Resonant Raman random lasing from disorder-structured material pumped by nanosecond-pulsed laser

P Srisamran1,2, P Pewkhom1,2, S Boonsit1,2, P Kalasuwan1,2, P van Dommelen1,2 and C Daengngam1,2*

1Department of Physics, Faculty of Science, Prince of Songkla University, Songkhla, 90110, Thailand
2Thailand Center of Excellence in Physics, Commission on Higher Education, Bangkok, 10400, Thailand

*E-mail: chalongrat.d@psu.ac.th

Abstract. Raman spectroscopy can provide “chemical fingerprint”, unique for each chemical composition; nevertheless, spontaneous Raman scattering has low efficiency (10^-8-10^-10). In this study, we report the evidence of Raman random lasing (RRL) generated from disordered materials even pumped by a nanosecond-pulsed laser, resulting in enhancement of Raman signal. The 355 nm UV excitation pulses allowed higher Stokes intensity due to the resonant Raman effect, compensating for the comparatively wider pulse duration. For the experiment, the effects of sample packing densities on RRL efficiency were studied for Ba(NO3)2 powder. The RRL threshold of the loosely-packed structure was lower than the closely-packed structure, and the RRL power efficiency reached 4.25 × 10^-5, for the former case. It is consistent with the coherent backscattering results that indicated the longer transport mean free path for the loosely-packed structure, implying deeper photon penetration into the sample structure with lower density. Furthermore, the full-wave simulation on COMSOL Multiphysics was solved for the investigation of localization time and confined energy of electromagnetic wave in the random structures. The closely-packed structure showed better localization property. However, the loosely-packed structure allowed more incident light to penetrate into the medium, which affected more profoundly on RRL generation.

1. Introduction

Standoff Raman spectroscopy (ST-Raman) is a high-selectivity [1] technique, promising for several applications, i.e. resources exploration [2], agricultural [3], and forensic science [4,5]. ST-Raman does not require any sampling process in the proximity range to a target [6], which is an outstanding advantage of this method that makes it ideal for security applications [7,8]. However, a major drawback of this procedure is the low efficiency of the spontaneous Raman scattering process, typically on the order of 10^-8 to 10^-10. It leads to a low signal-to-noise ratio (SNR), which hinders operations in ambient light [9]. To overcome this, powerful pump sources with pulse durations in either picoseconds or femtoseconds might be required [10], or high-performance fast-gating detection devices might be added [11-13] in order to efficiently resolve the Raman signal from noise background. Therefore, another Raman enhancement mechanism beyond spontaneous emission was investigated.

Raman random lasing (RRL) is a new optical paradigm possible to enhance Raman signal, which could be achieved in a naturally disordered medium [14]. RRL allows the optical amplification of Raman signals through the stimulated Raman scattering (SRS) gain mechanism [15,16], while multiple
scattering inside a random structure provides light confinement, acting as a cavity for lasing generation [17,18]. However, Raman effect is an ultrafast process (sub-picosecond time scale) that requires ultrashort pump peaks to create population conversion in virtual states rather than in conventional electronic states [19,20]. Therefore, the lower efficiency of creating Stokes light with broader nanosecond pulse was compensated by the resonant Raman effect when using a UV pump pulses to escalate the virtual state level near to the electronic state [21].

In this paper, we report the investigation for RRL generation near the electronic resonance using a UV nanosecond-pulsed laser as a pump source. Barium nitrate (Ba(NO$_3$)$_2$) powders with different packing structures were selected as Raman active random media that provided multiple scatterings without the need of an external optical cavity. Laser threshold characteristics can be observed through Raman signal strength generated from various pump intensities. Multiple scattering parameters of sample were also determined by coherent backscattering (CBS) experiment. Furthermore, the behavior of electromagnetic waves in multiple scattering structures can be revealed using finite-element time domain (FETD) wave simulation based on COMSOL Multiphysics.

