

# Steady-state Raman gain in visible and near-infrared waveband of SrWO<sub>4</sub> and BaWO<sub>4</sub> crystals

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The steady-state stimulated Raman scattering (SRS) gain with different excitation wavelengths ranging from 400 to 1100 nm of tungstate crystals, SrWO<sub>4</sub> and BaWO<sub>4</sub>, is systematically researched. As excitation frequency is close to electronic transition frequency, molecular polarizability is not a constant, which has to be taken into account in our work. The experiment and theory agree well with each other and show that SRS gain is not only proportional to Stokes light frequency, but is also inversely proportional to biquadratic excitation frequency.

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The stimulated Raman scattering (SRS) based on the third-order nonlinear optical process<sup>[1]</sup> is widely popularized as an efficient method to expand new wavelength lasers for satisfying the requirements of various applications. Solid-state Raman lasers can offer flexible wavelength in visible<sup>[2,3]</sup> and infrared<sup>[4-8]</sup> spectral ranges. Due to the excellent mechanical properties, stable chemical properties, non-deliquescence, high laser-induced damage threshold, and large Raman gain, SrWO<sub>4</sub> and BaWO<sub>4</sub> crystals had aroused much attention in Raman laser fields<sup>[3,4,8]</sup>. The gain coefficient is the most dominating factor for Raman applications. Till now, the reported Raman gain coefficients of SrWO<sub>4</sub> and BaWO<sub>4</sub> crystals mainly concentrated on several individual wavelengths including 532, 1047, and 1064 nm and had no systemically characterization on visible light waveband.

In this letter, we present the SRS gain measurements of these two crystals in 410–600 nm waveband and deduce the Raman gain in near-infrared band using fitting formula. The experimental results are in good agreement with theory, which takes into account the electronic transitions. The Raman gain coefficients decrease rapidly with increase in excitation wavelengths for both the crystals, and at the same time BaWO<sub>4</sub> exhibits better Raman property than SrWO<sub>4</sub> crystal.

The experimental setup is shown in Fig. 1. The pump source was an Opolette HE 355 II tunable laser system whose emission wavelength ranged from 410 to 710 nm, and the pulse energy was tunable over the range of 0–5 mJ. A beam compression system was used to elevate the intensity of the pump beam. Using the knife-edge method, the diameter of the pump beam in the Raman crystal was

measured to be ~150 μm. Different filters were adopted, which had high reflection at the pump wavelength and high transmission at Raman scattering wavelength. The average excitation power was measured using an energy/power meter (LPE-1C). The scattering light was detected by a spectrograph (HR4000CG-UV-NIR, Ocean Optics Inc.).

We chose 10 representative wavelengths as incident wavelength (IWL) ranging from 410 to 600 nm at 300 K. Utilizing the equation  $M = P/f\tau S$ , where  $P$  is the threshold power,  $f = 20$  Hz is the pulse frequency,  $\tau$  is the pulse width, and  $S$  is light spot area, the SRS threshold  $M$  is calculated. Using steady-state Raman gain equation  $GML = 25$ , where  $L$  is the length of the Raman crystal<sup>[9]</sup>, the SRS gain  $G$  was obtained. Table 1 shows the measured results including the pump pulse widths  $\tau$ , first Stokes wavelengths (FSWLs), frequency shifts  $\Delta\nu_s$ , the pump thresholds, and Raman gain coefficients. It shows that the gain coefficient obviously decreased with the increase in excitation wavelength. For SrWO<sub>4</sub> and BaWO<sub>4</sub> crystals, the Raman

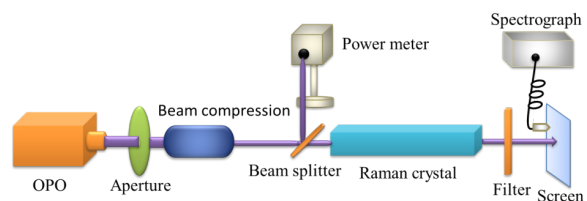


Fig. 1. Schematic of SRS experiment. OPO, optical parametric oscillator.

**Table 1.** Raman Gain and Other Parameters of SrWO<sub>4</sub> and BaWO<sub>4</sub> Crystals with Excitation Wavelength Varying from 410 to 600 nm

