / nm	441
Slit width / mm	0.01

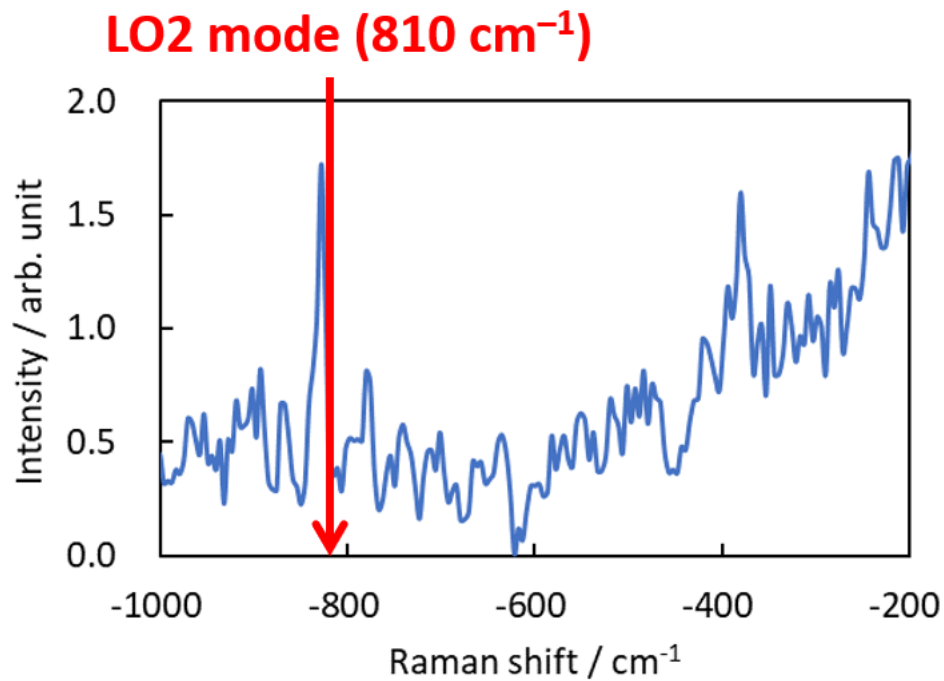


Figure 3-11 Stokes Raman spectrum of GaP.

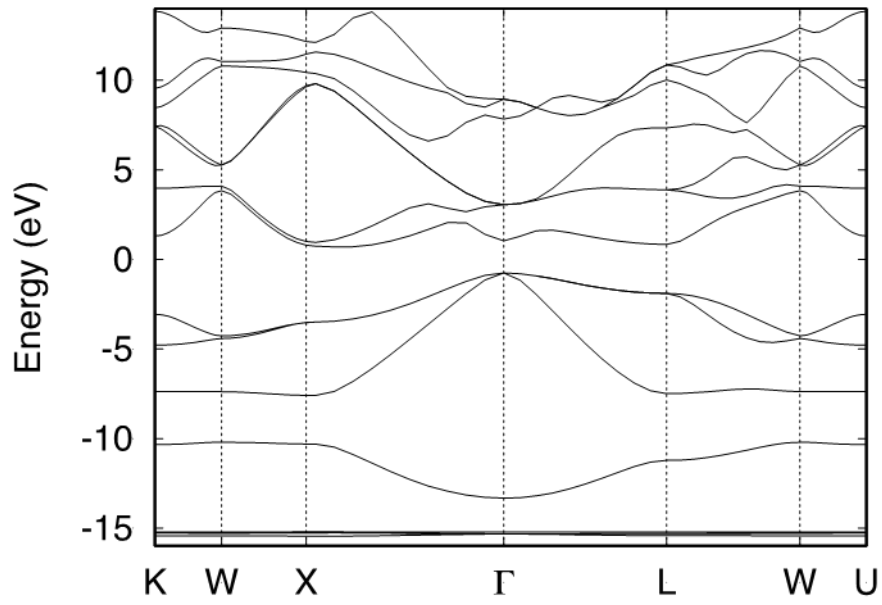


Figure 3-12 Electron energy band structures for GaP calculated with DFT method.

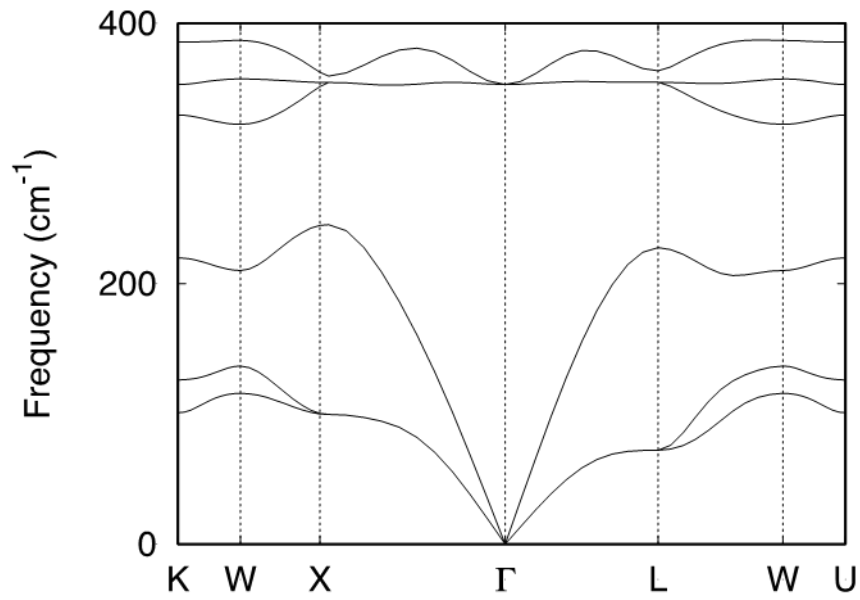


Figure 3-13 Phonon band structures for GaP calculated with DFT method.

The frequency of LO mode is slightly smaller than 400 cm^{-1} , and estimated 2LO should be less than 800 cm^{-1} . As obvious in the electron energy band, the bandgap energy is smaller in this case compared with YSZ or rutile. Therefore, the design of resonance Raman scattering measurements is reasonable. In such case, vertical direct transition at Γ -point estimated from this electron energy band diagram can be utilized.

3.4 Conclusion

Stokes Raman scattering light was successfully observed for GaP, while distinct signal was not obtained for YSZ and rutile. Anti-Stokes Raman scattering light could not be observed in all samples of YSZ, rutile, and GaP. A possible cause is that the excitation density of the probe laser used in this experiment is too high, as two-photon excitation by probe laser raise the noise level especially intense irradiation condition. Another possible reason for the inability to observe the signal is that it can only be measured by backscattering arrangement.

4. Stokes Raman Spectroscopy for chiral phonon excitation in alpha-quartz

4.1 Introduction

4.1.1 Chiral phonon excitation

The concept of chirality plays a significant role in multiple branches of sciences, such as physics, chemistry, and biology [38]-[40]. Chirality is also applied to the description of collective excitations of a system. Chiral phonon is the collective oscillation modes of a crystal lattice with a definite handedness, which is successfully observed in alpha-quartz [41], for example. It can couple with circularly polarized light and valley electrons and result in chiral selective optical transitions. In this section, I aim to excite chiral phonons by controlling the left and right circular polarization of excitation light using chiral crystals as samples.

4.1.2 alpha-quartz

In this chapter, alpha-quartz will be used as the sample. It is the most stable polymorph of SiO_2 found in nature. It has important applications in many industrial fields. Its lattice structure consists of SiO_4 tetrahedra bonded by oxygen. It is characterized by its chiral lattice structure, which is dextrorotatory or levorotatory. Alpha-quartz has 16 modes ($4A_1 + 4A_2 + 8E = 16$). This research targets the E mode located around 700 cm^{-1} [42].

4.2 Experiment

The main experimental equipment system is the same as in the previous chapter. Experimental setup is displayed in Figure 4-1. Lasers with two different wavelengths (532 and 785 nm) were used as probe lasers. In order to reduce the noise caused by aluminum as much as possible, I used a sample stage with a larger hole in the center than the previous one. All measurements were performed at room temperature. Dextrorotatory single crystal α -quartz (CRYSTAL GmbH) is purchased from a vendor. The sample size is $10 \times 10 \times 0.5$

mm for α -quartz.

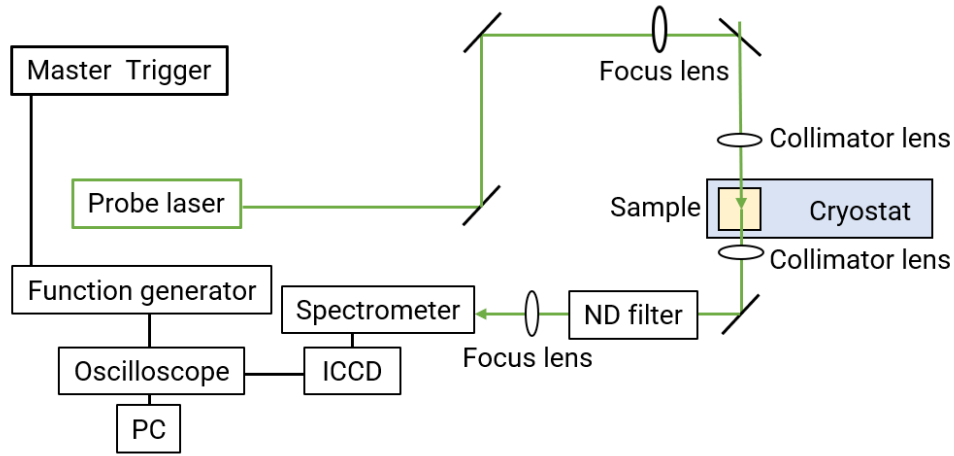


Figure 4-1 Schematic diagram of experimental equipment.

4.3 Results and discussion

I performed a preliminary measurement to observe the Stokes Raman scattering light of α -quartz using a 532 nm CW laser. I used a single-sided polished sample. The measurement conditions are shown in Table 4-1, and the spectrum is shown in Figure 4-2. The target mode was E mode located at 700 cm^{-1} , but no signal could be observed.

Raman measurements were also performed on single- and double-sided polished samples using a 785 nm diode laser. The experiment was conducted with direct incidence at an incident angle of 0° to the normal, and specular reflection light was collected to the spectrometer. The measurement conditions are shown in Table 4-2, and the spectra are shown in Figure 4-3. I was able to observe almost all the scattering band signals observed in reported studies [42]. This revealed that the signal could be observed even with the sample used in this experiment. In other words, it was found that the signal could be observed even if the surface orientation was different from previous research.

Table 4-1 The measuring conditions.

Probe laser intensity / mW	3	Slit width / mm	0.1
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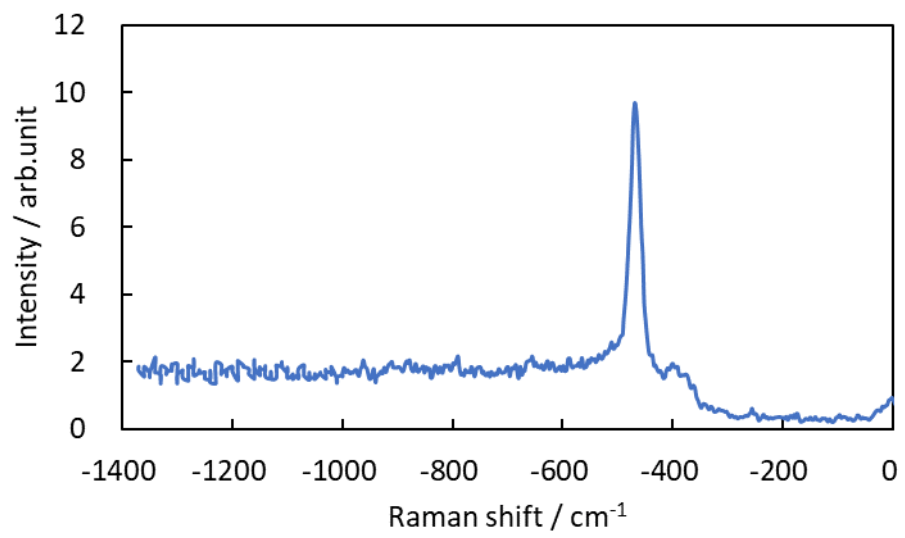


Figure 4-2 Stokes raman spectrum of alpha-quartz.

Table 4-2 The measuring conditions.

Probe laser intensity / mW	230	Slit width / mm	0.1
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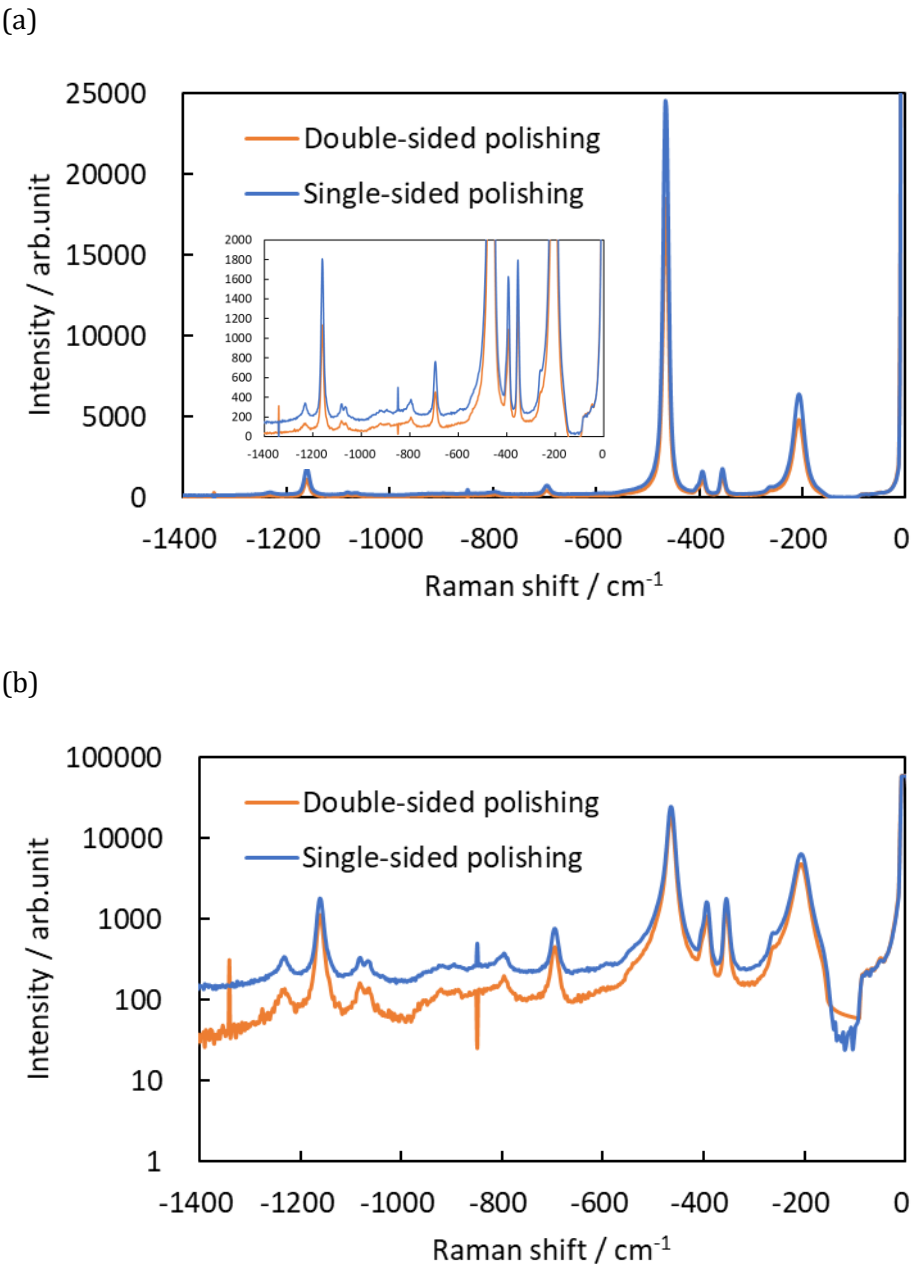


Figure 4-3 (a) Stokes Raman spectrum of α -quartz, (b) Logarithmic graph of (a).

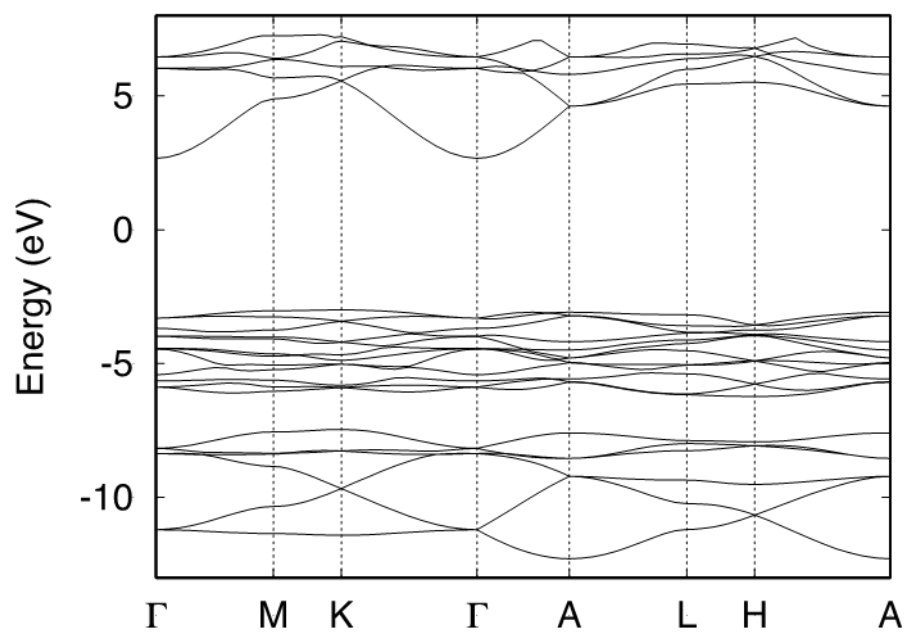


Figure 4-4 Electron energy band structures for α -quartz calculated with DFT method.

