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Raman Lasing and Cascaded Coherent Anti-Stokes Raman Scattering of Two-Phonon Raman Band

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Raman lasing of a two-phonon Raman band in anti-Stokes side is demonstrated. Two femtosecond light pulses with identical wavelengths is irradiated onto a SrTiO₃ crystal under cross-beam configuration. Under low excitation power, several wave-mixing signals with identical wavelengths are emitted. When the power exceeds over a critical value, cascaded Coherent anti-Stokes Raman Scattering (CARS) signals are emitted, the frequency step of which is coincident with that of the strongest two-phonon Raman band of 2TO₂. ©

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Stimulated Raman Scattering (SRS) is one of the earliest discovered nonlinear optical effects. In 1962, Woodbury and Ng detected an infrared component in the laser output while

studying Q-switching of a ruby laser with nitrobenzene Kerr cell. After this infrared output was recognized as the result of stimulated Raman emission (SRE), the SRE process was found in many other materials including gases and solids. Since then, useful applications have been developed by the effect, such as tunable coherent infrared and ultraviolet light sources, and high resolution spectroscopy.¹ Recently, multicolor generation using cascaded Raman process has attracted interests to generate ultrashort light pulses.^{2,3} Here, there is a question. Is the SRE possible for any Raman bands ? This is not necessarily an obvious problem. To our knowledge, one who gave this problem for two-phonon Raman bands for the first time was Shen.⁴ The two-phonon Raman bands come from the simultaneous creation and annihilation of two phonons. He examined the possibility of two-phonon Coherent Anti-Stokes Raman Scattering (CARS). Shen's answer was that the two-phonon CARS was possible but parametric amplification of one-phonon waves occurred in some condition. After it, the nonlinear spectroscopy of the two-phonon Raman bands has attracted very few interests. Recently, the two-phonon and the two-magnon Raman bands have attracted new interests. They are recognized as a stage of non-photon squeezing under strong electric field of femtosecond light pulses.⁵⁻⁹ The authors demonstrated that the quantum noise could be controlled via excitation of the second-order Raman bands. The second-order Raman bands have distinct nature against the first-order ones. Now, let's return to the original problem. Are the SRE possible for the two-phonon Raman bands ? In this letter, we report that cascaded CARS of the two-phonon Raman band is achieved by injecting a second femtosecond light pulse in a direction different from the main femtosecond pump pulse. The importance of SRE of the two-phonon Raman bands is not restricted to the scientific interests. Because the two-phonon Raman bands are broad and sometimes very strong, there is a possibility of

continuously tunable broadband solid-state Raman laser.

In this letter, a SrTiO₃ crystal, which has a cubic perovskite structure with a space group $Pm\bar{3}m$ (O_h^1) at room temperature is studied. Its phonon modes at the Brillouin zone center at room temperature are made up of one T_u acoustic mode and three T_{1u} and one T_{2u} optical modes. Each polar T_{1u} optical mode splits into one LO and doubly-degenerate TO modes.¹⁰ The specific feature of this crystal is that even though it has no Raman-active one-phonon modes, it has broad and strong Raman bands, all of which are the combination bands of two phonon waves.¹¹ It is an ideal material to study the SRS of two-phonon band because there's no direct path of excitation of the one-phonon Raman bands.

Photo-excitation is executed using a femtosecond regenerative amplifier system (Tsunami+Spitfire, Spectra Physic Co.). The experimental setup is shown in Fig.1. The pulse width is 130 fs and the spectral width is about 250 cm⁻¹. The repetition rate is 1 kHz. The light pulses from the regenerative amplifier are divided into two pulses and irradiated onto the sample. The laser pulses are focused onto the sample through a lens with a crossing angle of 2 degrees and a spot size of about 100 μm. One of the optical path lengths are controlled by a retroreflector set on an electrically controlled translational stage. When two light pulses overlap spatially and temporally well, several coherent light spots are observed at outside of the two incident light signals. The emitted light is picked-up by an optical fiber with 200- μm core radius. The optical fiber is fixed on an arm installed to an electrically controlled rotational stage so as to be rotated around the sample. The distance between the fiber and the sample is 40 mm. The collected light is measured by a visible multi channel spectrometer (USB2000, Ocean Optics Co.). A 1 mm-thick plate with a (100) surface is used for the optical measurement. All the polarizations of the incident light are vertical, which

direct the same direction of the crystal axis. The crystal surface is directed to nearly normal to the direction of the laser irradiation. When the polarizations of the excitation light pulses are crossed, no higher-order signals are observed. All the experiments are carried out at room temperature.