2. Theory and methodology

2.1. Theory

RRL is an optical process that amplifies the scattered light at Raman wavelength. Analogous to a conventional laser system, RRL requires two major components: gain mechanism and optical feedback. Here, the gain mechanism is originated from the third-order nonlinear SRS process. The SRS requires that the frequency difference between the pump pulse ($\omega_p$) and the Stokes pulse ($\omega_s$) matches to the vibrational mode frequency ($Q$) of the molecule, i.e., $Q = \omega_p - \omega_s$. The intensity of the Stokes wavelength along the propagation amplified by the SRS process can be described by,

$$I_s(z) = \exp(\alpha_{eff} z) I_s(0),$$  \hspace{1cm} (1)

where $I_s(0)$ is the initial Stokes intensity (spontaneous), and $\alpha_{eff} = \alpha_s - \alpha_a$ is the effective gain coefficient which accounts for the contribution of SRS gain ($\alpha_s$) and absorption loss ($\alpha_a$). The SRS gain coefficient is also a function of pump intensity as it reads [22],

$$\alpha_s = \frac{3}{2 k v n_p c^3} \chi^{(3)}(\omega_s) I_p,$$  \hspace{1cm} (2)

where $\chi^{(3)}(\omega_s)$ is the third-ranked nonlinear susceptibility respect to Raman signal, $I_p$ is the pump intensity, $c_0$ is the permittivity of free space, $k_s$ is the wavevector of Stokes signal, $n_p$ is the refractive index of a medium at pump wavelength, and $c$ is the speed of light in free space. The $\alpha_s$ coefficient is related to optical loss process which is predominantly affected by the normal and stimulated absorption processes as described below [23],

$$\alpha_a = \alpha_0 + \frac{N_1 T_p}{2 n_p c_0} K I_p,$$  \hspace{1cm} (3)

where $\alpha_0$ is the efficiency related to the normal absorption process, $N_1$ is the number of electrons in ground state, $T_p$ is the incident pulsed duration, $K$ is the efficiency of the absorption, and $n_p$ is the refractive index of the medium with respect to the pump wavelength.

2.2. Experimental setup

Schematic of the experimental setup for the incident beam is presented in figure 1(a). The pump pulse was provided by an optical parametric oscillator (OPO) system (Opolette 355, OPOTEK), at wavelength of 355 nm, 10 ns pulse width, and 20 Hz repetition rate. The peak intensity of the pump pulse can be adjusted from 0 to ~21 MW/cm$^2$ by changing the relative angle between the pump beam polarization and the axis of a Glan-laser polarizer. A quarter waveplate was placed to convert the linear polarization
into a circular polarization, thus eliminating any effect that may arise from the preferred direction of the incident polarization onto a sample. A laser line cleanup filter (FLH355-10, Thorlabs) was applied to filter any possible fluorescence and unwanted wavelengths from the optical components with blocking OD > 5. Pump beam was reduced from 4 mm to 2 mm and collimated using a beam-size reducer.

Commercially-available barium nitrate (Ba(NO$_3$)$_2$) powder (GRM351-500G, HIMEDIA) was used as a model material for random Raman active medium. Two different powder structures were studied in comparison, including the original powder form and the compressed powder structure with ~300 MPa pressure, designated as loosely-packed and closely-packed structure, respectively. The scattered lights were filtered by a filter set to reduce the Rayleigh component and possible fluorescence. The signal was coupled through an optical fiber, and analyzed by a spectrometer (Exemplar plus, BWTEK) as shown in figure 1(b). The signal strength at the major Raman peak of Ba(NO$_3$)$_2$, ~ 10$^{34}$ cm$^{-1}$, was also measured at varied pump intensity.

A CBS experiment was also performed to evaluate the degree of multiple scattering and absorption of the random structure. These parameters are important to gain insight into RRL processes of particular structures. They can be calculated from the angular intensity profile of the CBS beam leaving the random medium. The CBS experiment is presented in figure 1(c). A coupled-charged device camera (CCD camera) was used to capture the scattered light from the sample, covering a small angle from the center of incident. The transport mean free path ($l_t$) and the absorption length ($l_a$) were determined by the fitting the backscattered intensity profile with the following function [24,25],

$$I(\theta)=1+\frac{(E_{\exp}-1)\gamma_c(\theta,l_t,l_a)}{(E-1)\gamma_l(\theta,l_t,l_a)},$$

where $I(\theta)$ is the backscattered intensity at any backscattered angle, $E$ is the enchantment factor, $\gamma_c(\theta,l_t,l_a)$ and $\gamma_l(\theta,l_t,l_a)$ is the bistatic coefficient for coherent and diffuse background, respectively.