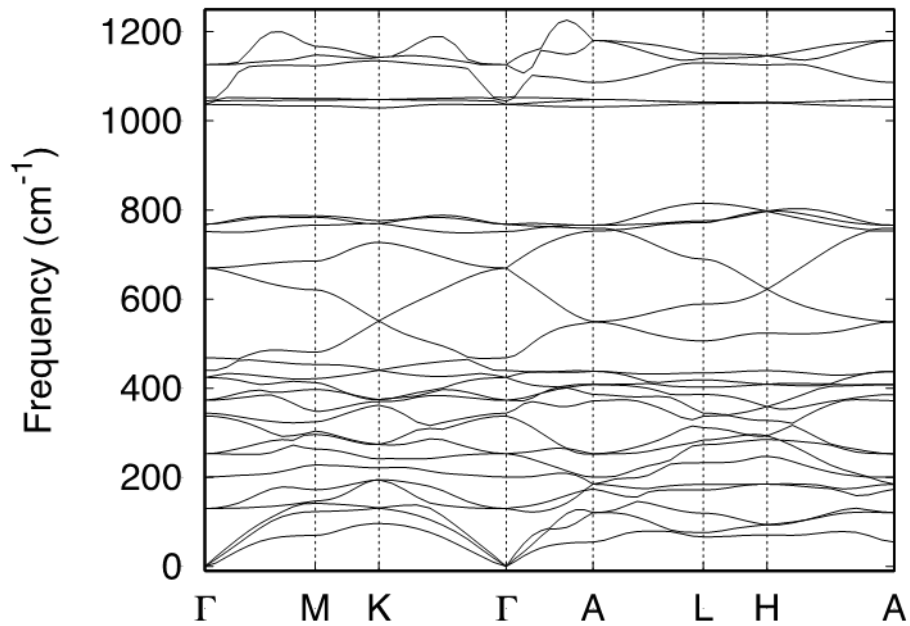


Figure 4-5 Phonon band structures for α -quartz calculated with DFT method.

Calculated electron energy band and phonon band are presented in Figure 4-4 and Figure 4-5. Direct interband transition and bandgap transition are calculated to be around 5.9 eV, which is around 4.8 eV (260 nm) in reported optical spectra. These values account for why 785 nm laser evade obstructive level of noise stemmed from two- or three-photon excitations. A half of the wavelength of 532 nm is 266 nm, quite close to 260 nm, and it will explain the considerable noise level observed in Figure 4-2.

4.4 Conclusion

Almost all modes could be observed with the 785 nm diode laser, but only the peak around 460 cm^{-1} could be observed with the 532 nm CW laser.

It is speculated from first-principles electron energy band calculations and reported absorption spectra that the probe laser of shorter wavelength generates higher level of stray-light photoluminescence through two-photon excitation.

5. First-principles electronic-structure calculations of the in-gap states and optimization of local structures around substitutional defects in La- or Nb-doped n-type SrTiO₃

5.1 Introduction

In this chapter, an example of the materials design based on density-functional theory calculation is presented. With the investigations on the electron band structures around bandgap, I can perform resonant Raman spectroscopy to detect phonon modes of weak signals. Especially, when it is applied to the in-gap dopant states in wide-gap semiconductors, particular modes concerning dopants can be selectively resonated.

A typical wide-gap semiconductor, SrTiO₃, has a bandgap of 3.2 eV [43]. As for the n-type doping of the SrTiO₃, La-doped SrTiO₃ (La:SiO₃) and Nb-doped SrTiO₃ (Nb:SrTiO₃) are well-known, and they are among the key materials in the oxide electronics [44]. The electron-dope mechanism to induce n-type conductivity in SrTiO₃ is widely investigated [45]-[49]. A wide variety of the electronic, thermoelectric and optical properties are emerged through electron doping, and it is accomplished by substitution of La to Sr, or Nb to Ti. Nature of in-gap states, which are defined as localized states emergent in the energy gap between conduction and valence bands introduced by doping [50][51], is especially important to discuss the type of conduction, whether it is classified as a polaron conduction or not, for example [52]. Electron doping is also enabled by introduction of O vacancy, and it is confirmed and investigated by a simulation [53]. In this context, both experimental and computational approaches have been taken to clarify the bandgap electronic states, which arise as an effect of the substitution of cations with dopants. Another study with the ab-initio electronic structure calculations for La- or Nb-doped STO were performed by Wunderlich et al [54]. They investigated the doping effect through estimation of the effects of dopant concentrations and lattice volumes on the effective mass of the carriers in the crystal.

Recently, an experimental study putting an emphasis on the in-gap states and local

structures around dopants have been made on the La- or Nb-doped n-type SrTiO_3 [50]. It proved that O ions around the dopants are attracted toward the substituted ions, and the conduction band bottoms are intersected by Fermi energy level to produce sharp in-gap-state bands. The in-gap-state bands can be observed with, such as, photoelectron spectroscopy [50][55]. The emergence of such bands, which are positioned just under the Fermi energy level, results from local lattice distortion introduced by the La/Nb substitution for electron doping and should lead to n-type conductivity. It is also confirmed that the La-doping hardly transforms cubic lattice of undoped SrTiO_3 into tetragonal structure, and slightly introduce local lattice distortion around the substitutional defects to generate symmetrical displacement of the nearest-neighbor O atoms toward the dopant ions [50]. Therefore, such transformation or distortion hardly alter the symmetry. This is consistent with the fact that the Raman activities of the vibrational modes in cubic SrTiO_3 is scarcely altered by doping [56].

In typical metal oxide perovskites, charge carriers for the p- or n-type semiconductors by doping or by oxygen deficiency conduct in (002) and its equivalent planes composed of metal and oxygen ions [50][57], in order to exhibit functionality through high mobility. In-gap electronic states introduced by hole or electron doping should be organized by the orbitals in metal or oxygen ions and their hybridizations, because metal-oxygen network in the plane can be the conduction path.

In the present study, I perform first-principles calculations on the La- or Nb-doped n-type SrTiO_3 to investigate the local structures and in-gap electronic structures induced by electron doping. The distorted lattice around the substitutional dopants is reproduced, and the components of the sharp in-gap-state bands just below the Fermi energy level are analyzed.

5.2 Computational details

Quantum ESPRESSO program suite [58][59], version 6.6, was used for the electronic structure and lattice structure relaxation calculations. The density functional theory (DFT) within the generalized-gradient approximation (GGA)[60] was chosen. With the Hubbard U

correction named as the DFT+ U method [61][62], I intended to improve the prediction of the electronic structure around bandgap and the local structures. In this study, the correction with + U was applied only to Ti atoms.

As for the pseudopotentials, PSLibrary [63] was used. The Projected Augmented Wave (PAW) type [64] pseudopotential files for the revised PerdewBurke-Ernzerhof (PBE) exchange-correlation functionals for solids (PBEsol) [65] were selected for Sr (Sr.pbesol-spn-kjpaw psl.1.0.0.UPF), Ti (Ti.pbesol-spn-kjpaw psl.1.0.0.UPF) and O (O.pbesol-n-kjpaw psl.1.0.0.UPF), respectively. As for La and Nb, however, the PBEsol files are not provided. I used pseudopotential files for PBE [66] instead (La.pbe-spn-kjpaw psl.1.0.0.UPF, Nb.pbe-spn-kjpaw psl.1.0.0.UPF) for the PBEsol functional calculations by specifying 'input dft = pbesol' [67]. Kinetic energy cutoff for wavefunctions ('ecutwfc') and for charge density and potential ('ecutrho') were set to the largest values among those suggested in the PBEsol pseudopotential files specified above, which were 'ecutwfc = 52' Ry and 'ecutrho = 576' Ry.

Simulation supercells were constructed by assembling unit cells illustrated in Figure 5-1. For La:SrTiO₃, $2 \times 2 \times 2$ unit cells (Sr₈Ti₈O₂₄) were used, and Sr atom at the center of the supercell was substituted with La atom. For Nb:SrTiO₃, $3 \times 3 \times 3$ unit cells (Sr₂₇Ti₂₇O₈₁) were used, and Ti atom at the center was substituted with Nb. As I discuss later, these cell sizes are the minimum to investigate into the atomic coordinations and their relaxations which accompany La- or Nb-doping, and the electronic structures including those of the Ti-O planes surrounding the substitutional defects above under periodic boundary condition. The lattice planes are indicated as those for the unit cell in Figure 5-1. All faces of the unit cell in Figure 5-1 are (100) and its equivalent planes, and those of Ti and O are (200) and its equivalent planes. Preliminary calculations with undoped SrTiO₃ were executed for the single unit cell.

The k -point sampling grids with Monkhorst-Pack method [68] of $6 \times 6 \times 6$ k points were used for the undoped crystal calculation, and $3 \times 3 \times 3$ k points were used for the larger supercells for the doped crystals. The total energy convergence criterion for self-consistent field (SCF) calculations was 1.0×10^{-6} Ry for supercell. The structural optimizations were performed until atomic forces were smaller than 1.0×10^{-4} Ry. All atoms in the supercell were relaxed to find the optimized structure during calculations for the La or Nb

substitution. Cubic structure was assumed for the undoped SrTiO_3 , while tetragonal structures were assumed for the La- or Nb-doped SrTiO_3 .

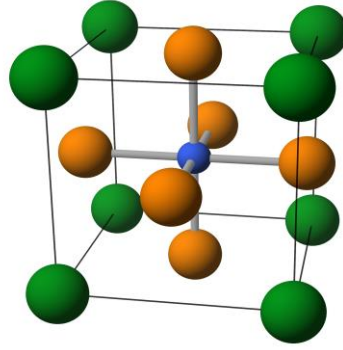


Figure 5-1 Schematics for the unit cells of cubic SrTiO_3 used for the simulations for La:SrTiO_3 and Nb:SrTiO_3 . The Sr, Ti and O atoms are colored with green, blue and orange, respectively.

5.3 Results and discussion

5.3.1 Calculations for SrTiO_3

In order to optimize the value of U in DFT+ U method, the lattice constant, a , obtained in the structural relaxation and the electronic band structure for the relaxed structure, especially direct (E_0) and indirect energy gaps (E_g), were calculated and confirmed. Results are summarized in Table 5-1 and in Figure 5-2 and Figure 5-3. The calculated lattice constant for the relaxed structure was close to the experimental value at around $U = 3.0$ eV. On the other hand, the values for E_0 and E_g reached to their extrema and were the closest to the experimental values at $U = 9.0$ eV. For all the values of U , indirect bandgaps were for the R to Γ transitions, which were consistent with those observed in the experimental study [69]. A reported study for the undoped SrTiO_3 by DFT+ U with PBE instead of PBEsol [71] did not have such extrema up to $U \leq 14.5$ eV with an overestimation of the lattice constant even at $U = 0$. Another report with PBE [72] improved the bandgap estimation with a smaller U of 6.0 eV on Ti, while the authors chose to assign extra uncommon U of 3.0 eV on Sr, which is not a transition element. Dependence of the band structure on U in PBE+ U method was

investigated to study La:SrTiO₃, and confirmed that the extremum to give a better prediction of the bandgap was at $U = 7.5$ eV [73]. Some reports claimed that too large U caused emergence of unreal bandgap states in the bandgap when applied to anatase TiO₂, and recommended $U \leq 3.0$ eV [74]. There was also a calculation for SrTiO₃ with a smaller U , such as 3.0 eV, with PBE+ U or LDA+ U [75]. Nevertheless, as I have seen in Figure 5-2, no unreal mid-gap states were observed in our calculations. It is therefore no reason to choose the U of inferior prediction at anywhere along the way to reach the maximum of the bandgap energy (E_g), especially when the best prediction is obtained at its extremum as I see in Figure 5-3. In the present study, the DFT+ U calculations were performed not only at $U = 9.0$ eV, but also at 0, 3.0 and 6.0 eV, in order to make comparison with other reports.

The calculated Löwdin charges [76] are compiled in Table 5-2. Initial charges (number of valence electrons) are Sr: 10.00(4s: 2.00; 5s: 2.00; 4p: 6.00); Ti: 12.00(3s: 2.00; 4s: 2.00; 3p: 6.00; 3d: 2.00) and O: 6.00(2s: 2.00; 2p: 4.00), respectively, which are defined in the pseudopotential library files. Qualitatively, increase of charge number means negativity of atoms, while decrease means positivity.

The calculated total and partial density of states are presented in Figure 5-4. For all U except $U = 9.0$ eV, conduction band bottoms were composed of Ti 3d orbitals. At $U = 9.0$ eV, Ti 3d orbitals were hybridized with O 2s orbitals. The valence band tops were composed of O 2p orbitals.

Table 5-1 Calculated direct gap at Γ point (E_0), indirect bandgap between valence band top at R and conduction band bottom at Γ points (E_g) and lattice constant for cubic SrTiO_3 (a) for U in DFT+ U method. Experimental values (Expt.) for E_0 , E_g [69] and a [70] are also presented.

U (eV)	E_0 (eV)	E_g (eV)	a ($\text{\AA}$)
0	2.18	1.85	3.892
2.0	2.34	1.98	3.900
3.0	2.41	2.05	3.904
4.0	2.52	2.13	3.908
5.0	2.63	2.23	3.912
6.0	2.77	2.34	3.918
7.0	2.92	2.48	3.923
8.0	3.10	2.54	3.931
8.8	3.28	2.80	3.937
9.0	3.29	2.81	3.939
9.2	3.23	2.74	3.941
9.5	3.15	2.65	3.945
10.0	3.02	2.51	3.950
Expt.	3.75	3.25	3.905

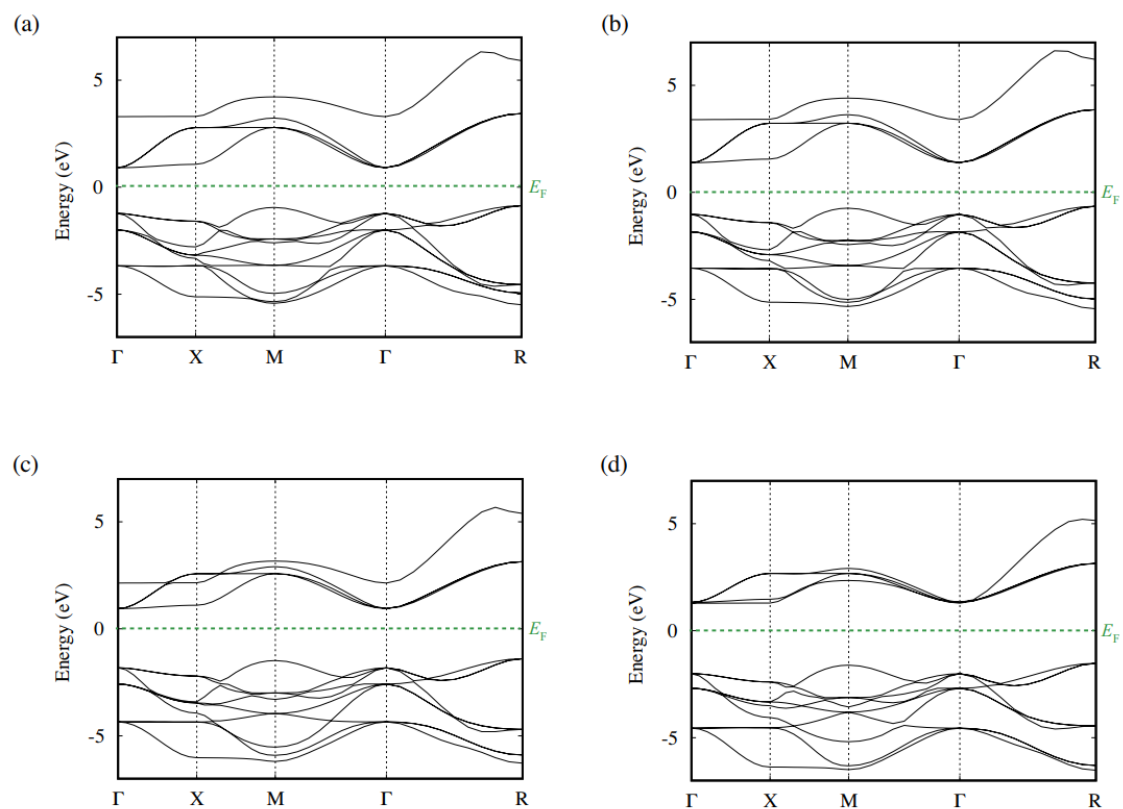


Figure 5-2 Band structures for cubic SrTiO₃ calculated with DFT+ U method: U = (a) 0, (b) 3.0, (c) 6.0 and (d) 9.0 eV. Fermi energy (E_F) is set to the origin of energy.

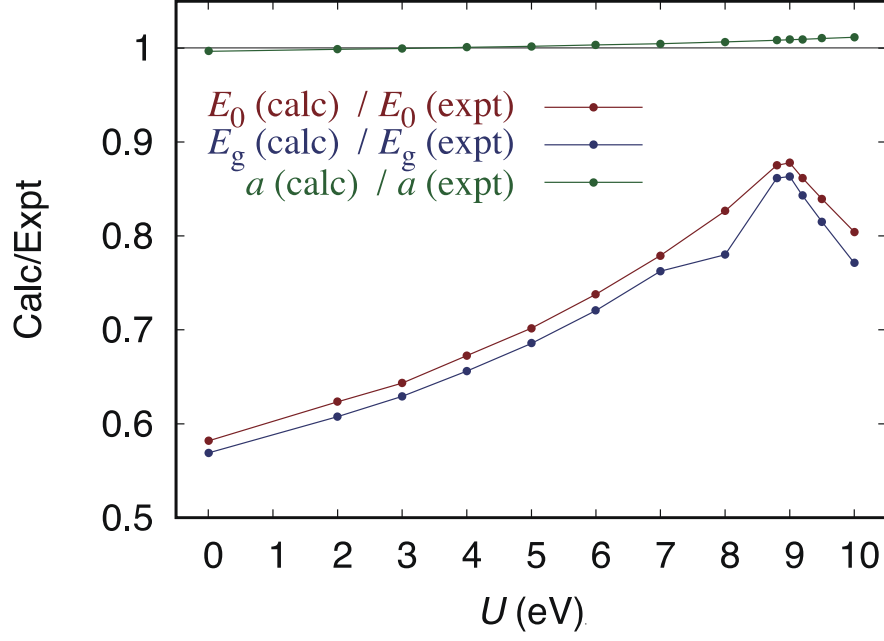


Figure 5-3 Calculated direct gap at Γ point (E_0), indirect bandgap between valence band top at R and conduction band bottom at Γ points (E_g) and lattice constant for cubic SrTiO_3 (a) compared with experimental values for U in DFT+ U method. The ratio of the calculated values to the corresponding experimental values are indicated.