Figure 2(a) and (b) show the angle-resolved spectra for the degenerate two-beam excitation at low and high irradiation power. No sensitivity calibration of the spectra has been carried out. When the power is low, higher-order signals, the frequencies of which are the same as that of the incident light, are emitted in the direction of $\mathbf{k}_n = \mathbf{k}_1 + n(\mathbf{k}_1 - \mathbf{k}_2)$, ($n=0, \pm 1, \pm 2, \pm 3 \dots$) where \mathbf{k}_1 and \mathbf{k}_2 are the wavevectors of the two incident light. As the power increases, the spectral shape distorts and new peaks appear at different frequencies. When the power is over 1mW, another clear series of light pulse train with frequency shift of 370 cm^{-1} is observed. The higher-order signals are the clearest when the relative delay is set to be 243 fs, where light pulse of \mathbf{k}_1 arrives earlier than that of \mathbf{k}_2 . Within the spectral width of the incident light, there are one degenerate Raman-active second-order Raman band of $\text{TO}_2\text{-TO}_1$ and $\text{TO}_2\text{-TA}$ with 81 cm^{-1} ,¹¹ Raman-inactive one-phonon modes of TO_1 with 176 cm^{-1} and degenerate TO_1 and TA with 84 cm^{-1} .¹⁰ The observed value 370 cm^{-1} corresponds to that of the strongest second-order Raman band of 2TO_2 . It is noted that the spectral width of the incident light is only 250 cm^{-1} and the 370 cm^{-1} mode can not be excited directly by the impulsive stimulated Raman scattering process. When only one beam is irradiated, the spectrum of the emitted signal becomes very complex due to the higher-order nonlinearity as the irradiation power is increased. The crystal is damaged before SRE resonant with the two-phonon band is observed. Figure 3 shows the frequencies of the emitted signals against the emitting angles. It is obvious that the wavevectors of the frequency-shifting series lie also

on a straight line $\mathbf{k}_1 + n\Delta\mathbf{k}$ ($n=0,1,2,3,\dots$). Comparing with the direction of the signals at low excitation power there is a small mismatch between $\Delta\mathbf{k}$ and $\mathbf{k}_1 - \mathbf{k}_2$ about 110 cm^{-1} .

When the irradiation power is low, a series of discrete signals with the identical frequencies and in different directions are observed. They are generated by the degenerate four-wave mixing process. The third-order nonlinear polarization governing the case of one-color cross-beam excitation is written as the following.

$$\begin{aligned} \mathbf{P}_s^{(3)}(\omega_s) &= \mathbf{P}_s^{(3)}(\mathbf{k}_1 + \mathbf{k}_1 - \mathbf{k}_2, \omega_s = \omega + \omega - \omega) \\ &= \chi^{(3)}(\omega, \omega, -\omega) : \mathbf{E}_1(\mathbf{k}_1, \omega)\mathbf{E}_1(\mathbf{k}_1, \omega)\mathbf{E}_2^*(-\mathbf{k}_2, -\omega). \end{aligned} \quad (1)$$

Equation (1) means that the two incident light with \mathbf{k}_1 and \mathbf{k}_2 generate a dynamic grating and the \mathbf{k}_1 light is diffracted from it. The emitted light has a wavevector $\mathbf{k}_1 + (\mathbf{k}_1 - \mathbf{k}_2) = 2\mathbf{k}_1 - \mathbf{k}_2$. This light mixes with \mathbf{k}_1 and \mathbf{k}_2 again. Then another light is emitted with a wavevector $2\mathbf{k}_1 - \mathbf{k}_2 + (\mathbf{k}_1 - \mathbf{k}_2) = \mathbf{k}_1 + 2(\mathbf{k}_1 - \mathbf{k}_2)$. This process is repeated to yield higher-order signals with $\mathbf{k}_1 + n(\mathbf{k}_1 - \mathbf{k}_2)$. Because the energy of the excitation photon is far lower than that of the band gap and there are no Raman-active mode other than the second-order difference band of $\text{TO}_2\text{-TO}_1$ and $\text{TO}_2\text{-TA}$, only the non-resonant term of $\chi^{(3)}$ contributes.

When the irradiation power is higher than 1mW, higher-order signals with a frequency shift of 2TO_2 are observed in larger frequency region. The stimulated Raman process to generate coherent light with larger frequency than that of the pump light is known as CARS. Under strong excitation condition, the SRE is amplified from quantum fluctuations. Once the SRE is build up to sufficient strength, the anti-Stokes signal is amplified by the four-wave mixing process among pump pulse and the Stokes pulse, where the pump pulse is used twice in the process.

