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Stimulated Raman scattering in anatase TiO_2

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Abstract. We report an experimental study of stimulated Raman scattering in anatase TiO_2 at 4K under both resonance and off-resonance conditions. Efficient first- and higher-order stimulated Raman emission of the lowest optical mode was observed, especially for the resonance case. From the dependence of the first-order Stokes emission on laser intensity, we estimate values of the Raman gain coefficient which are large compared with those reported for other crystalline materials. The large gain values are attributed to the narrow linewidth of the Raman line at low temperatures.

1. Introduction

Stimulated Raman scattering (SRS) is one of the nonlinear optical processes driven by coherent interactions between light and elementary excitations of materials [1]. Over the years, many applications such as Raman lasers [2] and attosecond pulse generation [3] have been developed out of this process. Spectroscopic applications of SRS have also been developed to obtain valuable information on the materials under investigation. It was pointed out that the major criteria for a material with efficient SRS are a narrow Raman linewidth and a high Raman scattering cross section [4]. Beattie and Gilson [5] observed a very intense Raman line in anatase TiO_2 which is well known as a photocatalyst material. Thus anatase is expected to be a good candidate for SRS. We shall report an investigation of SRS in anatase under off-resonant and resonant excitation.

2. Experimental

The samples used were single crystals of anatase TiO_2 grown by chemical transport reactions. They were kept in a continuous flow helium cryostat. For our measurements of stimulated Raman emission, an optical parametric amplifier (1.94 eV or 3.14 eV, 10 Hz repetition rate, 2 ns duration) pumped by the third harmonic of a Nd:YAG laser was used as the excitation source. The laser beam was focused into the sample by a lens of 25-cm focal length. Light scattered at nearly the right angle to the incident beam was analyzed with a double-grating monochromator equipped with a CCD detector. Spectral resolution of our setup was 0.2 (0.6) cm^{-1} for 1.94 (3.14) eV excitation.

3. Results and discussion

Figure 1 shows the spontaneous Raman spectrum of anatase TiO_2 measured at 5K. A cw He-Ne laser, 1.96 eV was used as the excitation source. Since the sample is not oriented, all the Raman-active vibrational modes with different polarizability tensors ($1A_{1g}+2B_{1g}+3E_g$) are detected [6]. It is found that the spectrum of the lowest E_g phonon at 137 cm^{-1} is quite sharp and intense, indicating a large scattering cross section for this mode [5]. These properties are the major criteria for a high gain Raman

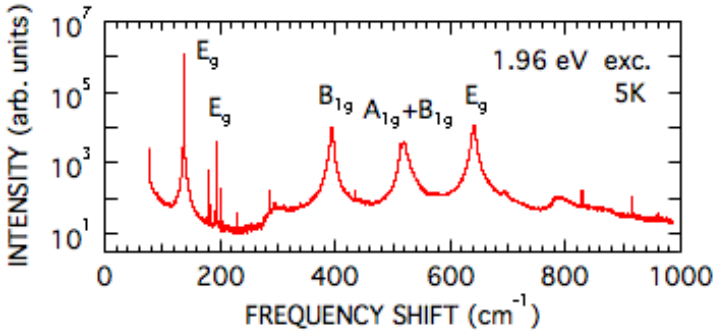

Figure 1. Spontaneous Raman spectrum of anatase at 5K excited with the 632.8 nm line of a cw He-Ne laser. The spectrum is plotted on a semi-log scale. Vibrational mode symmetries of the Raman lines are indicated. The other weak lines are plasma lines of the laser.

material [4].

Figure 2 shows the stimulated Raman spectra at 4 K and its dependence on incident laser intensity. Since the laser photon energy, 1.94 eV was well below the band-gap energy of anatase, 3.2 eV [7], the spectra were measured under the off-resonant excitation. At low excitation intensity, as shown in figure 2 (a), the spectrum is similar to the spontaneous Raman spectrum (figure 1). In addition, a weak anti-Stokes component (AS) due to the lowest E_g mode is seen. At higher intensities, the first-order Stokes emission of the E_g mode is strongly amplified through nonlinear coupling with the laser wave (figure 2(b)). As the excitation intensity is increased further, new Stokes lines appear, as shown in figure 2(c). There are intense lines at shifts of two and three times the frequency of the E_g phonon. Such higher-order Stokes components have been often observed in SRS experiments [1]. When the first-order Stokes emission becomes sufficiently intense, it acts as a source for the amplification of a light wave at the second-order Stokes energy. This process is iterated generating higher-order Stokes waves. It is found that the anti-Stokes component is also amplified.