Table 5-2 Löwdin charges for the atoms in the relaxed local structure of SrTiO₃ for $U = 0, 3.0, 6.0, 9.0$.

U (eV)		Sr	Ti	O
0	total	8.79	10.26	6.89
	<i>s</i>	2.23	2.28	1.68
	<i>p</i>	6.58	5.99	5.21
	<i>d</i>	0.00	1.99	0.00
3.0	total	8.80	10.21	6.91
	<i>s</i>	2.23	2.29	1.68
	<i>p</i>	6.57	5.99	5.23
	<i>d</i>	0.00	1.93	0.00
6.0	total	8.80	10.13	6.93
	<i>s</i>	2.23	2.29	1.68
	<i>p</i>	6.57	5.99	5.25
	<i>d</i>	0.00	1.85	0.00
9.0	total	8.82	10.03	6.95
	<i>s</i>	2.24	2.29	1.68
	<i>p</i>	6.58	5.99	5.27
	<i>d</i>	0.00	1.75	0.00

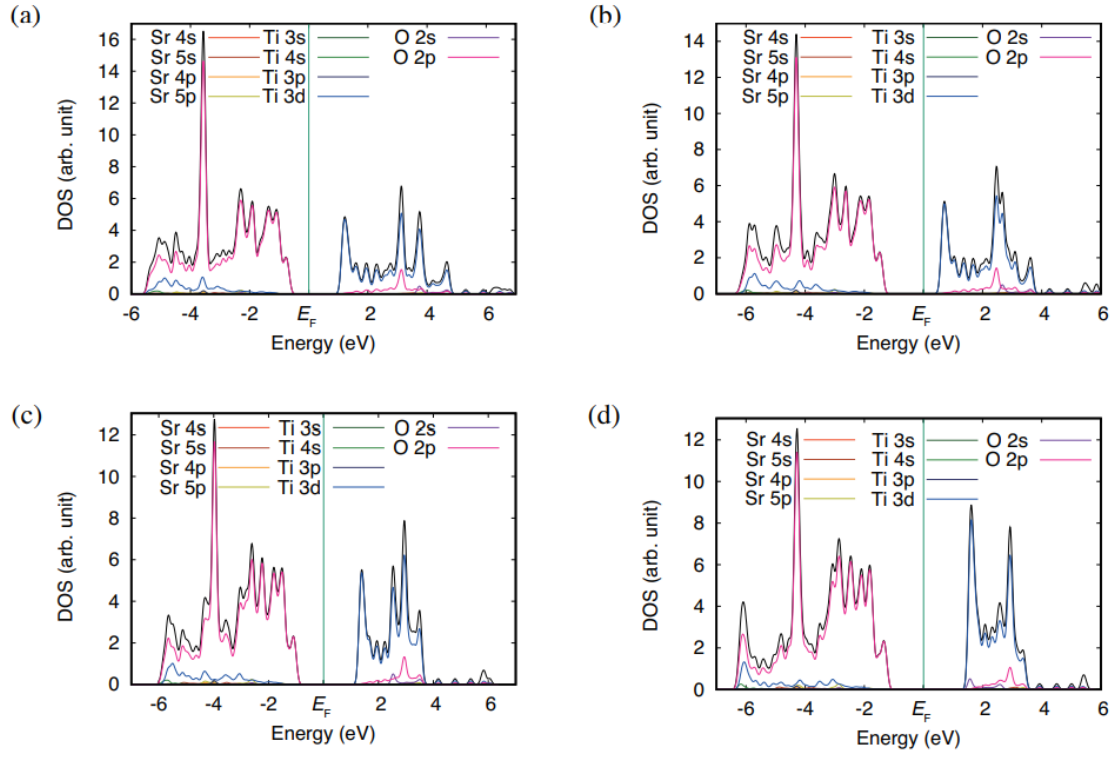


Figure 5-4 Total and partial density of states for SrTiO_3 calculated with DFT+ U method for $U =$ (a) 0, (b) 3.0, (c) 6.0 and (d) 9.0 eV. Total density of states is drawn in solid black line, and partial density of states are labeled in legend.

5.3.2 Calculations for La:SrTiO₃

Although La is one of the lanthanoid, the 4f orbital of the element is empty. Therefore, it is not common to assign non-zero U to this element in DFT+ U method unlike other lanthanoid elements. I confirmed U of 0, 3.0, 6.0, 9.0 eV, which were assigned only to Ti. The parameters to describe atomic arrangements around the dopant La atoms are defined in Figure 5-5. The band structures are given in Figure 5-6, and presented in Figure 5-7 are the calculated total and partial density of states corresponding to the band structures. The in-gap states emergent with La-doping are also displayed as those localized around Ti in Figure 5-5, which are evident from band structure and density of states as I see later. Results of the relaxation of atomic positions and lattice parameters to investigate the local structure around La substitutional defects are compiled in Table 5-3. Even though I have assumed tetragonal structure for the unit cell, cubic structure, $a = c$, was obtained through structural relaxation calculation. Therefore, I used the lattice constant of a only. The angle and the distances indicate that the O atoms neighboring the substitutional La slightly moved toward the dopants. The reported parameters were 2.719 Å (EXAFS, 20 K) or 2.761 Å (XRD, room temperature) for the Sr-O distance, 2.533 Å (EXAFS, 20 K) for the La-O distance, and $\sim 170^\circ$ for the angle α in Figure 5-5 which was estimated from the distances at 20 K derived with EXAFS [50]. The lattice constants for a and c were 3.906 Å and 3.907 Å derived with Rietveld analysis of the XRD spectra [50]. The $a/\sqrt{2}$ was 2.762 Å for that value.

The band structures in Figure 5-6 and the calculated total and partial density of states in Figure 5-7 show that the Fermi energy level crossed the conduction band bottoms as an effect of the La-doping. Such electronic structure gives n-type conductivity of electrons near Fermi energy in SrTiO₃. The intersection of Fermi energy level at conduction band bottom yields a sharp band in photoelectron spectroscopy observed at the higher energy end [50][55]. It is investigated in the literature which orbitals consist this sharp band, doping conducting electrons to be n-type carriers in the crystals. I confirmed that this was composed of 3d orbitals in Ti. This is consistent with the literature which proved that the conduction band bottom was mainly composed of 3d orbitals in Ti [50][55]. While the conduction bottom was calculated to be at Γ point, the lowest part of the conduction band intersected by Fermi energy level was revealed to be stretched toward the X point direction.

With the calculations of charge transfer between constituent atoms, spatial distribution of charges, and rearrangements of atomic positions around dopants, I can make deduction on the mechanism how to emerge n-type conduction carriers by doping. The calculated Löwdin charges are compiled in Table 5-4. Initial charges (number of valence electrons) are Sr: 10.00(4s : 2.00; 5s : 2.00; 4p : 6.00); La: 11.00(5s : 2.00; 6s : 1.50; 5p : 6.00; 6p : 0.50; 5d : 1.00; 4f : 0.00); Ti: 12.00(3s : 2.00; 4s : 2.00; 3p : 6.00; 3d : 2.00) and O: 6.00(2s : 2.00; 2p : 4.00), respectively, which are defined in the pseudopotential library files. As discussed in the previous subsection, those calculated for undoped SrTiO₃ for $U = 9.0$ eV were Sr: 8.82; Ti: 10.03; and O: 6.95 as I have seen in Table 5-2. With La-doping, positivity of Ti atoms decreased by $\sim 0.4 - 0.6$ and negativity of O atoms decreased by $\sim 0.2 - 0.3$ through transformation of some of the p electrons in O into the d electrons in Ti. Such rearrangements of charge were milder for the larger U . Substitution of Sr by La were replacement of +1.1 positive ions by +0.3 – 0.4 positive ions. As I will show later in the charge density plots, La-doping caused decrease in charge density localized around La site compared with those of Sr sites. Although Table 5-4 indicates that small number of electrons occupied f-orbitals, Figure 5-7 shows the effect on the electronic structure of the occupied states is negligible.

The 2D charge density plots for La:SrTiO₃ calculated with DFT+ U method plotted for the (110) plane: $U =$ (a) 0, (b) 3, (c) 6 and (d) 9 eV are shown in Figure 5-8. The charge densities presented here are integrated to the number of electrons in each atom. As I see especially in Figure 5-8 (a), O atoms neighboring Sr, not only those neighboring La, also moved inward when $U = 0$. The Ti-O-Ti angles neighboring Sr reduced to 172.4° for $U = 0$, while they were 179.0° for $U = 3.0$, 178.9° for $U = 6.0$ and 178.9° for $U = 9.0$. As will be described in the next subsection for the Nb-substitution, the smaller distortions near substituted La atom compared with those observed in experiments [50] are likely to be because of the limitation in the simulation cell size.

By introducing the less positive La cations in the crystal, native cations, Sr or Ti, in the matrix crystal should also be less positive. To transfer some of the electrons to Ti atoms, the 3d orbitals, which are originally situated at the nearest to the Fermi energy, should be the electron transfer destination. Thus, some of the electrons in O, whose 2p electrons are

located at the valence band top, are transferred to the Ti 3*d* orbitals, and the Fermi energy level intersects the conduction band bottom, while Ti sites are spatially distanced from La by the presence of distorted O atoms. This is also illustrated in Figure 5-5 as in-gap states at Ti sites.

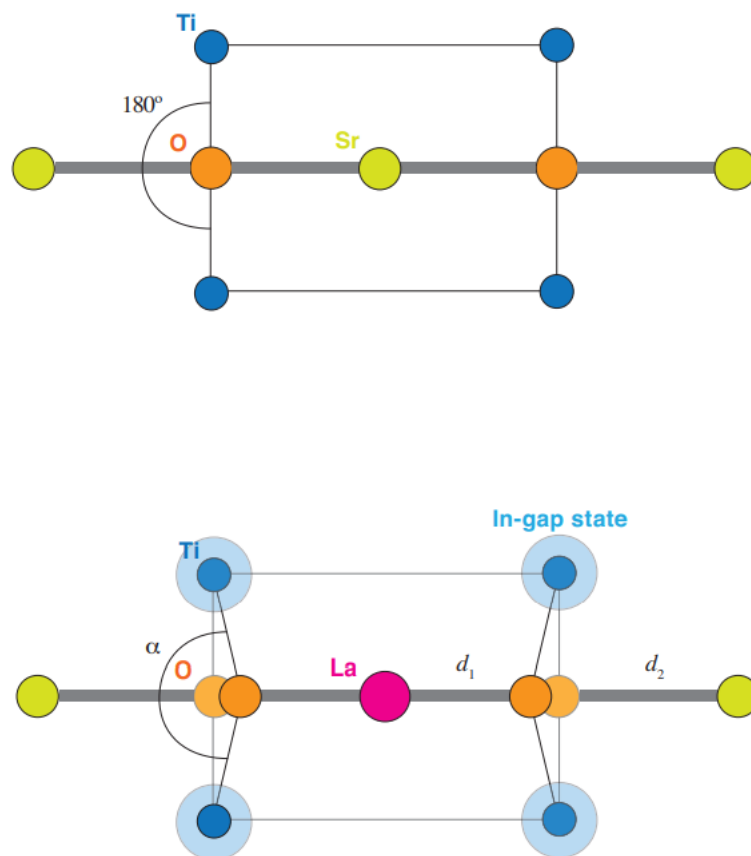


Figure 5-5 Schematics for the atomic arrangements in a (110) plane around a Sr replaced by La (upper panel) before and (lower panel) after the doping.

Table 5-3 Parameters for the relaxed local structure around doped La in La:SrTiO₃. The angle (α) and the distances (d_1, d_2) are defined in Figure 5-5.

U (eV)	α (°)	d_1 (Å)	d_2 (Å)	$a/\sqrt{2}$ (Å)
0	176.6	2.747	2.832	2.754
3.0	176.8	2.712	2.812	2.762
6.0	176.6	2.717	2.826	2.771
9.0	176.6	2.747	2.832	2.799

Table 5-4 Löwdin charges for the atoms in the relaxed local structure around doped La in La:SrTiO₃. Annotations (n) and (d) index atomic positions at neighboring and distant sites of La.

<i>U</i> (eV)		Sr(n)	Sr(n)	La	Ti(n)	Ti(d)	O(n)	O(d)
0	total	8.85	8.85	10.62	10.66	10.66	6.67	6.75
	<i>s</i>	2.17	2.17	2.17	2.26	2.26	1.70	1.72
	<i>p</i>	6.68	6.68	6.67	5.99	5.99	4.97	5.03
	<i>d</i>	0.00	0.00	1.53	2.41	2.41	0.00	0.00
	<i>f</i>	0.00	0.00	0.25	0.00	0.00	0.00	0.00
3.0	total	8.86	8.86	10.64	10.59	10.59	6.70	6.76
	<i>s</i>	2.17	2.17	2.17	2.26	2.26	1.70	1.72
	<i>p</i>	6.69	6.69	6.68	5.99	5.99	5.00	5.04
	<i>d</i>	0.00	0.00	1.53	2.34	2.34	0.00	0.00
	<i>f</i>	0.00	0.00	0.26	0.00	0.00	0.00	0.00
6.0	total	8.87	8.87	10.65	10.51	10.51	6.72	6.79
	<i>s</i>	2.18	2.18	2.18	2.27	2.27	1.71	1.72
	<i>p</i>	6.69	6.69	6.68	5.99	5.99	5.01	5.07
	<i>d</i>	0.00	0.00	1.53	2.25	2.25	0.00	0.00
	<i>f</i>	0.00	0.00	0.26	0.00	0.00	0.00	0.00
9.0	total	8.89	8.89	10.66	10.38	10.38	6.75	6.82
	<i>s</i>	2.19	2.19	2.19	2.27	2.27	1.71	1.72
	<i>p</i>	6.70	6.70	6.69	5.99	5.99	5.04	5.10
	<i>d</i>	0.00	0.00	1.52	2.12	2.12	0.00	0.00
	<i>f</i>	0.00	0.00	0.26	0.00	0.00	0.00	0.00

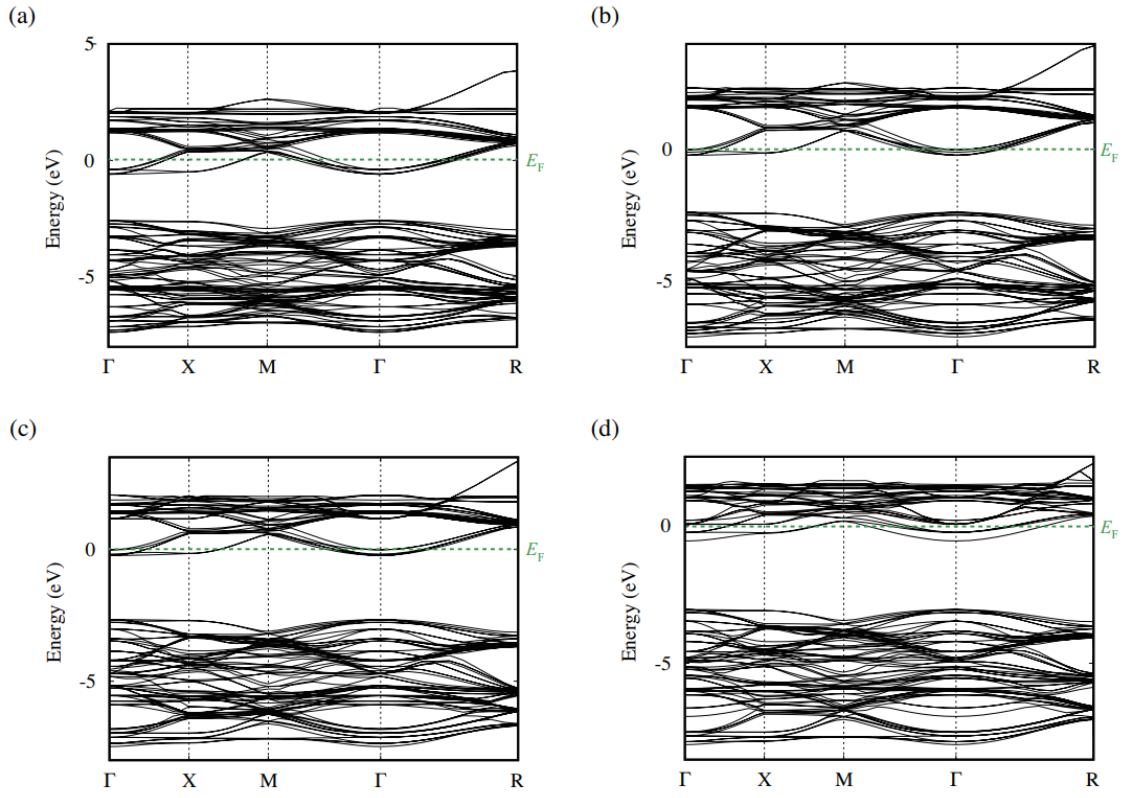


Figure 5-6 Band structures for La:SrTiO_3 calculated with DFT+ U method using a simulation box of 2×2 unit cells: $U =$ (a) 0, (b) 3.0, (c) 6.0 and (d) 9.0 eV. Fermi energy (E_F) is set to the origin of energy.