We have reported that higher-order CARS signals are efficiently generated from solids by two-color cross-beam excitation.¹² Even in the one-color excitation case, there are two advantages in the cross-beam excitation over the single-beam excitation. Firstly, the additional pulse reduces the threshold of the excitation power for SRE. Secondly, the anti-Stokes light is emitted as a beam, whereas it is emitted conically in the single-beam excitation.

In the one-color cross-beam excitation case, the \mathbf{k}_2 wave is supplied by the SRE of the two-phonon Raman band. Once the SRE is build up to sufficient strength, the anti-Stokes signal is amplified by the CARS process,

$$\begin{aligned} \mathbf{P}_s^{(3)}(\omega_s) &= \mathbf{P}_s^{(3)}(\mathbf{k}_1 + \mathbf{k}_1 - \mathbf{k}_2, \omega_s = \omega + \omega_p) \\ &= \chi^{(3)}(\omega, \omega, -\omega_2) : \mathbf{E}_1(\mathbf{k}_1, \omega) \mathbf{E}_1(\mathbf{k}_1, \omega) \mathbf{E}_2^*(-\mathbf{k}_2, -\omega_2), \end{aligned} \quad (2)$$

where $\omega_2 = \omega - \omega_p$ is the first Stokes frequency. The third-order nonlinear susceptibility $\chi^{(3)}$ for two-phonon CARS which depends on the phonon-amplitude was derived by Shen.⁴ When phonons are pumped to sufficient intensities by the stimulated Raman process, the resonant term can overcome the nonresonant term. Under efficient excitation of the anti-Stokes light, the anti-Stokes light mixes with the pump and the first Stokes light again. Then a higher-order CARS signal, the frequency of which is shifted by ω_p , is emitted in a new direction. This wave mixing process is repeated to generate higher-order signals with shifting frequency, $\omega_n = \omega + n(\omega - \omega_2) = \omega + n\omega_p$. The mismatch of the wavevector 110 cm^{-1} shows that the two-phonon wave is amplified at a definite wavevector. The Raman bands of SrTiO₃ observed in a spontaneous Raman scattering spectrum are moderately sharp, even though they are second-order ones. These suggest that the two-phonon states of SrTiO₃ form well-defined quantum states.

It is interesting to compare the above results with that of the wavevector overtone spectroscopy of LiTaO_3 by Brennan and Nelson.¹³ In their experiment, two light pulses with 35 fs duration are crossed on a crystal to generate a transient grating. A third pulse is overlapped with them as a probe beam. They found up to 9 th overtone of a phonon frequency in the transient signal of the 5 th spatially diffracted signal of the probe beam when the pump pulse power was 130 μJ . In their result, several overtones of a phonon frequency are observed in a wavevector overtone. It is contrast with our result, where the overtones of the two-phonon Raman frequency are observed in the different wavevector overtones. This means that the cascaded two-phonon CARS originates from not the overtone of the two-phonon mode but the multiple diffraction from it.

In summary, we have observed SRE of two-phonon Raman band from SrTiO_3 under cross-beam configuration using two identical color femtosecond light pulses. The SRE couples with the pump beam to generate cascaded CARS, the frequency step of which is the same as 2TO_2 .

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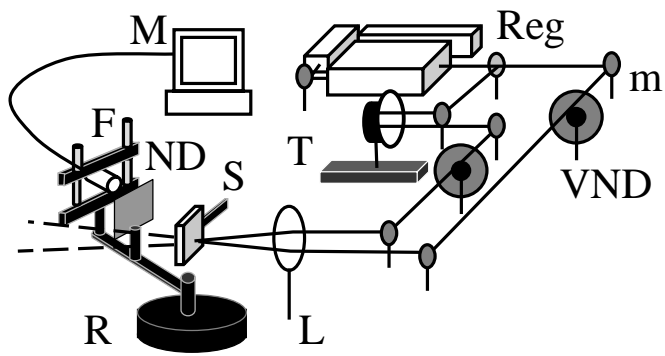


Fig. 1.

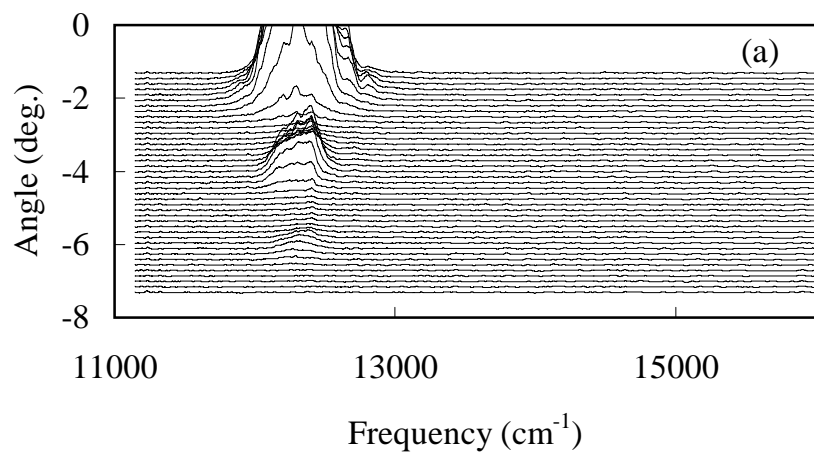


Fig.2(a)