Next we investigate the SRS process in resonant-scattering regime. Figure 3 shows the observed Raman spectra for incident laser energy of 3.14 eV which is slightly below the band-gap energy. As in the case of the off-resonant excitation, Stokes emission of the E_g mode is strongly amplified and the

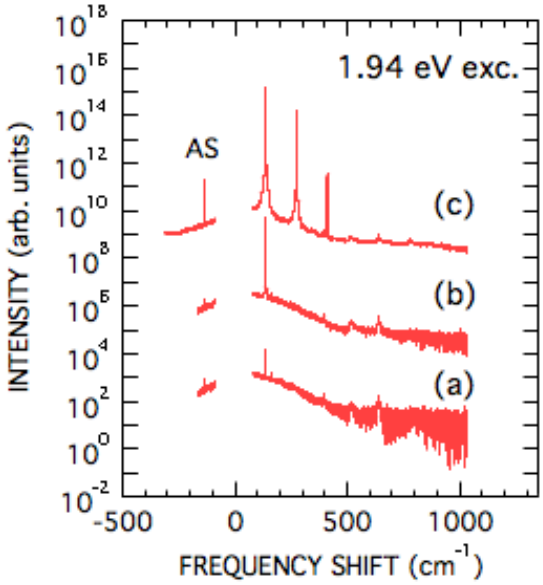

Figure 2. Stimulated Raman spectra at 4 K under off-resonant excitation for laser intensities equal to (a) 300, (b) 740 and (c) 2000 MW/cm^2, respectively. Each spectrum is offset by three decades for clarity.

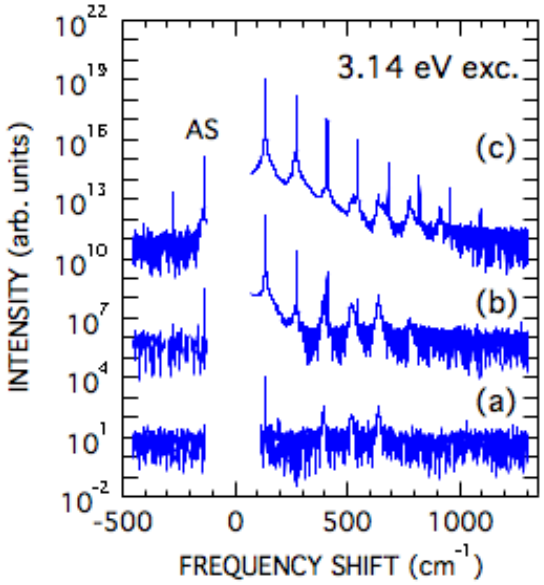

Figure 3. Stimulated Raman spectra at 4 K under resonant excitation for laser intensities equal to (a) 80, (b) 370 and (c) 1200 MW/cm^2, respectively. Each spectrum is offset by five decades for clarity.

number of the Stokes components increases with increasing excitation intensity. We observe the Stokes emission up to the eighth-order at laser intensity of 1.2 GW/cm^2 as shown in figure 3(c). Thus the number of the Stokes components in figure 3(c) is larger than that in figure 2(c) in spite of the low laser intensity compared with that in figure 2(c), indicating the resonant enhancement of Raman scattering efficiency.

Besides the sharp Stokes components, there are several bands in the range above 700 cm^{-1} in figures 3(b) and 3(c). These bands arise from spontaneous Raman scattering caused by the Stokes components. For example, the band at 777 cm^{-1} corresponds to the spontaneous Raman emission of the 640 cm^{-1}-mode (E_g symmetry) induced by the first-order Stokes emission. This fact indicates that the conversion efficiency of laser into the Stokes emission is high. Several anti-Stokes components are also observed in figures 3 (b) and 3(c). These components are produced by Raman-induced four-wave mixing processes [1].

The observed intensities of the first- and second-order Stokes emission are plotted as functions of the laser intensity in figure 4 for 1.94 eV excitation and in figure 5 for 3.14 eV excitation. For comparison, the intensity of the 395 cm^{-1}-mode (B_{1g}) is also shown. For both excitation energies, while the B_{1g} emission shows a linear dependence on incident laser intensity over the whole intensity range investigated (as shown by thin solid lines), the Stokes components show different behaviors depending on the laser intensity. With reference to [8], four different regions can be distinguished for the first-order Stokes emission : (A) at low intensities, the Stokes emission increases linearly with laser intensity (thin solid lines), indicating that spontaneous Raman scattering dominates ; (B) amplification of the Stokes emission occurs ; (C) substantial growth of the Stokes emission is observed, as shown by dotted lines (the lines are guides to the eye.) ; (D) the Stokes emission saturates under the resonant excitation (figure 5).

SRS is observed in the regions (B),(C) and (D). The threshold for SRS occurs at laser intensity of 340 (80) MW/cm^2 for 1.94 (3.14) eV excitation. We can estimate values of the Raman gain coefficient g by fitting an equation I_{Stokes}=(const)Ie^{gIl} to the first-order Stokes data in the region (B) [9]. Here I is the incident laser intensity and l is an effective interaction length. The bold solid curves in figures 4 and 5 were obtained by the fitting. Taking l = 0.5 mm (the sample size), the Raman gain coefficient is estimated to be 0.12 (0.14) cm/MW for 1.94 (3.14) eV excitation at 4 K (the accuracy of the gain values is approximately ±60% due to the possible errors in estimating I and l). These values are large