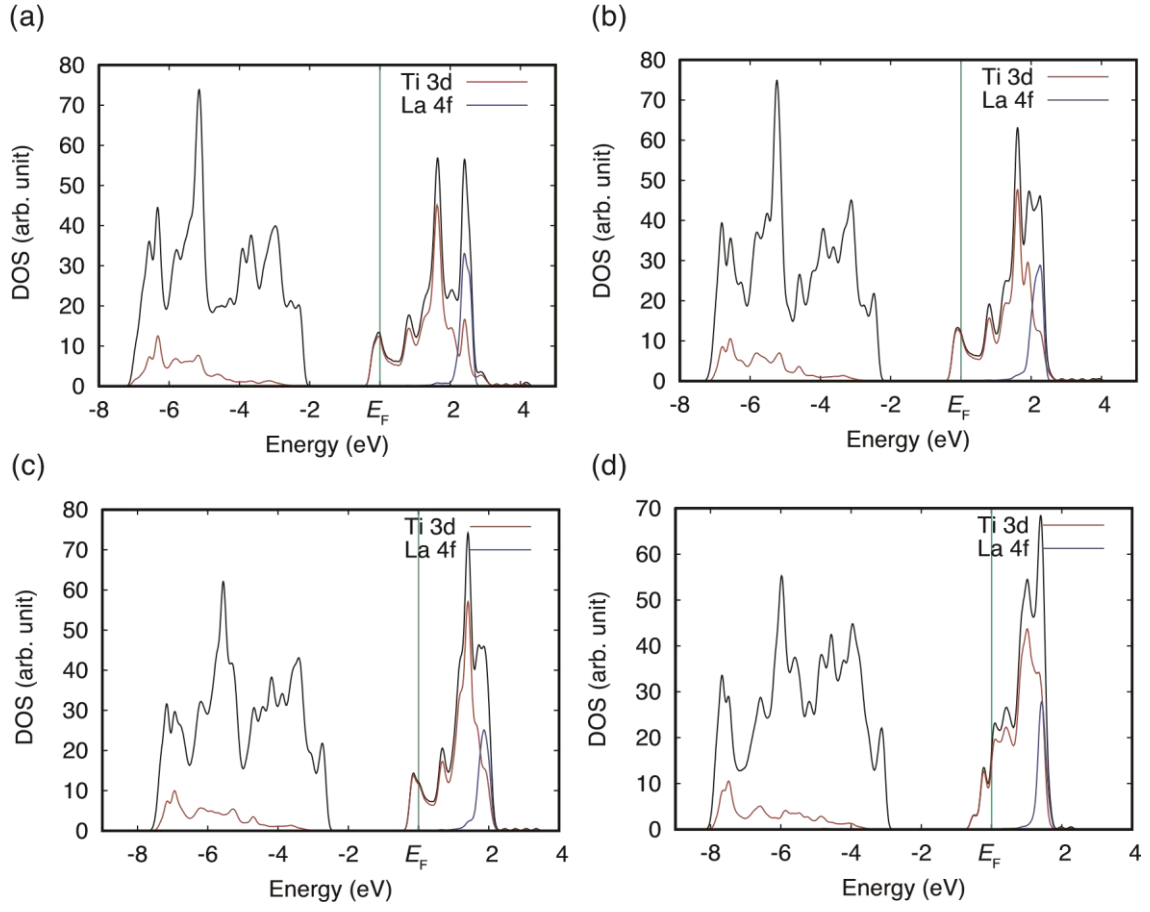


Figure 5-7 Total and partial density of states for La:SrTiO₃ calculated with DFT+ U method using a simulation box of 2×2 unit cells: U = (a) 0, (b) 3.0, (c) 6.0 and (d) 9.0 eV. Total density of states is drawn in solid black line, and partial density of states are labeled in legend.

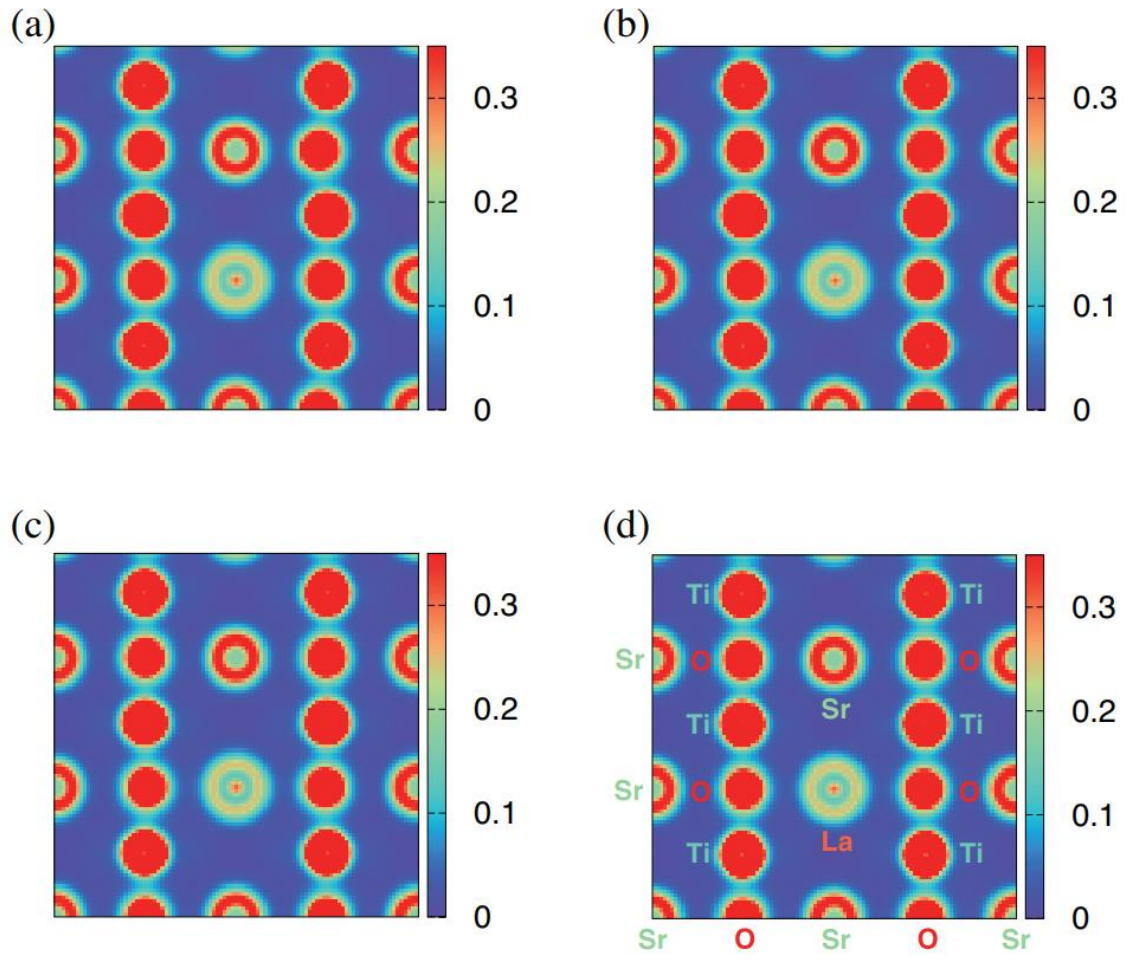


Figure 5-8 2D charge density plots for La:SrTiO_3 calculated with DFT+ U method plotted for the (110) plane: $U =$ (a) 0, (b) 3.0, (c) 6.0 and (d) 9.0 eV. Atoms are labelled in (d).

5.3.3 Calculations for Nb:SrTiO₃

As for the Nb:SrTiO₃, cubic structure were proved to be stable again. The parameters for the relaxed local structure around dopant Nb defined in Figure 5-9 are calculated and compiled in Table 5-5. The relations of the values, $\alpha < 180^\circ$ and $a/2 < d_1 < d_2$, result from the relaxed atomic arrangements that the O atoms neighboring Nb are attracted toward the dopant Nb atoms, and that the Ti atoms at the nearest neighbors of Nb are repelled away from the dopant. As I will see later in the 2D charge density plots, the (002) and all other equivalent planes of Ti and O are not distorted at Ti site despite the relations above. The cube surrounded by those planes isotropically expands, and its inside shrinks.

The calculated Löwdin charges are compiled in Table 5-6. Initial charges (number of valence electrons) are Sr: 10.00 (4s : 2.00; 5s : 2.00; 4p : 6.00); Nb: 13.00 (4s : 2.00; 5s : 2.00; 4p : 6.00; 4d : 3.00); Ti: 12.00 (3s : 2.00; 4s : 2.00; 3p : 6.00; 3d : 2.00) and O: 6.00 (2s : 2.00; 2p : 4.00), respectively, which are defined in the pseudopotential library files. As compiled in Table 5-6, charge rearrangements did not differ so much from La-doping case. With Nb-doping, positivity of Ti atoms decreased by $\sim 0.4 - 0.7$, and negativity of O atoms decreased by $\sim 0.1 - 0.3$. Rearrangements of the charges were milder for the larger U . Substitution of Ti by Nb were replacement of $+1.3 - 1.5$ positive ions by $+0.4 - 0.5$ positive ions.

The band structures are given in Figure 5-10, and presented in Figure 5-11 are the calculated total and partial density of states corresponding to the band structures. A reported calculation for the metallic state of the lightly electron-doped SrTiO₃ [77] appeals that the sharp band observed in photoelectron spectroscopy just below the Fermi energy level consists mainly of Ti 3d states with a slight hybridization of O 2p states. This coincides with the present calculation for $U = 9.0$ eV, which is shown in Figure 5-11 (d), while the partial density of states for O 2p is non-zero but small near E_F . In addition, the lowest part of the conduction band intersected by Fermi energy level was stretched toward the X point direction, which was same as the La-doping case. As displayed in Figure 5-11, the in-gap states at the conduction band bottom are of Ti 3d orbitals, and consist not only of the first nearest-neighbor Ti, but also of the second and third nearest-neighbor Ti atoms. The isotropic expanding of the cube of the (002) planes and its equivalents including Nb at its center leads to simultaneous repelling of all the 1st, 2nd and 3rd nearest neighbor (NN) Ti

atoms away from the substitutional Nb atoms, and corresponds to the emergence of the in-gap states containing the $3d$ orbitals in, not one, but all of these NN Ti atoms. The simultaneous repelling, or isotropic expanding, is also reflected in the 2D charge density plots presented in Figure 5-12. Apparently, Nb-doping did not bring about so much modulation in charge density as presented in Figure 5-12. As a consequence, intrusion of Fermi energy level into conduction-band density of states, and atomic rearrangements near Nb substitutional defects, were milder than those in La-substitution, even though I have used a larger simulation cell for the Nb-substitution. The rearrangements are concentrated in the single unit cell containing the dopant, and the Fermi energy level intrude into the conduction bands of the Ti-O planes outside the cell not containing the dopants. Nevertheless, the small rearrangements in atomic positions are still because of my simulation cell size. The present small shrinkage around Nb comes from a partial offset of an attractive force acting on O atom from the neighboring Nb atoms by another attractive force from another Nb located outside the simulation box toward opposite direction under periodic boundary condition. In our $3 \times 3 \times 3$ unit-cell simulation box, the unit cell at the center containing O atoms shifted toward the substituted Nb are located in the expanded cubic cage of the (002) planes and its equivalents composed of the Ti-O network. In order to describe the lattice relaxation of these planes, I need $3 \times 3 \times 3$ unit cells as the minimum, because another Nb-substituted cell generated by the periodic boundary condition does not contact directly at the planes with that size. As a proof of it, if I calculate with $2 \times 2 \times 2$ simulation box, the balance of the attractive forces between two toward opposite directions is exactly held at the (002) plane, and variation of the angle α from 180° disappears at the same time. Consequently, it is probable that the twist at angle α can be more sharp if I calculate with a larger periodicity. The minimum size supercell in this sense for the La-substituted cell is composed of $2 \times 2 \times 2$ unit cells.

The result that the sharp band just below the Fermi level consists of the isotropic expanding cube of the (002) planes of Ti-O and its equivalents around the substitutional Nb also means that the carriers doped in n-type does not need to transport across the electronic states containing the Nb defects. The doped electron carriers can conduct within Ti-O network without scattering by defects. Therefore, the substitution of Ti with Nb is not inferior to that of Sr with La, although the Nb dopants are embedded in the Ti-O network while Sr is not

contained in the network. As replacing Sr by La does not disturb the n-type carrier transportation within Ti-O conduction planes, Nb doping forms the conduction path which bypasses the unit cell containing the dopants. Taking the mild alternation of the local atomic arrangements also into account, Nb:SrTiO₃ is as appropriate as La:SrTiO₃ for an n-type semiconductor, which is confirmed in the experiments [78].

Table 5-5 Parameters for the relaxed local structure around doped Nb in Nb:SrTiO₃. The angle (α) and the distances (d_1, d_2) are defined in Figure 5-5.

U (eV)	α (°)	d_1 (Å)	d_2 (Å)	$a/2$ (Å)
0	179.1	1.962	1.967	1.949
3.0	179.0	1.963	1.974	1.954
6.0	178.8	1.964	1.982	1.961
9.0	178.5	1.968	1.995	1.972

Table 5-6 Löwdin charges for the atoms in the relaxed local structure around doped Nb in Nb:SrTiO₃. Annotations (n) and (d) index atomic positions at neighboring and distant sites of Nb.

<i>U</i> (eV)		Sr(n)	Sr(n)	Nb	Ti(n)	Ti(d)	O(n)	O(d)
0	total	8.81	8.85	12.56	10.71	10.70	6.67	6.74
	<i>s</i>	2.13	2.15	2.25	2.26	2.26	1.67	1.72
	<i>p</i>	6.68	6.70	7.03	5.99	5.99	5.00	5.02
	<i>d</i>	0.00	0.00	3.28	2.46	2.45	0.00	0.00
3.0	total	8.82	8.86	12.50	10.59	10.59	6.64	6.76
	<i>s</i>	2.13	2.15	2.25	2.27	2.27	1.67	1.72
	<i>p</i>	6.68	6.71	7.04	5.99	5.99	4.97	5.04
	<i>d</i>	0.00	0.00	3.21	2.33	2.33	0.00	0.00
6.0	total	8.83	8.87	12.51	10.50	10.49	6.65	6.78
	<i>s</i>	2.14	2.16	2.26	2.27	2.27	1.67	1.72
	<i>p</i>	6.69	6.71	7.04	5.99	5.98	4.98	5.06
	<i>d</i>	0.00	0.00	3.21	2.24	2.24	0.00	0.00
9.0	total	8.84	8.89	12.54	10.41	10.38	6.62	6.82
	<i>s</i>	2.14	2.16	2.25	2.27	2.28	1.65	1.73
	<i>p</i>	6.70	6.73	7.04	5.99	5.99	4.97	5.09
	<i>d</i>	0.00	0.00	3.25	2.15	2.11	0.00	0.00

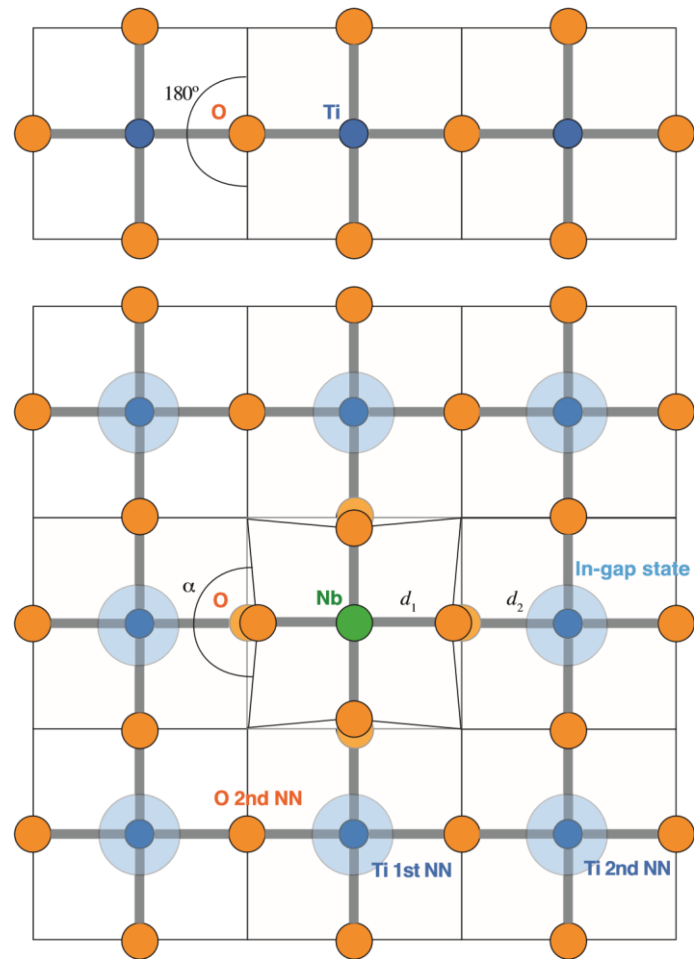


Figure 5-9 Schematic for the atomic arrangements in a (002) plane around a Ti replaced by Nb (upper panel) before and (lower panel) after the doping.

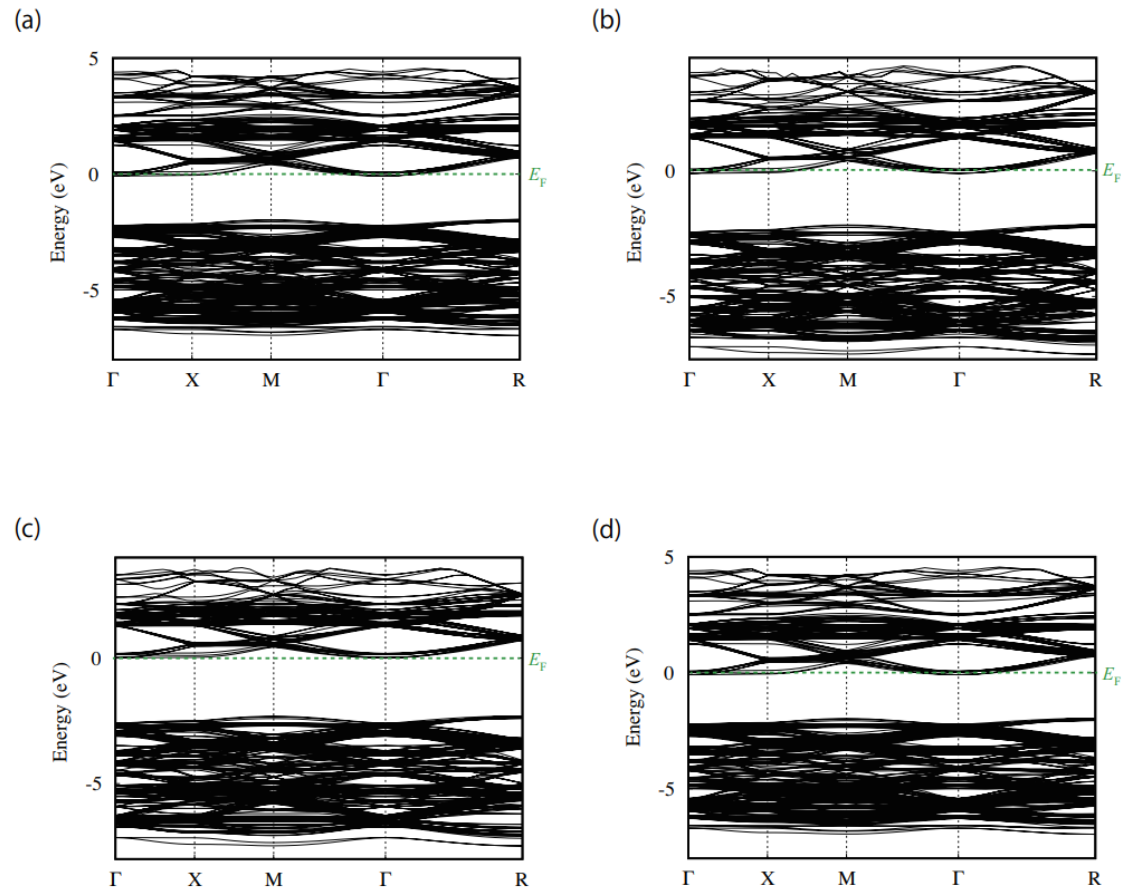


Figure 5-10 Band structures for Nb:SrTiO₃ calculated with DFT+*U* method using a simulation box of $3 \times 3 \times 3$ unit cells: $U =$ (a) 0, (b) 3.0, (c) 6.0 and (d) 9.0 eV. Fermi energy (E_F) is set to the origin of energy.