IWL (nm)	$\tau$ (ns)	SrWO <sub>4</sub> ( $L = 48.61$ nm, $K \perp C_4$ , $E // C_4^a$ )				BaWO <sub>4</sub> ( $L = 21.24$ nm, $K \perp C_4$ , $E // C_4^a$ )			
		FSWL (nm)	$\Delta\nu_s$ (cm <sup>-1</sup> )	$M$ (MW/cm <sup>2</sup> )	$G$ (cm/GW)	FSWL (nm)	$\Delta\nu_s$ (cm <sup>-1</sup> )	$M$ (MW/cm <sup>2</sup> )	$G$ (cm/GW)
410	4.7	426.1	921.6	148.1	79.4	426.2	927.1	57.4	89.5
430	4.6	447.8	924.4	231.1	50.9	447.9	929.4	71.1	72.4
450	4.7	469.5	923.0	314.4	37.4	469.6	927.5	85.9	59.9
470	4.4	491.3	922.4	359.1	32.8	491.4	926.6	100.1	51.4
490	4.5	513.2	922.6	407.4	28.9	513.3	926.4	111.2	46.3
510	4.5	535.2	923.2	458.5	25.7	535.3	926.7	125.1	41.1
530	4.2	557.3	924.3	533.2	22.1	557.4	927.5	135.3	38.0
550	4.1	579.4	922.6	641.9	18.3	579.6	928.5	159.4	32.3
580	4.3	612.8	922.8	712.5	16.5	613.0	928.2	186.4	27.6
600	4.3	635.2	923.6	766.7	15.4	635.4	928.5	211.5	24.3

<sup>a</sup> $C_4$  is the optic principal axis.

gain coefficients varied from 79.4 and 89.5 to 15.4 and 24.3 cm/GW, respectively, as the excitation wavelength changed from 410 to 600 nm. Owing to the accuracy of our spectrometer (0.3 nm), the Raman shifts which should be on the same value of a certain Raman crystal in theory had a small change. The average Raman shifts of SrWO<sub>4</sub> and BaWO<sub>4</sub> crystals were 923.0 and 927.6 cm<sup>-1</sup>, which was close to the previously reported 921.5 and 926 cm<sup>-1</sup>[10]. The discrepancies might be originated from the difference in crystal growing conditions, which decreased the cell parameters by a small degree and slightly decreased the distance of W–O bond further. So the frequency shifts, which were caused by the symmetrical stretching vibration of [WO<sub>4</sub>]<sup>2-</sup> tetrahedron, had a small blue shift.

It is known<sup>[9,11]</sup> that the gain is related to the frequency of Stokes and scattering cross (Eq. (1)), and the scattering cross is in connection with the molecular polarizability  $\partial a / \partial q$  (Eq. (2)). When the excitation frequency  $\nu_p$  is far away from the electronic transition frequency,  $\partial a / \partial q$  is regarded as a constant, therefore Raman gain is proportional to Stokes light frequency (Eq. (3)). But when the pump frequency is much close to the electronic transition angular frequency  $\omega_1 - \omega_i$  or  $\omega_f - \omega_1$ ,

it appears a resonant enhancement based on Eq. (4)<sup>[9]</sup> and Raman scattering gain can be expressed as Eq. (5) according to<sup>[12,13]</sup>

$$g(\nu_s) = \frac{A}{\nu_s^3} \left( \frac{\partial \sigma}{\partial \Omega} \right), \quad (1)$$

$$\left( \frac{\partial \sigma}{\partial \Omega} \right) = B \nu_s^4 \left( \frac{\partial a}{\partial q} \right)^2, \quad (2)$$

$$g(\nu_s) = C_0 \nu_s = \frac{C}{\lambda_s} = C \left( \frac{1}{\lambda_p} - \Delta \nu_s \right), \quad (3)$$

$$\left( \frac{\partial a}{\partial q} \right) = D_0 \left| \sum_l \left( \frac{p_{il} p_{lf}}{\nu_1 - \nu_i - \nu_p} + \frac{p_{il} p_{lf}}{\nu_1 - \nu_f + \nu_p} \right) \right|, \quad (4)$$

$$g(\nu_p) = D \frac{\nu_s}{(\nu_c^2 - \nu_p^2)^2} = D \frac{(1/\lambda_p - \Delta \nu_s)}{[\nu_c^2 - (1/\lambda_p)^2]^2}, \quad (5)$$

where  $A$ ,  $B$ ,  $C_0$ ,  $C$ ,  $D_0$ , and  $D$  are constants,  $g$  is the Raman gain,  $\partial \sigma / \partial \Omega$  is the scattering cross,  $\nu_c$ ,  $\nu_s$ , and  $\nu_p$  are the resonant electronic transition frequency, the Stokes, and pumping light frequencies,  $\lambda_s$  and  $\lambda_p$  are the Stokes and pumping light wavelengths,  $p_{il}$  and  $p_{lf}$  represent the dipole matrix elements,  $h\nu_i$ ,  $h\nu_l$ , and  $h\nu_f$  describe the energies of molecular states ( $i$ ,  $l$ , and  $f$  are initial, intermediate, and final states of Raman transition), and  $\Delta \nu_s$  is Raman frequency shift.

The fitting results with Eqs. (3) and (5) are shown in Figs. 2 and 3, respectively. Figure 2 shows huge discrepancies between experiment data and theoretical curve which means that Raman gain is not proportional to Stokes frequency, that is, molecular polarizability is not a constant in present conditions.