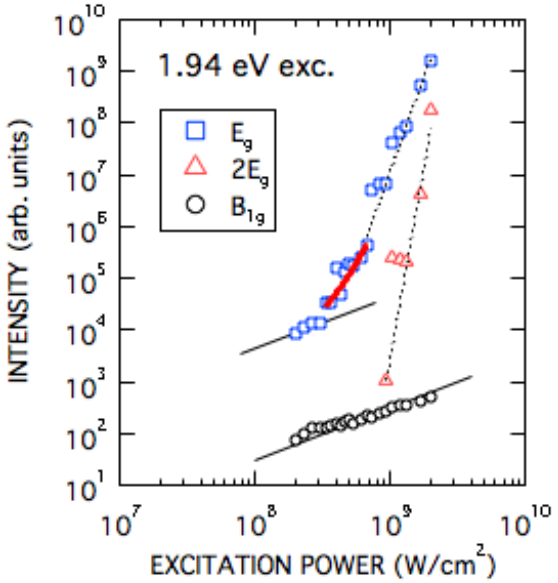

Figure 4. Experimental intensities of several Stokes lines for incident laser energy of 1.94 eV as functions of excitation power.

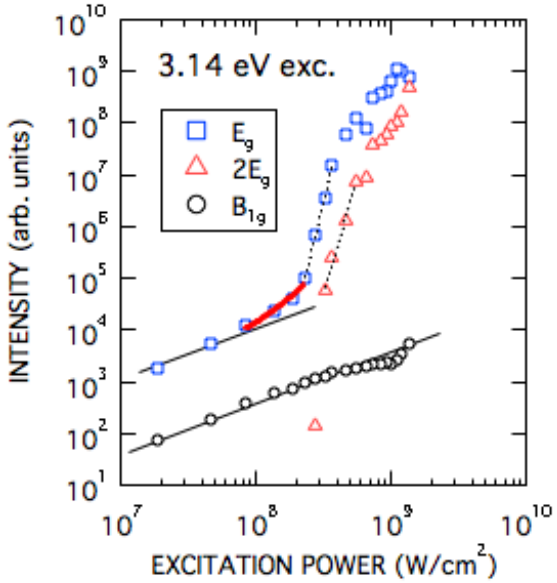

Figure 5. Same as figure 4, with incident laser energy of 3.14 eV.

compared with reported values for other crystalline materials. For example, gain values of 0.04 cm/MW for the 521 cm^{-1}-mode in Si at 77K [9] and 0.044 cm/MW for the 1066 cm^{-1}-mode in $NaNO_3$ at room temperature [10] have been reported. The gain coefficient is inversely proportional to the Raman linewidth [1]. The linewidth of the lowest E_g mode in anatase at 4 K is below our instrumental resolution (0.2 cm^{-1} full width at half-intensity-maximum) and is much smaller than the linewidths of 0.8 cm^{-1} for Si and of 2.0 cm^{-1} for $NaNO_3$. Thus it is concluded that the observed large gain is (at least partly) due to the narrow Raman linewidth. In fact, we did not observe SRS in anatase at room temperature where the Raman line of the E_g mode broadened considerably (about 7 cm^{-1}). It is seen that the estimated gain coefficient in resonance condition is almost equal to that in off-resonance condition. We have shown that intense photoexcitation with energies slightly below the band-gap energy induced resonant two-photon transitions at low temperatures [7]. Two-photon absorption at the laser frequency may suppress the Raman gain in resonance condition. Since the gain is inversely proportional to the cube of the Stokes frequency [1], the factor also contributes to the suppression.

In the region (C), the first-order Stokes emission increases sharply with increasing excitation intensity. The results are similar to those found in SRS experiments for liquid O_2 and N_2 [8]. In [8], the authors ascribed the results to the onset of Raman oscillation caused by feedback of Stokes emission via Rayleigh scattering. Since our sample is not a parallel-sided slab, it is unlikely that the onset of oscillation arises from reflection at the sample surfaces. Then it is inferred that the feedback via Rayleigh scattering is the cause of oscillation, as in the case of [8]. It is to be noted that substantial growth of the second-order Stokes emission is also observed in the region (C), as shown by dotted lines (the lines are guides to the eye.).

Under the resonant excitation (figure 5), at higher laser intensities above 1 GW/cm^2, the Stokes emission saturated and further increase in laser intensity resulted in reduction of the emission intensity due to damage to the crystal. As mentioned above, resonant two-photon transition occurs under intense photoexcitation at 3.14 eV, thus producing many electron-hole pairs in the crystal [7]. Then the two-photon excitation is expected to act as a competing nonlinear process in the region (D).

4. Conclusion

We have studied stimulated Raman effect in anatase TiO_2 at 4 K under the off-resonance and resonance conditions. It is found that anatase exhibits highly efficient first-order stimulated Stokes emission associated with the E_g mode at 137 cm^{-1}. We also observe the high-order Stokes and anti-Stokes emission, when we increase the incident laser intensity, especially for the resonant case. The large gain values estimated from the stimulated Raman emission are assigned to the narrow linewidth of the Raman line of the E_g mode at low temperatures. Our results show that anatase has large Raman nonlinearity and suggest the possibility of stimulated Raman effect to control the material property through excitation of intense coherent lattice vibrations.

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