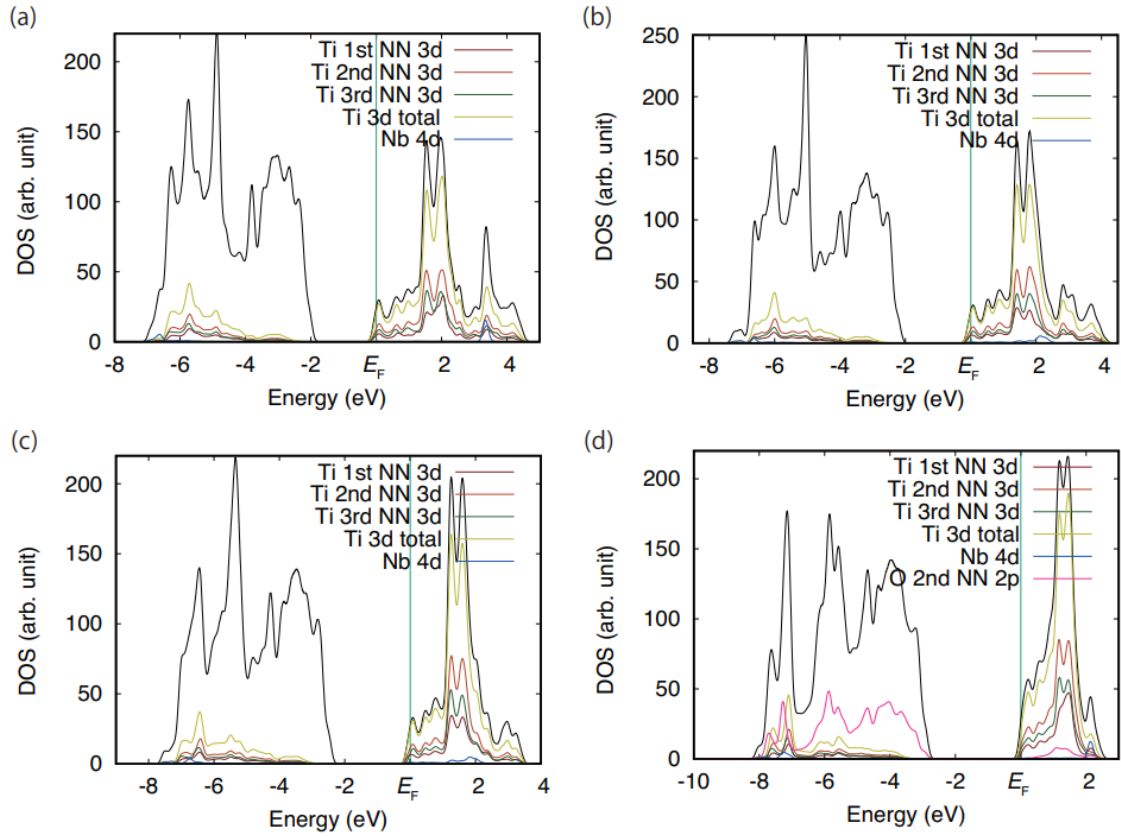


Figure 5-11 Total and partial density of states for Nb:SrTiO₃ calculated with DFT+*U* method using a simulation box of $3 \times 3 \times 3$ unit cells: *U* = (a) 0, (b) 3.0, (c) 6.0 and (d) 9.0 eV. The 1st and 2nd nearest neighbor (NN) positions are defined in Figure 5-9, and the 3rd NN positions are defined as the remaining Ti sites in the cube consists of the (002) planes and their equivalents. Total density of states is drawn in solid black line, and partial density of states are labeled in legend.

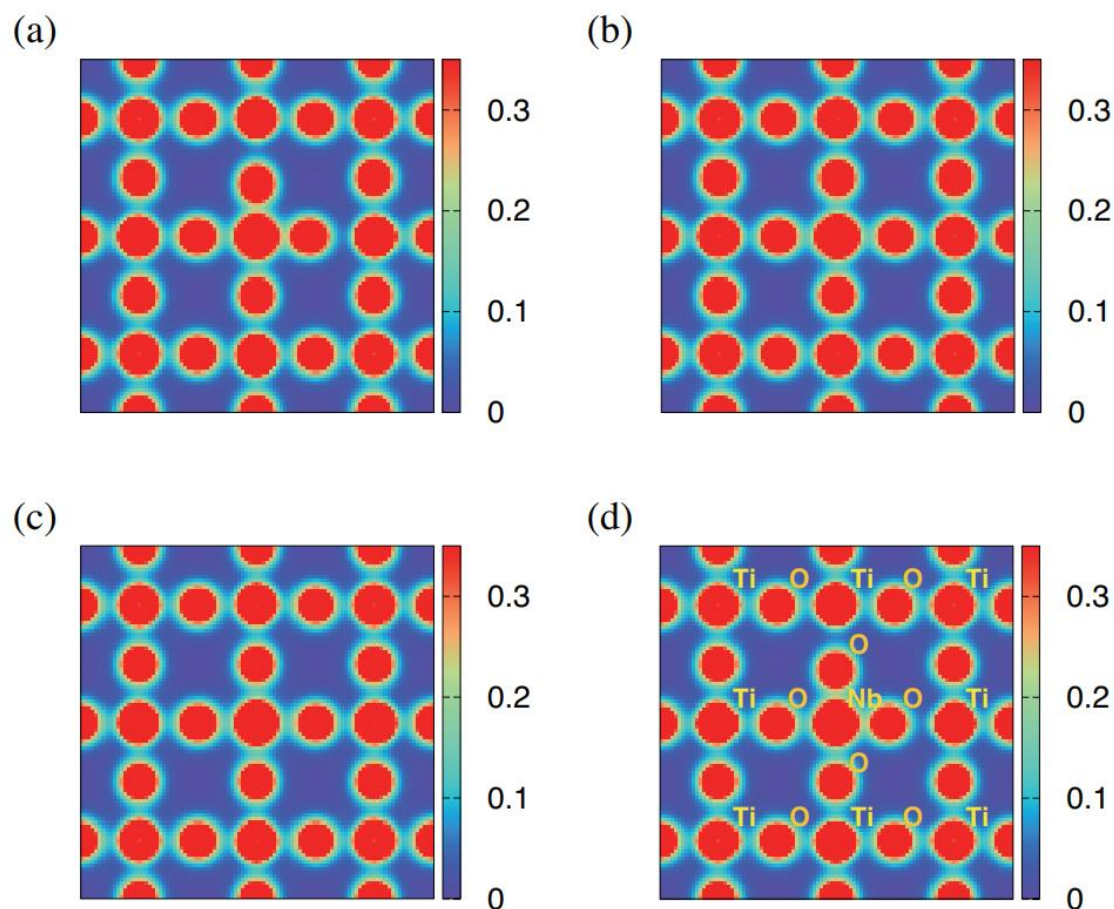


Figure 5-12 2D charge density plots for Nb:SrTiO₃ calculated with DFT+*U* method plotted for the (002) plane: *U* = (a) 0, (b) 3.0, (c) 6.0 and (d) 9.0 eV.

5.4 Conclusion

First-principles calculations with DFT+*U* were performed on the local structures and the in-gap electronic states of n-type SrTiO₃ introduced by substitution of Sr by La or Ti by Nb.

Preliminary calculations for the undoped SrTiO₃ revealed that the direct and indirect energy gaps in the band structures were better reproduced by assigning a large *U* on Ti.

For La-doped SrTiO₃, cubic structures, $a = c$, were proved to be stable by the structural relaxation calculations, even though the tetragonal structures were assumed for the unit cell. The O atoms neighboring the substitutional La slightly moved toward the dopants. The sharp electron band, which gave n-type conductivity and resulted from the intersection of

Fermi energy level at the conduction band bottom with La-doping, was composed of $3d$ orbitals in Ti. The La-doping transformed some of the p electrons in O into the d electrons in Ti, which contributed to n-type conduction.

For Nb-doped SrTiO_3 , cubic structure was proved to be stable again. The local structure around the Nb substitutional dopants to Ti was revealed that the O atoms neighboring the dopants were attracted toward the Nb atoms, while the Ti atoms at the nearest neighbors of the dopants were repelled away from the Nb atoms. The sharp band of the in-gap states just below the Fermi energy was not only of the first nearest-neighbor Ti atoms, but also of the second and third nearest-neighbor Ti atoms of the Nb dopants. The degree of Fermi energy level intrusion into conduction band and atomic rearrangements near Nb substitutional defects were milder than those of La substitutions.

Replacement of Sr by La not contained in Ti-O network does not disturb the electron transport within Ti-O conduction planes. Similarly, Nb-doping in Ti site does not interrupt the n-type carrier transportation through conduction path formation which bypasses the unit cell containing the dopants.

6. First-principles calculations of the electron and phonon band structure for CsAlCl₄ crystal

6.1 Introduction

The structure of $AX\text{-}AlX_3$ (A : alkaline metals; X : halogens) binary molten salts near stoichiometry solid phase compound composition (1 : 1 mixture) have long been in dispute [79]-[92]. Binary alkaline haloaluminates have originally attracted interest because they exhibit relatively low melting temperatures for inorganic salts [80]. This property enables many applications to be used as efficient electrolyte materials [91]. Investigations on the alkaline tetrahaloaluminate melt structure merge with those on organic cation - tetrahaloaluminate anion room temperature ionic liquids [86] which have great impact on electrochemical surface finishing and energy storage technology [93], and they are essential to develop and design new electrolytes.

As for $A = \text{Cs}$ and $X = \text{Cl}$, anion structure is known to change sharply from AlCl_4^- to Al_2Cl_7^- at the 1 : 1 composition [83]. AlCl_4^- anion takes shape of tetrahedron, which places Al atom at its center and Cl atoms at its corners. With increasing AlCl_3 composition, transition of the shape of anion from single AlCl_4^- tetrahedron to corner-sharing double AlCl_4^- tetrahedra, takes place. Vibrational spectroscopy, Raman and infrared spectroscopy, has been effectively used to investigate the sharp change of the melt structures at the stoichiometry composition [83]-[85].

The CsAlCl_4 crystal, solid-state 1 : 1 stoichiometry phase, is an indispensable key to investigate into the drastic melt structure change against composition [94][95]. The reported crystal structure [96][97] claims that anion site of this phase is composed of AlCl_4^- tetrahedron. Vibrational spectroscopy is the essential tool for the structural study of this solid crystal phase either [94][95]. Although the electron band structure of this phase to be compared with UV-vis-NIR spectroscopy is hardly found but reported and included in a database [98], no phonon dispersion calculation to be compared with vibrational spectroscopy cannot be found.

I made first-principles calculations of the electron and phonon band structure for CsAlCl_4

crystal. The crystal and coordination structures were optimized. The electronic structure was checked and phonon modes were visualized and analyzed to compare with the reported Raman spectroscopy results.

6.2 Computational details

Quantum ESPRESSO program suite [58][59], version 6.7, was used for the electronic structure and lattice structure relaxation calculations. The density functional theory (DFT) within the generalized-gradient approximation (GGA) [60] was chosen.

The PSlibrary [63] was used for the pseudopotentials. The Projected Augmented Wave (PAW) [64] pseudopotentials for the revised Perdew-BurkeErnzerhof (PBE) exchange-correlation functionals for solids (PBEsol) [65] were selected for Cs (Cs.pbesol-spn-kjpaw psl.1.0.0.UPF), Al (Al.pbesol-nkjpaw psl.1.0.0.UPF) and Cl (Cl.pbesol-nl-kjpaw psl.1.0.0.UPF), respectively. Kinetic energy cutoff for wavefunctions ('ecutwfc' [67]) and for charge density and potential ('ecutrho' [67]) were set to the largest values among those suggested in the PBEsol pseudopotential files specified above, which were 'ecutwfc = 45' Ry and 'ecutrho = 258' Ry. The suggested values for the kinetic energy cutoff values are 34 Ry for Cs, 30 Ry for Al and 45 Ry for Cl, respectively. Similarly, those for the charge density and potential cutoff are 258 Ry for Cs, 144 Ry for Al and 182 Ry for Cl, respectively, which are recommended to be more than 4-times larger than the kinetic energy cutoff [67]. As I will see later, variation of the total energy for unit cell for the present discussion should have the deviation smaller than 0.01 Ry per unit cell. Total energy calculations with kinetic energy cutoff values of 42.5, 45, 47.5, 50 and 52.5 Ry, and charge density cutoff of 256 Ry, give a same value if I round the calculated total energy values off with this accuracy

The k -point sampling grid with Monkhorst-Pack method [68] of $2 \times 2 \times 2$ k -points was used for the electron band calculation. The number of sampling points were limited because of the rather large supercell equal to the large unit cell of the crystal containing 24 atoms (4 Cs⁺ cations and 4 AlCl₄⁻ anions). The total energy convergence criterion for self-consistent field (SCF) calculations was 1.0×10^{-6} Ry for supercell. The structural optimizations were performed until atomic forces were smaller than 1.0×10^{-4} Ry. All atoms in the supercell

were relaxed to find the optimized structure.

Phonon band frequency dispersion and density of states were calculated with the program in Quantum ESPRESSO package, based on density-functional perturbation theory (DFPT) [99]. The “ASR=‘crystal’ ” setting was used to enforce the acoustic sum rule (ASR) [67]. Threshold for self-consistency in phonon calculation (‘tr2 ph’ [67]) was set to 1.0×10^{-14} . A grid of q -points for direct calculation of the entire phonon band dispersion relation (‘nq1, nq2, nq3’ [67]) was $2 \times 2 \times 2$. A k -point grid for the phonon density of states calculation (‘nk1, nk2, nk3’ [67]) was $8 \times 8 \times 8$.

XCrySDen program [100] was used to visualize the crystal structure and phonon vibration modes.

6.3 Results and discussions

Figure 6-1 and Table 6-1 show optimized structure through crystal coordinate relaxation in a fixed cell (‘relax’ program [99]), and then, through crystal coordinate and cell parameter relaxations (‘vc-relax’ program [99]). The reported crystal structure refined through X-ray diffraction study [96] was used for the initial coordinate. I use atom number in Table 1 (#) hereafter. A set of 5 sites in the unit cell defines the crystal structure for CsAlCl₄ as displayed in Table 1 in Ref [94], and here, all the other sites can be successfully derived through symmetry operation to the set of coordinates, for example, the set of #24 Al, #4 Cs, #20 Cl, #14 Cl and #11 Cl. In addition to Cs and Al, the Cl sites are derived from #20 Cl for #17-20, from #14 Cl for #13-16, from #11 Cl for #10, and from the pair of # 11 and #10 Cl for #5-12. This symmetry, including the distinction of Cl sites, is maintained both in electronic and phonon structures as I see later. The final optimized values for the lattice parameters were $a = 11.5867 \text{ \AA}$, $b = 7.05541 \text{ \AA}$ and $c = 9.34341 \text{ \AA}$, which were reported to be 11.641, 7.116 and 9.373 $\text{\AA}$, respectively [94][96]. Lattice volume of $763.813 \text{ \AA}^3$ corresponding to the unit cell composed of these lattice parameters gives lowest total energy if I simply check the energy to the volume relation in Figure 6-2. The volumes to calculate the total energies in Figure 6-2 were set by multiplying single scale factor to all of three lattice parameters. The best-fit parabola is also displayed in the Figure 6-2. The formula for the parabola is $y = f(x)$

$= Ax^2 + Bx + C$, $A = 9.37563 \times 10^{-6}$, $B = -0.014447$ and $C = -3036.18$, while parameter x is volume. As I discuss for the phonon dispersion calculation, the derived structure is not assured to be stable against any distortion at 0 K in the strict sense with this volume-energy relation. Nevertheless, as lattice vibration energy for the unit cell of 24 atoms, $\frac{3}{2} \times 24 \times (\text{Boltzmann constant}) \times (\text{absolute temperature})$, is 0.02 Ry for 80 K and 0.07 Ry for 298 K. The volume-energy relation curve in Figure 6-2 implies that these values correspond to sufficient deviations of volume, and the optimized lattice structure gains stability at these finite temperatures. The optimized structure is close to that of the experimentally observed [96][97]. As summarized in a database [101], CsAlCl_4 phase belongs to the orthorhombic Pnma space group. In this structure, three inequivalent Cl sites exist. One Cl is bonded to three equivalent Cs and one Al. Another Cl is bonded to one Cs and one Al. The remaining Cl is bonded to three equivalent Cs and one Al. Bond lengths and bond angles for the structure in Table 6-1 and Figure 6-1 are compiled in Table 6-2. Note that Cl 13 and Cl 15 cross the supercell boundary, and fourfold coordination of Cl around Al for AlCl_4^- is configured but apparently obscured. Four Al-Cl bonds around each Al are also indicated to be classified into two/one/one bonds of three types. The lengths of first group of bonds between each Al and Cl 5-12 are slightly longer, 2.1555 Å. Those between each Al and Cl 17-20 are 2.1452 Å. Those between each Al and Cl 13-16 are 2.1397 Å and slightly shorter. The slight difference in lengths is important because degeneracy of modes resolves. This classification is also valid to Cs-Cl bonds. As I see later, the existence of three different Cl sites is reflected in three different types of partial density of states and Löwdin charges for Cl. Cs is bonded to ten Cl atoms. Al is bonded to four Cl atoms to form a tetrahedron. The Cs-Cl and Al-Cl bond lengths are a little longer than those reported [96]. As a results, some of the Cl-Al-Cl bond angles in tetrahedral AlCl_4^- are slightly smaller than those observed [96], because the optimized lattice volume to pack all of these bonds into is rather smaller at the same time.