![Figure 1](image_url). Schematics of the experimental setup for incident pump beam (a), observation of Raman random lasing signal (b), and coherent backscattering setup (c).
2.3. Simulation
The full-wave simulation based on FETD method was carried out using COMSOL Multiphysics solver to investigate the multiple scattering behaviors in random medium. Here, spherical particles were used as medium grains with an average particle size of 0.9 ± 0.2 µm, randomly generated with Gaussian size distribution inside a square domain of 25 µm × 25 µm. The refractive index of the generated particles was set at 1.5756, related to the Ba(NO$_3$)$_2$ material. The geometry was surrounded by air background. Fill factor of the geometry was assigned as 0.5 and 0.8 representing loosely-packed and closely-packed structures, respectively.

COMSOL Multiphysics was used to solve for transient electromagnetic wave propagating through this random structure via the following expression,

$$\nabla \times (\nabla \times A) + \mu_0 \frac{\partial}{\partial t}(\epsilon_0 \epsilon_r \frac{\partial A}{\partial t}) = 0,$$

(5)

where $A$ is the magnetic vector potential, $\mu_0$ is the electric permeability of the free space, $\epsilon_0$ is the electric permittivity of the free space, and $\epsilon_r = n^2$ is the relative permittivity of the medium. The simulation based on dielectric, non-magnetic material which defines $\sigma = 0$ and $\mu_r = 1$. The decay of the electromagnetic wave energy stored in the structure over time can be estimated by,

$$E(t) = E_0 e^{-t/\tau},$$

(6)

where $E_0$ is the initial energy stored in the structure, and $\tau$ is the decay time constant.

3. Results and discussion

3.1. Raman random lasing experimental results
Raman spectra of samples shown in figure 2(a) reveal scattering information of both Rayleigh and Raman. Here, the Rayleigh peak at Raman shift equal to zero was intentionally acquired. The major Raman peak of the NO$_3^-$-group can be found at 1034 cm$^{-1}$, which agrees with the standard spectrum of Ba(NO$_3$)$_2$. Signal strength at the dominant Raman peak was observed at various pump intensities as shown in figure 2(b). In general, the Raman signal from the loosely-packed medium is about one order of magnitude stronger when compared with the closely-packed counterpart. For both structures, Raman signals are growing quite linearly with increasing pump intensity at lower values, i.e. below 2 MW/cm$^2$, which can be attributed to spontaneous Raman emission. At moderate pump intensity values, beyond 2 MW/cm$^2$, increasing rates of the Raman signals drop. This nonlinear decrease of the Raman intensity can be described by a stimulated absorption process at the pump wavelength, explained by equation (3), which reduces the excitation and thus the Raman. However, by increasing the pump intensity further, surpassing 18 MW/cm$^2$, a rapid increase of the Raman signal was found for the loosely-packed sample. This indicates the lasing threshold characteristic, where the SRS gain starts to supersede the loss caused by stimulated absorption. The estimated Raman conversion efficiency at pump intensity 21.30 MW/cm$^2$ is 4.25 x 10$^{-4}$, which is several orders of magnitude higher than the spontaneous Raman scattering (on the order of 10$^{-8}$-10$^{-10}$). However, the laser threshold characteristics under the same range of pump intensity cannot be observed in the case of the closely-packed structure, although it contains higher density of Raman active particles. It confirms the better capability of the loosely-packed structure to support pump beam penetration into the medium. A higher intense pump penetration and a higher degree of multiple scattering lead to a higher RRL efficiency.
Figure 2. Raman spectra of the Ba(NO$_3$)$_2$ for two different types of structure (a) and the signal strength of the dominant Raman peak at 1034 cm$^{-1}$ at various pump intensities (b).