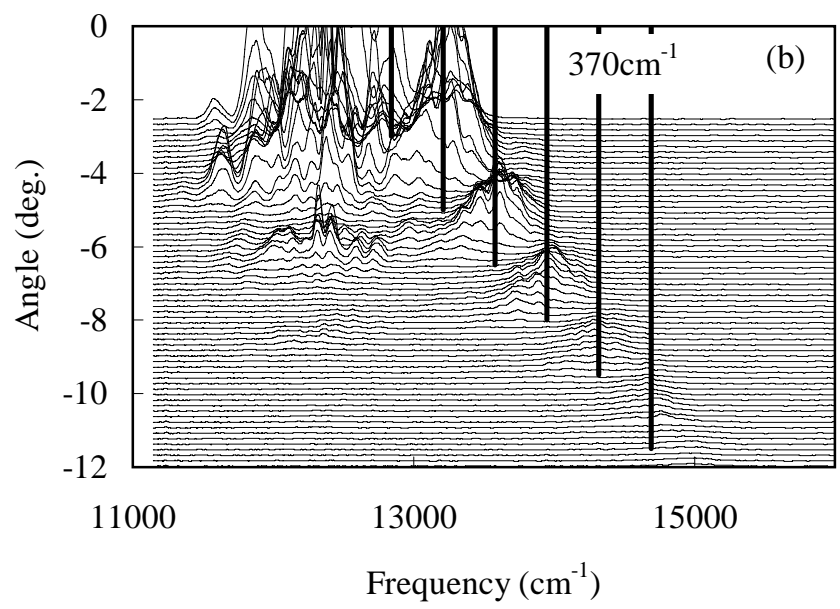


Fig.2(b)

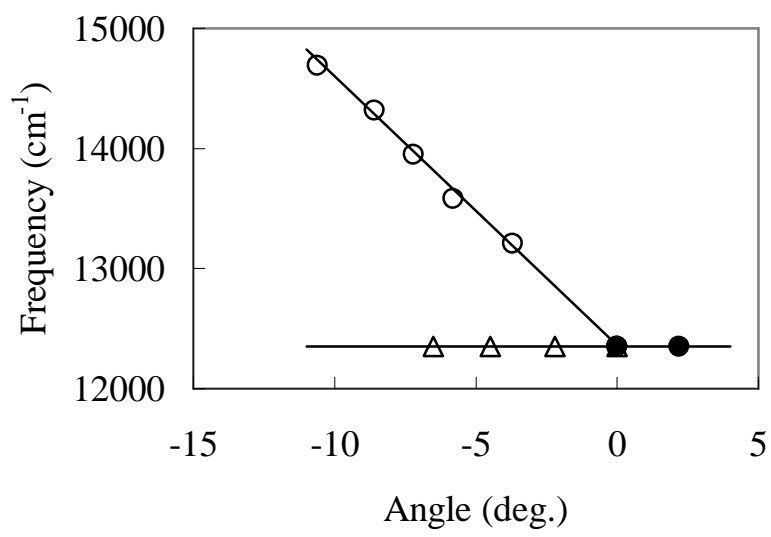


Fig.3

A. Figure Captions

Fig.1 : Setup of angle-resolved measurement. Reg : femtosecond regenerative amplifier system, m : mirror, VND : variable ND filter, T : translational stage, L : lens, M : monochromator and PC, F : optical fiber, ND : ND filter, R : rotational stage, S : sample (SrTiO_3).

Fig.2 : Angle-resolved spectrum. (a) $P_1=P_2=0.5\text{mW}$ and (b) $P_1=P_2=2.0\text{mW}$. The light pulses are injected at the angle of 0 and 2 deg. The vertical lines show the peak positions. Their spacing is 370 cm^{-1} .

Fig.3 : Peak frequencies of the higher-order signals against the emitting angle. Filled circle : incident light, open circle : wave-mixing signals at $P_1=P_2=0.5\text{mW}$, open triangle : wave-mixing signals with shifting wavenumber at $P_1=P_2=2.0\text{mW}$.