The electronic band structure is presented in Figure 6-3. Fermi energy, which is located in the middle of the bandgap in insulators and semiconductors, is calculated in the program package and derived with smearing scheme by assuming thermal broadening of the bands [29]. I chose Gaussian smearing scheme and spreading parameter of 0.01 Ry. The

characteristic structure near conduction band bottom at Γ -point and flat structure of bands in valence band do not differ from those reported, but valence band top located between Γ - and Z-point is different from the reported one at Y-point [98]. Indirect bandgap of 5.401 eV is close to the reported value of 5.392 eV [98]. Direct transition at Γ -point is 5.403 eV. Though structural optimization does not alter the crystal symmetry, exact atomic positions in the unit cell are not the same [98]. Therefore, the present calculated electron band structure has exhibited a little difference.

The calculated total and partial density of states are displayed in Figure 6-4. As common to ionic crystals, the conduction band is mainly composed of orbitals in positive atoms, Cs and Al, and the valence band is mainly composed of those in negative atom, Cl, while Al-Cl bondings in AlCl_4^- anions and coordinations of Cl around Cs is reflected in valence band. The partial densities of states for Cl indicate three different shapes of spectra.

The calculated Löwdin charges [76] are compiled in Table 6-3. Initial charges (number of valence electrons) are Cs: 9.00 (5s : 2.00; 6s : 1.00; 5p : 6.00); Al: 3.00 (3s : 2.00; 3p : 1.00) and Cl: 7.00 (3s : 2.00; 3p : 5.00), respectively, which are defined in the pseudopotential library files. Qualitatively, increase of charge number means negativity of atoms, while decrease means positivity. In this case, positivity(+) and negativity(-) are estimated as +0.8023 for Cs #1-4, -0.3409 for Cl #5-12, -0.3246 for Cl #13-16, -0.3280 for Cl #17-20 and +0.7711 for Al #21-24. It is possible that the small values of polarization lead to longer Cs-Cl and Al-Cl bond lengths and smaller Cl-Al-Cl angles.

Figure 6-5 shows phonon band frequency dispersion and Table 6-4, Table 6-5 and Table 6-6 compile calculated phonon frequencies at Γ -point to be compared with those reported and read from experimental Raman scattering spectra [94]. Each calculated frequency, such as $522.555753 \text{ cm}^{-1}$, is rounded to the first decimal place and displayed as 522.6 cm^{-1} . Too much digits for the frequencies are meaningless for comparison with numbers I read from the peak positions of experimental Raman scattering bands. Negative frequencies were obtained at Γ -point and at Γ -Y, Γ -X, X-S, S-Y and Γ -Z branches even for the optimized structure derived with the relaxation algorithms. Apparently, they seem to correspond to imaginary phonon modes which often appear in DFPT calculations based on harmonic approximation [102]-[104]. In those cases, they indicate dynamic instability of the high temperature phase

under low temperature conditions to transform into low temperature phase observed for cubic ZrO_2 [105], SrTiO_3 [106] and $\beta\text{-Ti}$ [102]. In the reported phase diagrams for CsCl-AlCl_3 binary system at the temperatures above 0 °C, there exists no phase transition for the 1 : 1 stoichiometry phase at the temperature region from around 273 K to its melting point, 660.7 K [91][92]. Nevertheless, regardless of whether the origin of the imaginary mode in the present case is dynamical instability or other factors, such as technical or material specific issues [103], wave numbers of the higher frequency modes at Γ -point can be compared with those confirmed with the experimental Raman and IR spectroscopy. The calculated frequencies were about 10 cm^{-1} higher than experimental scattering peak in low-frequency region, about $10 - 20\text{ cm}^{-1}$ lower in medium-frequency region, and about 3–30 lower in high-frequency region. A little shrinkage of the calculated volume [94][96] leads to the rise of the global mode frequency in low-frequency region, and a little elongation of the bonds [95][96] results in the lowering of the local mode frequency in medium- and high-frequency regions.

The calculated total and partial phonon density of states are given in Figure 6-6. The Cs-related modes are concentrated in the low-frequency region especially at the lower side, because of their large effective mass of the modes. It is suggested from Figure 6-5 and Figure 6-6 that not only $a \neq b \neq c$ orthorhombic crystal structure but also existence of three inequivalent Cl sites make electron and phonon band structure non-degenerated and congested.

The experimentally observable phonon vibration modes in Raman spectra measurement [94] demonstrated in Table 6-4, Table 6-5 and Table 6-6 are visualized in Figure 6-7. The distinct motions of Cs atoms are only observed in low-frequency modes as illustrated in the example for mode 11 and 18, and for 15 as a faint. In these modes and in the other low-frequency mode 16, center of mass for each tetrahedral AlCl_4^- anion is highly mobile with vibration, which is characteristic for global modes. It is particularly the case in mode 15, where the bond-lengths of the medium-length bonds are totally frozen, and those of other shorter or longer bonds are faintly deviate. Therefore, all of four Cl atoms around each Al atom move on with its central Al in this mode. The remaining medium- and high-frequency modes are local modes of AlCl_4^- . This is why it is important to analyze solid crystal

vibrational modes in order to investigate into neutral melt structure at stoichiometry composition [95]. As for mode #38-60, vibrational motions are similar to normal modes of tetrahedral methane, such as symmetric (#60) stretching modes, bending mode (#42, 43), and torsional mode (#38, 39). Those correspond to asymmetric modes are not obvious. The modes #46-54 involve central Al motions, and it is possible that such Al motions are accompanied by either of the normal modes of tetrahedral molecules. The high-frequency modes of #63-71 are also local modes, while bond-length deviation is concentrated on one out of four Al-Cl bonds around each Al atom. Since symmetric stretching mode of #60 at 341.4 cm^{-1} is rather categorized as a high-frequency mode, local mode of higher frequency whose bond-stretching is concentrated on either of four bonds with significant motion of Al would be regarded as a variant of stretching mode which is asymmetric. Therefore, the high-frequency modes are considered to be divided into two small classifications depending on whether they have total symmetry or not. The localization of motions and the lightness of the effective mass of each mode raise the frequencies of the asymmetric stretching vibrations further.

Table 6-1 Optimized structural data for CsAlCl₄ in orthorhombic unit cell with space group Pnma. Atomic positions are displayed in relative coordinates of the lattice constants, *a*, *b*, *c*. Lattice parameters are *a* = 11.5867, *b* = 7.05541, *c* = 9.34341.

Atom #	Species	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
1	Cs	0.1806501981	0.2500000000	0.3363431620
2	Cs	0.3193498019	0.7500000000	0.8363431620
3	Cs	0.8193498019	0.7500000000	0.6636568380
4	Cs	0.6806501981	0.2500000000	0.1636568380
5	Cl	0.0854881311	0.0031310290	0.6696051979
6	Cl	0.4145118689	0.5031310290	0.1696051979
7	Cl	0.4145118689	0.9968689710	0.1696051979
8	Cl	0.9145118689	0.5031310290	0.3303948021
9	Cl	0.9145118689	0.9968689710	0.3303948021
10	Cl	0.5854881311	0.4968689710	0.8303948021
11	Cl	0.5854881311	0.0031310290	0.8303948021
12	Cl	0.0854881311	0.4968689710	0.6696051979
13	Cl	0.0938789623	0.7500000000	0.0911700652
14	Cl	0.4061210377	0.2500000000	0.5911700652
15	Cl	0.9061210377	0.2500000000	0.9088299348
16	Cl	0.5938789623	0.7500000000	0.4088299348
17	Cl	0.2120070879	0.2500000000	0.9529978207
18	Cl	0.2879929121	0.7500000000	0.4529978207
19	Cl	0.7879929121	0.7500000000	0.0470021793
20	Cl	0.7120070879	0.2500000000	0.5470021793
21	Al	0.0705344262	0.2500000000	0.8052497467
22	Al	0.4294655738	0.7500000000	0.3052497467
23	Al	0.9294655738	0.7500000000	0.1947502533
24	Al	0.5705344262	0.2500000000	0.6947502533

Table 6-2 Bond lengths and bond angles for the optimized crystal structure presented in Table 6-1.

Bond	Length (Å)	Bond	Length (Å)
Cs 1 - Cl 5	3.7226	Al 22 - Cl 6	2.1501
Cs 1 - Cl 6	3.5910	Al 22 - Cl 7	2.1501
Cs 1 - Cl 12	3.7226	Al 22 - Cl 16	2.1345
Cs 1 - Cl 14	3.5294	Al 22 - Cl 18	2.1400
Cs 2 - Cl 10	3.5561	Al 21 - Cl 5	2.1501
Cs 2 - Cl 12	3.5910	Al 21 - Cl 12	2.1501
Cs 2 - Cl 18	3.5916	Al 21 - Cl 17	2.1400
Cs 3 - Cl 8	3.7226	Al 24 - Cl 10	2.1501
Cs 3 - Cl 9	3.7226	Al 24 - Cl 11	2.1501
Cs 3 - Cl 16	3.5294	Al 24 - Cl 14	2.1345
Cs 3 - Cl 10	3.5910	Al 24 - Cl 20	2.1400
Cs 4 - Cl 6	3.5561	Al 23 - Cl 8	2.1501
Cs 4 - Cl 8	3.5910	Al 23 - Cl 9	2.1501
Cs 4 - Cl 20	3.5916	Al 23 - Cl 19	2.1400

Bonds	Angle (deg)	Bonds	Angle (deg)
Cl 5 - Al 21 - Cl 17	108.469	Cl 8 - Al 23 - Cl 9	107.182
Cl 5 - Al 21 - Cl 12	107.182	Cl 8 - Al 23 - Cl 19	108.469
Cl 12 - Al 21 - Cl 17	108.469	Cl 9 - Al 23 - Cl 19	108.469
Cl 6 - Al 22 - Cl 7	107.182	Cl 10 - Al 24 - Cl 14	109.744
Cl 6 - Al 22 - Cl 16	109.744	Cl 11 - Al 24 - Cl 10	107.182
Cl 7 - Al 22 - Cl 16	109.744	Cl 11 - Al 24 - Cl 14	109.744
Cl 16 - Al 22 - Cl 18	113.051	Cl 11 - Al 24 - Cl 20	108.469
Cl 18 - Al 22 - Cl 6	108.469	Cl 20 - Al 24 - Cl 10	108.469
Cl 18 - Al 22 - Cl 7	108.469	Cl 20 - Al 24 - Cl 14	113.051

Table 6-3 Löwdin charges for the atoms in the relaxed local structure of CsAlCl₄. $N(s)$ and $N(p)$ denote numbers of electrons in s - and p -orbitals, respectively.

Species	Atom #	Total	$N(s)$	$N(p)$
Cs	1 - 4	8.1983	2.2140	5.9843
Cl	5 - 12	7.3403	1.8156	5.5247
Cl	13 - 16	7.3234	1.8116	5.5118
Cl	17 - 20	7.3272	1.8148	5.5124
Al	21 - 24	2.2302	0.7074	1.5228

Table 6-4 Calculated frequencies for Γ -point, assigned types of vibration modes based on D_{2h} point group and mode activities. Reported experimentally observed Raman scattering frequencies at 298 and 80 K are also indicated.

Mode #	Frequency (cm^{-1})	Assignment	Activity	Raman scattering [94]	
				(cm^{-1}) 298 K	(cm^{-1}) 80 K
1	-21.9	B_{2u}	I		
2	-18.5	A_g	R		
3	-8.2	B_{1u}	I		
4	-7.9	B_{2u}	I		
5	-1.3	B_{3u}	I		
6	13.0	B_{2g}	R		
7	16.1	B_{3u}	I		
8	18.1	A_u			
9	25.2	B_{1u}	I		
10	27.1	B_{1g}	R		
11	33.7	B_{3g}	R		
12	34.1	A_g	R	22	23
13	39.2	A_u			
14	39.4	B_{3g}	R		
15	41.0	B_{1g}	R	48	48
16	41.1	A_g	R		
17	42.6	B_{2g}	R	26	25
18	44.9	B_{2u}	I	33	34
19	48.6	B_{2g}	R		
20	51.0	B_{1u}	I		
21	52.1	A_u			
22	53.8	B_{1g}	R		
23	54.7	B_{2u}	I		
24	56.6	B_{3u}	I		
25	58.4	A_u			
26	58.6	B_{3g}	R		
27	58.7	B_{2g}	R		
28	60.7	B_{1u}	I		
29	60.8	A_g	R		
30	61.6	B_{1g}	R		

Table 6-5 Calculated frequencies for Γ -point, assigned types of vibration modes based on D_{2h} point group and mode activities. Reported experimentally observed Raman scattering frequencies at 298 and 80 K are also indicated. (Continued)

Mode #	Frequency (cm^{-1})	Assignment	Activity	Raman scattering [94] (cm^{-1})	
				298 K	80 K
31	64.0	B_{3g}	R		
32	67.0	B_{3u}	I		
33	69.1	B_{3g}	R		
34	72.3	B_{2u}	I		
35	74.2	B_{1u}	I		
36	77.3	A_g	R		
37	110.2	B_{1u}	I		
38	114.4	B_{3g}	R	130	132
39	115.7	B_{2u}	I		
40	116.1	A_g	R	126	127
41	118.9	B_{3u}	I		
42	119.9	B_{2g}	R		127
43	120.2	B_{1g}	R	128	128
44	126.4	A_u			
45	160.3	A_u			
46	164.0	A_g	R	179	178
47	164.7	B_{3u}	I		
48	165.6	B_{1u}	I		
49	167.3	B_{2u}	I		
50	169.0	B_{1g}	R	182	182
51	169.8	B_{2g}	R	189	190
52	173.1	B_{2u}	I		
53	174.6	B_{3g}	R		180
54	175.0	A_g	R	185	186
55	176.9	B_{1u}	I		
56	178.6	B_{3g}	R		180
57	344.3	B_{3g}	R		
58	344.4	B_{2u}	I		
59	345.8	B_{1u}	I		
60	346.5	A_g	R	354	348, 351, 354, 357*

R: Raman active; I: IR active

* The splitting at low temperature is assigned to the chlorine isotopic effect [94].

Table 6-6 Calculated frequencies for Γ -point, assigned types of vibration modes based on D_{2h} point group and mode activities. Reported experimentally observed Raman scattering frequencies at 298 and 80 K are also indicated. (Continued)

Mode #	Frequency (cm^{-1})	Assignment	Activity	Raman scattering [94]	
				(cm^{-1}) 298 K	(cm^{-1}) 80 K
61	475.8	A_u			
62	476.0	B_{3u}	I		
63	481.7	B_{1g}	R	484	489
64	483.8	B_{2g}	R	506	510
65	486.9	B_{1u}	I		
66	489.9	A_g	R	488	491
67	492.3	B_{2u}	I		
68	501.9	A_g	R	499	503
69	508.7	B_{2u}	I		
70	509.2	B_{3g}	R	484	489
71	511.9	B_{3g}	R	484	489
72	528.5	B_{1u}	I		

Table 6-7: Dielectric constant tensor, Born effective charge tensors in cartesian axis and mean charges. Charge neutrality is enforced by applying acoustic sum rule.

Dielectric constant tensor			
$\begin{pmatrix} 2.572189369 & 0.000000000 & 0.000000000 \\ 0.000000000 & 2.551933537 & 0.000000000 \\ 0.000000000 & 0.000000000 & 2.545838201 \end{pmatrix}$			
Species	Atom #	Born effective charge tensor	Mean charge
Cs	1, 3	$\begin{pmatrix} 1.41338 & 0.00000 & 0.02878 \\ 0.00000 & 1.31014 & 0.00000 \\ 0.00902 & 0.00000 & 1.35367 \end{pmatrix}$	1.35906
Cs	2, 4	$\begin{pmatrix} 1.41338 & 0.00000 & -0.02878 \\ 0.00000 & 1.31014 & 0.00000 \\ -0.00902 & 0.00000 & 1.35367 \end{pmatrix}$	1.35906
Cl	5, 7, 9, 11	$\begin{pmatrix} -0.71267 & 0.01980 & 0.03418 \\ 0.02187 & -1.18440 & -0.35649 \\ 0.00675 & -0.33763 & -0.91414 \end{pmatrix}$	-0.93707
Cl	6, 8, 10, 12	$\begin{pmatrix} -0.71267 & -0.01980 & -0.03418 \\ -0.02187 & -1.18440 & -0.35649 \\ -0.00675 & -0.33763 & -0.91414 \end{pmatrix}$	-0.93707
Cl	13, 15	$\begin{pmatrix} -1.33283 & 0.00000 & 0.42160 \\ 0.00000 & -0.59987 & 0.00000 \\ 0.39676 & 0.00000 & -0.79650 \end{pmatrix}$	-0.90973
Cl	14, 16	$\begin{pmatrix} -1.33283 & 0.00000 & -0.42160 \\ 0.00000 & -0.59987 & 0.00000 \\ -0.39676 & 0.00000 & -0.79650 \end{pmatrix}$	-0.90973
Cl	17, 19	$\begin{pmatrix} -1.01320 & 0.00000 & -0.35573 \\ 0.00000 & -0.67662 & 0.00000 \\ -0.41606 & 0.00000 & -1.03957 \end{pmatrix}$	-0.90980
Cl	18, 20	$\begin{pmatrix} -1.01320 & 0.00000 & 0.35573 \\ 0.00000 & -0.67662 & 0.00000 \\ 0.41606 & 0.00000 & -1.03957 \end{pmatrix}$	-0.90980
Al	21, 23	$\begin{pmatrix} 2.35799 & 0.00000 & -0.09574 \\ 0.00000 & 2.33516 & 0.00000 \\ 0.02916 & 0.00000 & 2.31068 \end{pmatrix}$	2.33461
Al	22, 24	$\begin{pmatrix} 2.35799 & 0.00000 & 0.09574 \\ 0.00000 & 2.33516 & 0.00000 \\ -0.02916 & 0.00000 & 2.31068 \end{pmatrix}$	2.33461

Table 6-8: Recalculated frequencies with non-analytical term correction for Γ -point, assigned types of vibration modes based on D_{2h} point group and mode activities.