CBS angular profiles of the loosely-packed and closely-packed structures are shown in figure 3(a) and (b), respectively. Normalized backscattered light intensity can be analyzed for the $l_t$ and $l_a$ by fitting it with the CBS model in equation (4). Fitting results various pump intensities and for each structure are shown in table 1.

Table 1. Transport mean free path and absorption length of the powder samples extracted from coherent backscattering experiments.

| Pump intensity (MW/cm$^2$) | Transport mean free path ($l_t$) | Absorption length ($l_a$) |
|-----------------------------|---------------------------------|--------------------------|
|                             | Loosely-packed sample (µm)      | Closely-packed sample (µm) | Loosely-packed sample (µm) | Closely-packed sample (µm) |
| 0.12±0.06                   | 7.4±0.7                        | 6.8±0.3                  | 51±3                      | 47±4                      |
| 6.9±0.1                     | 6.1±0.8                        | 5.7±0.6                  | 41±5                      | 38±4                      |
| 21.3±0.3                    | 5.2±0.6                        | 4.8±0.9                  | 34±4                      | 32±6                      |

From the CBS fitting, $l_t$ and $l_a$ evolve in the same trend for both samples. They become shorter at higher intensity. This indicates an increase of the scattering efficiency at higher pump intensities. Longer light penetration depth inside the loosely-packed structure can be expected when compared with the closely-packed structure, since it shows longer $l_t$ in the loosely-packed case. Also, a longer $l_a$ in the loosely-packed structure indicates a lower absorption loss of the penetrating light in the structure. As higher pump energy can penetrate further inside the medium structure and with lower loss, the Raman lasing efficiency of the loosely-packed structure is thus higher than of the closely-packed structure.

Figure 3. Results of coherent backscattering experiments for the loosely-packed structure (a), and the closely-packed structure (b).
3.2. Raman random lasing simulation results

The behavior of a short pulse penetration in a multiple scattering structure at different propagation times is illustrated in figure 4(a) and (b) for cases of low- and high-density media. The FETD results show laser pulse incident upon the random media with some portion of light energy generated from backscattered light, while another portion of the pulse energy penetrated into the medium and undergoes multiple scattering. The time evolution of the wave energy stored in the structure shows exponential decay behavior as displayed in figure 4(c). As expected, it was found that the low-density structure allows higher pulse energy to penetrate into the medium before decay. The decay time constants of the light energy stored are 117.94 fs and 151.93 fs for the loosely-packed and closely-packed media, respectively. Simulation results indicate that the degree of multiple scattering is higher in the high-density structure as it shows slower decay rates of the energy stored inside the medium. When compared to experimental results, it suggests that the initial amount of pump intensity plays a more significant role to generate the RRL, as higher pump intensities have more pronounced effects on the nonlinear SRS gain. The degree of multiple scattering may have minor contributions to RRL here as the process generally occurs in ultrafast time scales, with not many scattering cycles involved.

![Figure 4](image)

**Figure 4.** Time-evolution of light propagation in low-density (a) and high-density (b) structures, and the corresponding energy stored in the structure due to multiple scatterings (c).

4. Conclusion

In this study, the RRL generation from random structure was investigated using nanosecond laser pump at UV wavelength to improve efficiency via resonant enhancement. It was found that the packing density of the random structure has an effect for the RRL generation efficiency. In particular, the lower-density structure showed higher Raman single with clearer laser threshold characteristics at a pump intensity of 18 MW/cm². The maximum efficiency of RRL is $4.25 \times 10^{-4}$, which is several orders of magnitude higher than the conventional Raman scattering based on spontaneous emission. The CBS experiment indicates that the loosely-packed structure allows more pump power to penetrate for longer distance with lower absorption loss, compared to the closely-packed structure. Lastly, COMSOL simulation results for light penetrated into turbid structures agree with the CBS results that the low-density structure allows more pump energy to penetrate into the structure, whereas, the high-density structure reveals better light confinement property due to more multiple scattering. However, the experiment suggests that higher pump energy penetration is more critical than multiple scattering to generate RRL as it provides higher SRS gain.

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