Figure 3 shows good agreement between experimental data and theoretical fitting which implies that Raman

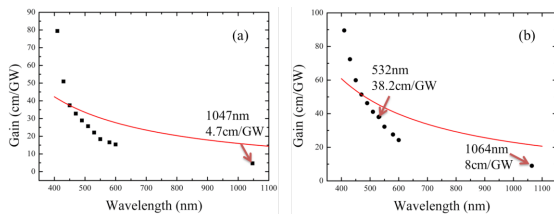


Fig. 2. Experimental data of Raman gain (dark spots) and fitting curves adopting Eq. (3) (red solid lines): (a) SrWO<sub>4</sub> and (b) BaWO<sub>4</sub> crystals.

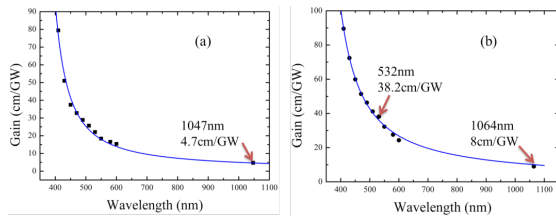


Fig. 3. Experimental data of Raman gain (dark spots) and fitting curve adopting Eq. (5) (blue solid lines): (a)  $\text{SrWO}_4$  and (b)  $\text{BaWO}_4$  crystals.

gain is proportional to Stokes frequency and inversely proportional to the biquadratic excitation frequency. It shows  $3.832 \times 10^{16} \text{ cm}^{-2} \text{ GW}^{-1}$  for proportionality coefficient  $D_S$  and  $3.06 \times 10^4 \text{ cm}^{-1}$  for resonance electronic frequency  $\nu_{eS}$  for  $\text{SrWO}_4$  crystal, and  $1.551 \times 10^{17} \text{ cm}^{-2} \text{ GW}^{-1}$  for proportionality coefficient  $D_B$  and  $3.51 \times 10^4 \text{ cm}^{-1}$  for resonance electronic frequency  $\nu_{eB}$  for  $\text{BaWO}_4$  crystal. From our fitting results,  $\text{SrWO}_4$  Raman gain is 4.6 cm/GW for 1047 nm excitation wavelength, which is much close to 4.7 cm/GW reported by Basiev *et al.* in 2004<sup>[14]</sup>. And the Raman gain coefficients of  $\text{BaWO}_4$  crystal are 36.0 and 10.0 cm/GW for 532 and 1064 nm excitation wavelengths, respectively, which is similar to the previous reports (38.2 and  $8 \pm 1.6$  cm/GW) by Černý *et al.* in 2001<sup>[15]</sup> and Lisinetskii *et al.* in 2005<sup>[12]</sup>. It indicates that although our measurement scope is 400–600 nm, yet the fitting curve is appropriate to the scope ranging from visible to near infrared.

In order to make sure that there is electronic transition in 410–600 nm spectral region for these two Raman crystals, we measure the photoluminescence spectra (270 nm light excitation) using high sensitive fluorescence spectrometer (FS920, Edinburgh) and the results are shown in Fig. 4. It can be seen that there are emission spectral lines ranging from 410 to 600 nm. According to Refs. [16,17], the blue luminescence band was related to the emission of regular  $[\text{WO}_4]^{2-}$  center, and green and red luminescence bands were caused by  $(\text{WO}_4+\text{F})$  center. According to Eq. (4), a resonant enhancement of SRS is excited when transition frequencies  $\nu_1 - \nu_i$  or  $\nu_f - \nu_1$  are close to the pump frequency  $\nu_p$ . So the molecular polarizability  $\partial\alpha/\partial q$  is not a simple constant again under this circumstance and Eq. (5) is more appropriate compared with Eq. (3).

In conclusion, we demonstrate the SRS gain performance of two important tungstate crystals,  $\text{SrWO}_4$  and  $\text{BaWO}_4$ . The Raman gain coefficients rapidly decrease with the increase in excitation wavelength. Using theoretical fitting analysis, we determine that SRS gain is proportional to Stokes light frequency and inversely proportional to biquadratic pump light frequency. It is evident that when the pump light approaches the electronic transition frequency, the molecular polarizability is not a constant. Our experiments show the Raman gain performance in the visible and near-infrared wavebands, and the  $\text{BaWO}_4$  crystal possess larger Raman gain than the

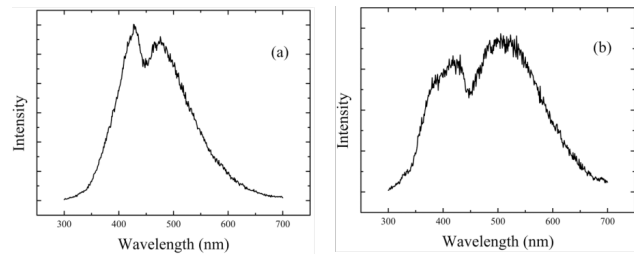


Fig. 4. Photoluminescence spectra: (a)  $\text{SrWO}_4$  and (b)  $\text{BaWO}_4$  crystals. Excitation: 270 nm.

$\text{SrWO}_4$  crystal. The fitting curves supply good references for different Raman applications of these two crystals.

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