Mode #	Frequency (cm^{-1})	Assignment	Activity	Mode #	Frequency (cm^{-1})	Assignment	Activity
1	-26.8	B_{2u}	I	29	58.5	B_{1g}	R
2	-23.6	A_g	R	30	59.1	B_{1u}	I
3	-21.1	B_{3u}	I	31	62.5	B_{3g}	R
4	-16.6	B_{1u}	I	32	63.4	B_{3u}	I
5	-15.9	B_{2u}	I	33	66.3	B_{3g}	R
6	2.2	B_{3u}	I	34	70.9	B_{2u}	I
7	8.2	B_{2g}	R	35	71.2	B_{1u}	I
8	16.1	A_u		36	75.4	A_g	R
9	20.6	B_{1u}	I	37	108.5	B_{1u}	I
10	24.8	B_{1g}	R	38	112.7	B_{3g}	R
11	31.6	B_{3g}	R	39	114.1	B_{2u}	I
12	32.6	A_g	R	40	114.5	A_g	R
13	36.2	A_u		41	117.0	B_{3u}	I
14	37.4	B_{3g}	R	42	118.2	B_{2g}	R
15	37.7	B_{1g}	R	43	118.5	B_{1g}	R
16	40.2	B_{2g}	R	44	125.1	A_u	
17	40.6	A_g	R	45	159.0	A_u	
18	44.0	B_{2u}	I	46	162.6	B_{3u}	I
19	44.2	B_{2g}	R	47	162.9	A_g	R
20	47.9	A_u		48	164.4	B_{1u}	I
21	50.3	B_{1g}	R	49	166.4	B_{2u}	I
22	50.7	B_{1u}	I	50	168.3	B_{1g}	R
23	51.7	B_{2u}	I	51	168.8	B_{2g}	R
24	51.9	B_{3u}	I	52	172.2	B_{2u}	I
25	55.8	B_{2g}	R	53	173.4	B_{3g}	R
26	56.2	A_u		54	174.2	A_g	R
27	57.6	B_{3g}	R	55	176.1	B_{1u}	I
28	58.0	A_g	R	56	177.8	B_{3g}	R

Table 6-9: Recalculated frequencies with non-analytical term correction for Γ -point, assigned types of vibration modes based on D_{2h} point group and mode activities. (Continued)

Mode #	Frequency (cm^{-1})	Assignment	Activity	Mode #	Frequency (cm^{-1})	Assignment	Activity
57	343.5	B_{3g}	R	65	486.9	B_{1u}	I
58	343.7	B_{2u}	I	66	489.8	A_g	R
59	345.1	B_{1u}	I	67	492.2	B_{2u}	I
60	345.8	A_g	R	68	501.9	A_g	R
61	475.8	A_u		69	508.6	B_{2u}	I
62	475.8	B_{3u}	I	70	509.2	B_{3g}	R
63	481.5	B_{1g}	R	71	511.9	B_{3g}	R
64	483.7	B_{2g}	R	72	528.6	B_{1u}	I

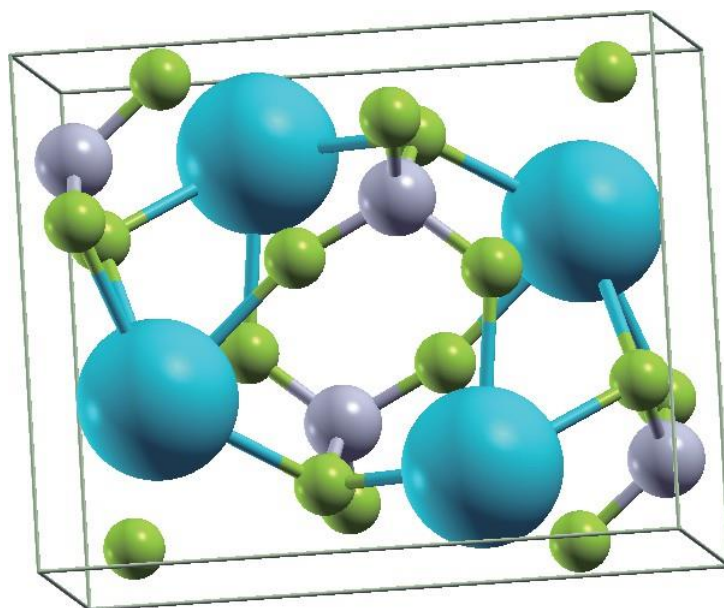


Figure 6-1 Schematic for the unit cell of orthorhombic CsAlCl_4 used for the calculations. The Cs, Al and Cl atoms are colored with turquoise, grey and lime green, respectively.

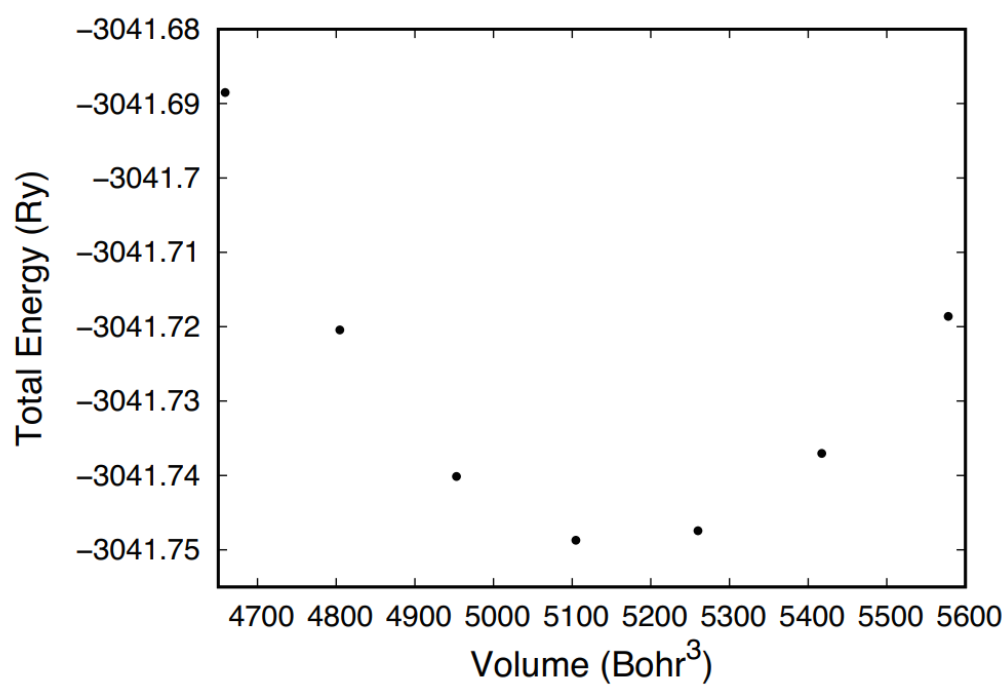


Figure 6-2 Calculated total electron energy for CsAlCl_4 against unit-cell volume.

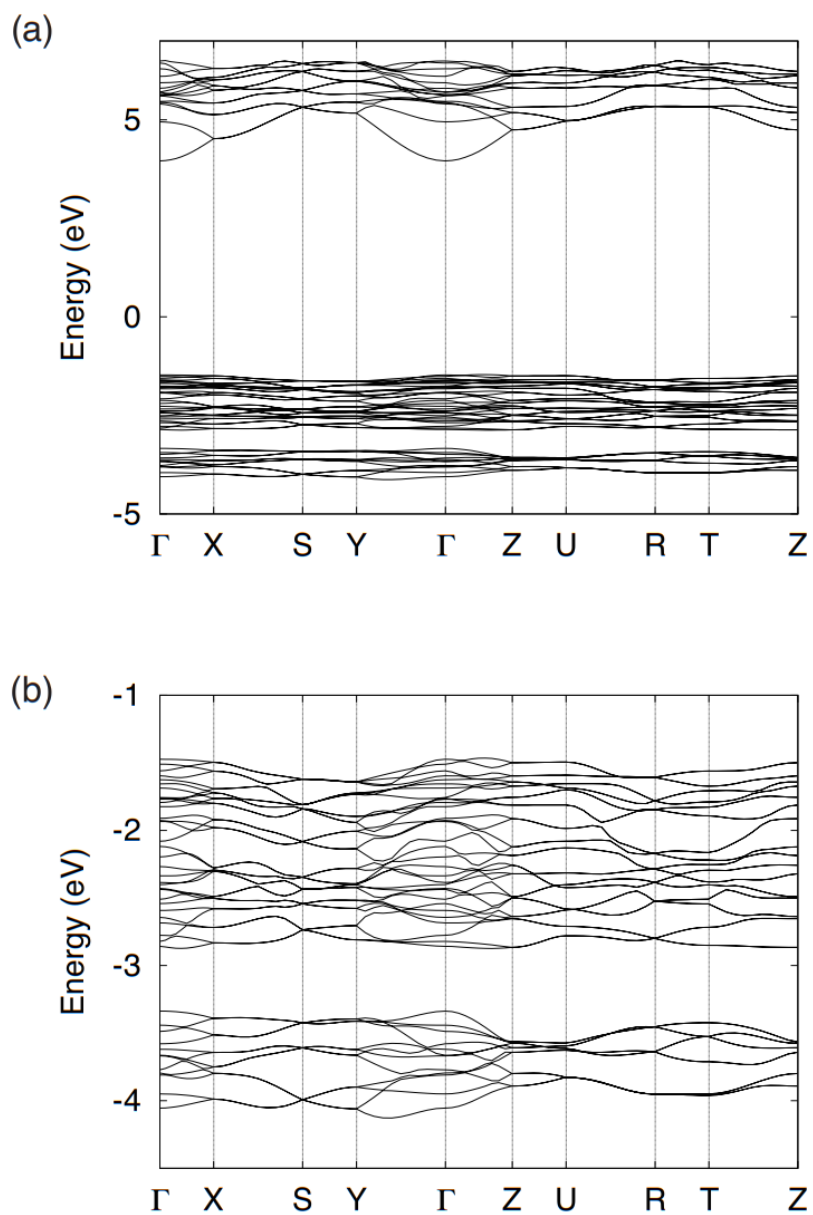


Figure 6-3 Electron band structures for CsAlCl₄ calculated for the optimized structure. Fermi energy (E_F) is set to the origin of energy: (a) all calculated bands and (b) calculated bands belong to valence band.

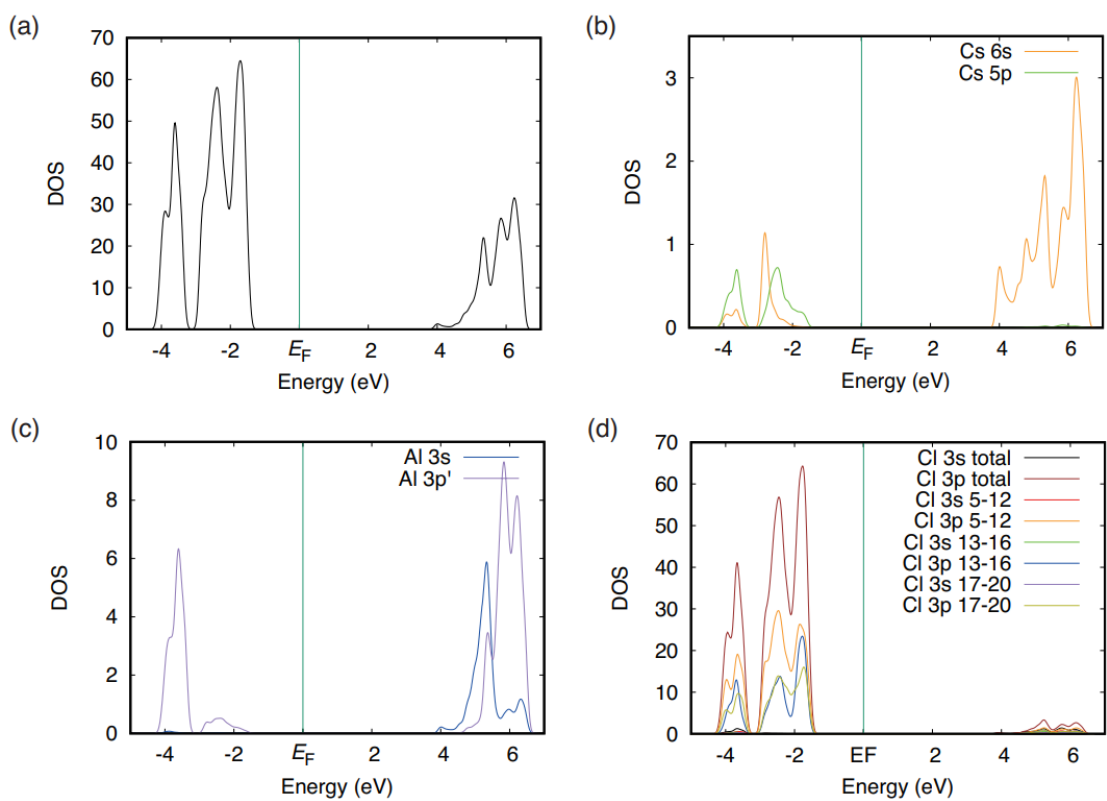


Figure 6-4 Total and partial electron density of states (DOS) for CsAlCl₄ calculated for the optimized structure: (a) total density of states, (b) Cs, (c) Al and (d) Cl partial density of states. Fermi energy (E_F) is set to the origin of energy.

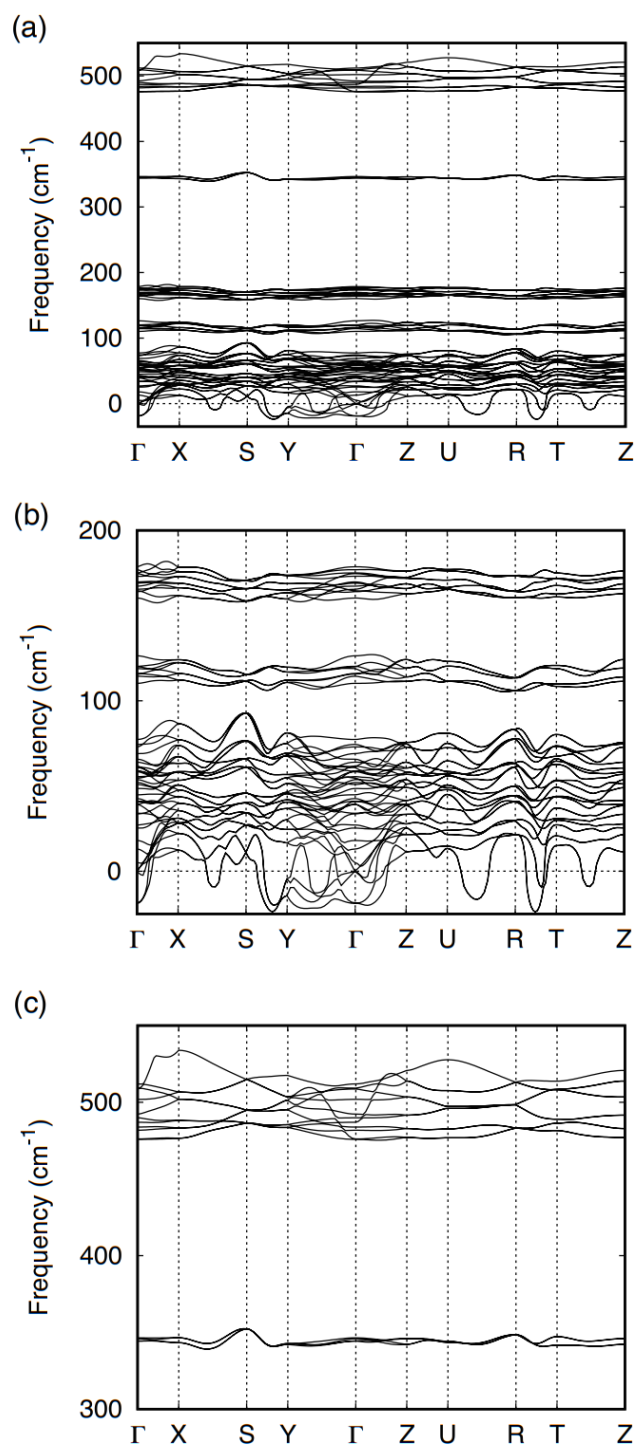


Figure 6-5 Calculated phonon band structure for CsAlCl₄ for the optimized structure: (a) all modes, (b) low frequency modes (mode #1-56) and (c) high frequency modes (mode #57-72).

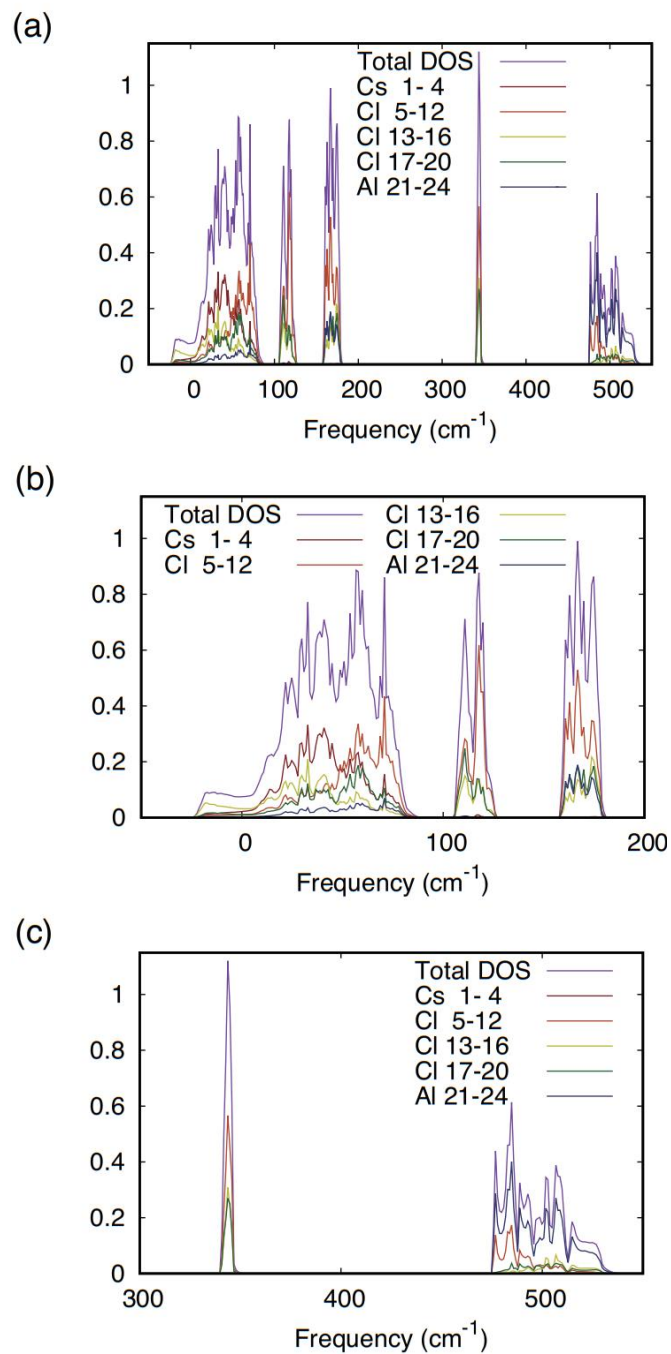


Figure 6-6 Calculated phonon density of states (DOS) spectra for CsAlCl₄ for the optimized structure: (a) all frequency, (b) frequency < 200 cm⁻¹, (c) frequency > 300 cm⁻¹.

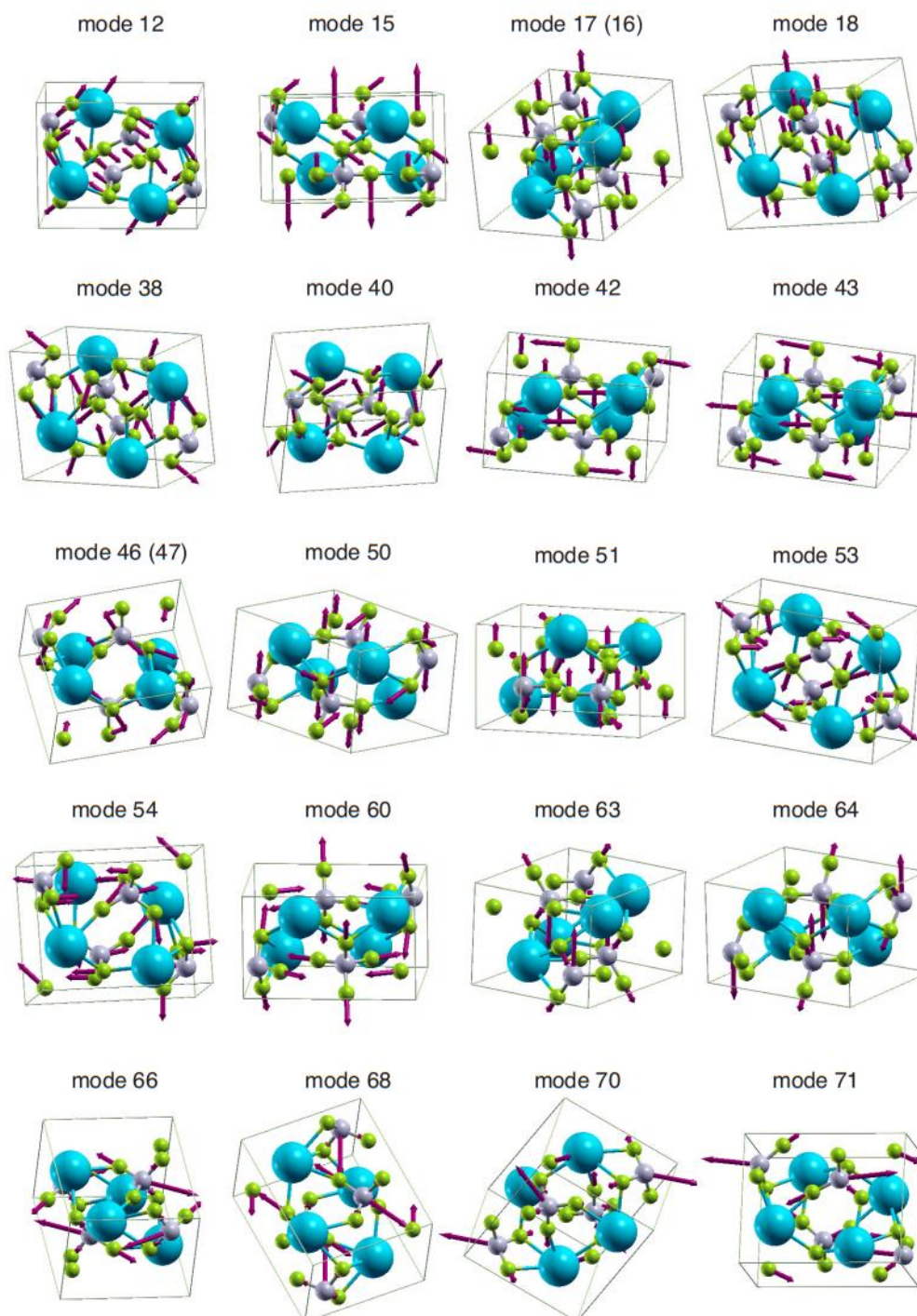


Figure 6-7 Visualized phonon vibration modes of CsAlCl_4 for the optimized structure. The Cs, Al and Cl atoms are colored with turquoise, grey and lime green, respectively. Mode numbers in brackets are correspond to those of the recalculation with non-analytical term correction.

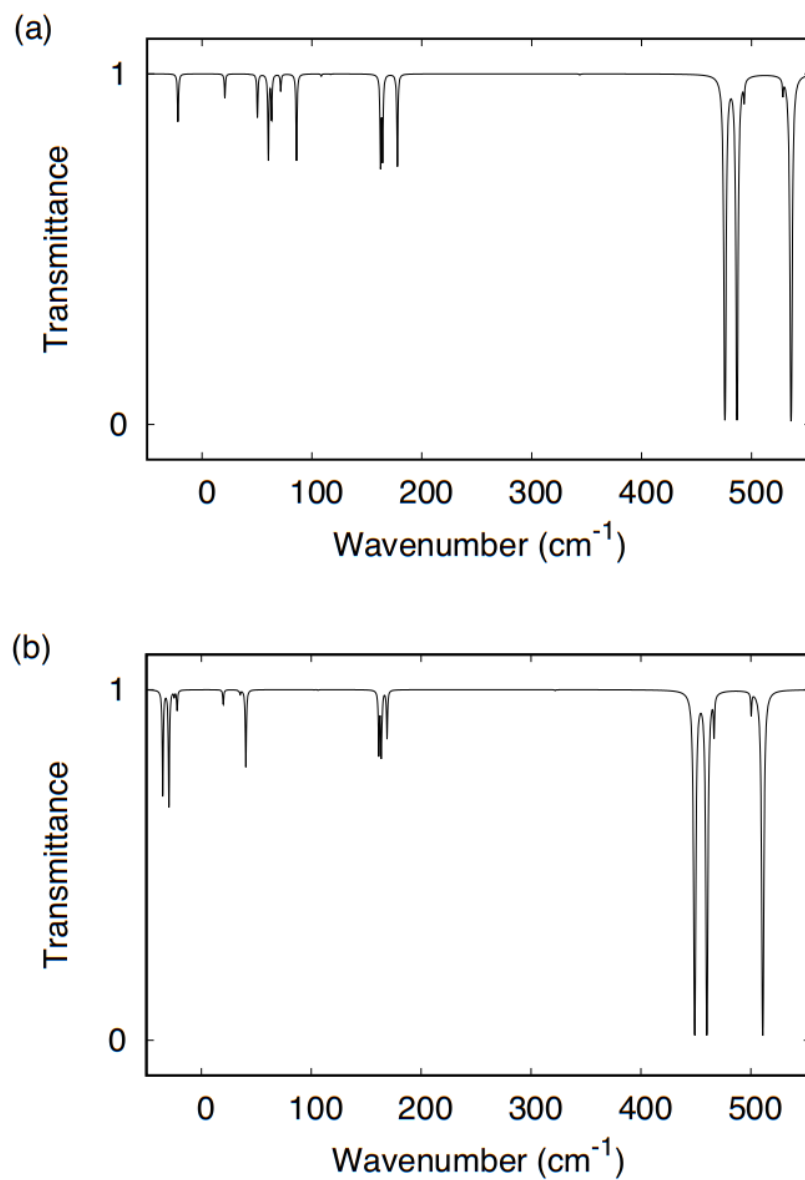


Figure 6-8 Simulated IR transmittance spectra calculated with (a) PBEsol exchange-correlation potential and PAW pseudopotentials, and (b) PZ exchange-correlation potential and NCP pseudopotentials for the recalculated phonon at Γ -point with non-analytical term correction.

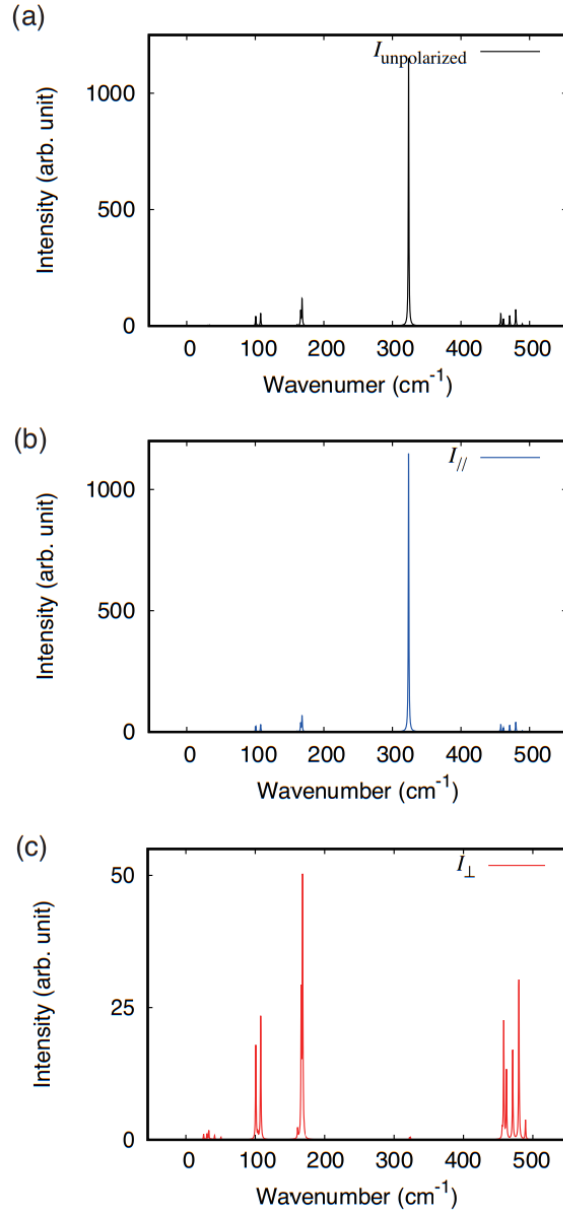


Figure 6-9 Simulated Raman scattering spectra calculated with PZ exchange-correlation potential and NCP pseudopotentials for the recalculated phonon at Γ -point with non-analytical term correction to be obtained for the polycrystalline samples through (a) non-polarized light excitation and detection, (b) detection of light with a polarization parallel to that of the excitation light, and (c) detection with a polarisation perpendicular to that of the excitation light.

6.4 Conclusion

First principles calculations were made on the electron and phonon band structure for the CsAlCl_4 crystal. The calculated phonon modes were analyzed and compared with the reported Raman spectroscopy results. For the optimized crystal structure, four Al-Cl bonds around each Al to form AlCl_4^- anions were classified into three types for their lengths. Band structure indicated an indirect bandgap of 5.401 eV between valence band top near Z-point and conduction band bottom at Γ -point. Electron density of states and Löwdin charges reflected three types of Cl sites. Phonon band frequency dispersion and phonon density of states revealed splitting of phonon vibration modes into those of low-, medium- and high-frequencies. In each bunch of modes, existence of three inequivalent Cl sites made its structure non-degenerated and congested. Visualized vibration modes exhibited distinct motions of Cs atoms only in low-frequency global modes with highly mobile tetrahedral AlCl_4^- anions, bending and torsional motions of tetrahedra as medium-frequency local modes, and stretching motions of Al-Cl bonds as high-frequency local modes of AlCl_4^- . The high-frequency modes were divided into two small classifications depending on whether they have total symmetry or not.

7. General conclusion

In Chapter 2, selective lattice vibration excitation method is applied to Raman-active but infrared-inactive mode using mid-infrared free-electron laser as a pump and solid-state green laser as a probe, taking diamond as an example. By using two-photon excitation in pump system, I succeeded in selective excitation of an inactive-infrared diamond T_{2g} mode with a sufficient distinction. Surface destruction by probe laser, red shift of the target signal and scattering-band broadening in previous study were resolved by reviewing the measurement system. Excited phonon lifetime was also estimated.

In Chapter 3, I tried to perform selective excitation of phonon modes in Raman inactive mode and weak signal mode. For that purpose, a preliminary study with Stokes Raman scattering was performed and successfully observed a signal for GaP, while distinct signal was not obtained for YSZ and rutile. Anti-Stokes Raman scattering light could not be observed in all of these samples.

In Chapter 4, I planned chiral phonon excitation using dextrorotatory α -quartz. Almost all modes could be observed with the 785 nm diode laser, while only the peak around 460 cm^{-1} could be observed with the 532 nm CW laser. It is speculated from first-principles electron energy band calculations and reported absorption spectra that the probe laser of shorter wavelength generates higher level of stray-light photoluminescence through two-photon excitation.

In Chapter 5, first-principles calculations with DFT+ U were performed on the local structures around bandgap and the in-gap electronic states, in order to design resonant Raman spectroscopy especially targeting local modes involving functional dopants. It is successfully applied to n-type SrTiO_3 doped with La or Nb.

For La-doped SrTiO_3 , the sharp electron band, which gave n-type conductivity and resulted from the intersection of Fermi energy level at the conduction band bottom with La-doping, was proved to be composed of $3d$ orbitals in Ti. The La-doping transformed some of the p electrons in O into the d electrons in Ti, which contributed to n-type conduction.

For Nb-doped SrTiO_3 , the sharp band of the in-gap states just below the Fermi energy was

not only of the first nearest-neighbor Ti atoms, but also of the second and third nearest-neighbor Ti atoms of the Nb dopants. Replacement of Sr by La not contained in Ti-O network does not disturb the electron transport within Ti-O conduction planes. Similarly, Nb-doping in Ti site does not interrupt the n-type carrier transportation through conduction path formation which bypasses the unit cell containing the dopants.

In Chapter 6, first-principles calculations were performed on the electron and phonon band structure for the CsAlCl_4 crystal. The calculated phonon modes were analyzed and compared with the reported Raman spectroscopy results. Band structure indicated an indirect bandgap of 5.401 eV between valence band top near Z-point and conduction band bottom at Γ -point. Phonon band frequency dispersion and phonon density of states revealed splitting of phonon vibration modes into those of low-, medium- and high-frequencies. Visualized vibration modes exhibited distinct motions of Cs atoms only in low-frequency global modes with highly mobile tetrahedral AlCl_4^- anions, bending and torsional motions of tetrahedra as medium-frequency local modes, and stretching motions of Al-Cl bonds as high-frequency local modes of AlCl_4^- . The high-frequency modes were divided into two small classifications depending on whether they have total symmetry or not.

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List of publications

Chapter 2

Rei Akasegawa, Heishun Zen, Kan Hachiya, Kyohei Yoshida, Takuya Goto, Takashi Sagawa and Hideaki Ohgaki

“Mode-selective excitation of an infrared-inactive phonon mode in diamond using mid-infrared free electron laser”

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Chapter 5

Rei Akasegawa, Kan Hachiya and Takashi Sagawa

“In-gap states and local structures around substitutional defects in La- or Nb-doped n-type SrTiO₃”

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Chapter 6

Rei Akasegawa, Kan Hachiya and Takashi Sagawa

“First-principles calculations of the electron and phonon band structure for CsAlCl₄ crystal”

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Chapter 3

Rei Akasegawa, Kan Hachiya and Takashi Sagawa

“Stokes Raman Spectroscopy for mode-selective phonon excitation in widegap semiconductors”

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Chapter 4

Rei Akasegawa, Kan Hachiya and Takashi Sagawa

“Stokes Raman Spectroscopy for chiral phonon excitation in alpha-quartz”

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List of presentations

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"Selective excitation of lattice vibration mode using mid-infrared free electron laser",

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Rei Akasegawa, Heishun Zen, Kyohei Yoshida, Kan Hachiya, Takashi Sagawa, Hideaki Ohgaki

"Selective phonon-mode excitation with mid-infrared free-electron laser probed by hyper-Raman scattering spectroscopy"

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赤瀬川 怜, 蜂谷 寛, 佐川 尚

「La/Nb ドープ n 型 SrTiO₃ のギャップ内電子構造」

2023 年第 70 回応用物理学会春季学術講演会、2023 年 3 月 15-18 日

上智大学 四谷キャンパス、東京都千代田区

赤瀬川 怜, 岡崎 豊, 塚本桂大, 蜂谷 寛, 佐川 尚

「汎用蛍光分子の一軸配向に基づく発光型円偏光コンバータの作製と評価」

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兵庫県民会館、兵庫県神戸市

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「中赤外自由電子レーザーを用いた選択的格子振動励起の実証」

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上智大学 四谷キャンパス、東京都千代田区

赤瀬川 怜、佐藤央至、吉田恭平、全 炳俊、蜂谷 寛、後藤琢也、佐川 尚、大垣英明

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“Generation of time-multiplexed chiroptical information from multilayer-type luminescence-based circular polarization conversion films”

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Ju Yoon Hnin Bo, Heishun Zen, Kyohei Yoshida, Kan Hachiya, Rei Akasegawa, Hideaki Ohgaki
“Observation of selective excitation of Raman inactive phonon mode of strontium titanate through anti-Stokes hyper-Raman scattering process”

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Ju Yoon Hnin Bo, Heishun Zen, Rei Akasegawa, Kan Hachiya, Kyohei Yoshida, Hideaki Ohgaki
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