Stimulated Raman Scattering in Yttrium, Gadolinium, and Calcium Orthovanadate Crystals with Single and Combined Frequency Shifts under Synchronous Picosecond Pumping for Sub-Picosecond or Multi-Wavelength Generation around 1.2 μm

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Abstract: Comparative investigation of stimulated Raman scattering (SRS) characteristics in the YVO₄, GdVO₄, and Ca₃(VO₄)₂ orthovanadate crystals at both low and high frequency anionic group vibrations is presented. It was found that GdVO₄ is the most perspective for SRS generation on both the ν₁ stretching and ν₂ bending modes of internal anionic group vibrations with the strongest SRS pulse shortening under synchronous picosecond pumping. It is as a result of GdVO₄’s widest linewidth (17 cm⁻¹) of the homogeneously broadened scheelite-type component of the bending ν₂ Raman line that led to the strongest SRS pulse shortening down to the dephasing time of the widest (scheelite-type) Raman mode at the secondary intracavity short-shifted SRS conversion. It allowed us to achieve SRS pulses with sub-picosecond duration under tens-of-picoseconds pumping due to the strongest 42-fold pulse shortening. Using the Ca₃(VO₄)₂ crystal with essentially wider Raman lines (~50 cm⁻¹) did not allow us to generate SRS pulses shorter than 1 ps. It can be explained by inhomogeneous broadening of the Raman lines in Ca₃(VO₄)₂ because of its structural disordering. Using the measured SRS pulse duration, the homogeneous broadening of the inhomogeneously broadened bending Raman line of Ca₃(VO₄)₂ was estimated to be ~9 cm⁻¹. Among the orthovanadate crystals, the YVO₄ crystal with the highest gain and with homogeneous broadened Raman lines allowed us to realize the most efficient SRS lasing and SRS pulse shortening truly down to inverse half-width of the bending Raman line.

Keywords: vanadate crystals; stretching and bending Raman modes; stimulated Raman scattering

1. Introduction

Yttrium, gadolinium, and calcium orthovanadate crystals are well-known as the laser host materials [1,2]. These crystals can also be used as the active materials for stimulated Raman scattering (SRS) and even for self-Raman lasing at the most intense Raman mode with the highest frequency of ν₁~854–889 cm⁻¹. This Raman mode corresponds to totally symmetric V-O stretching internal...
vibration in the tetrahedral (VO$_4$)$^{2-}$ anionic group [3–6]. Recently, self-Raman lasing was also obtained on secondary Raman modes in Nd:YVO$_4$ and Nd:GdVO$_4$ with frequencies of ~380 cm$^{-1}$ (O-V-O stretching mode) [7,8] and ~260 cm$^{-1}$ (Y-O stretching mode in YVO$_4$) [9,10]. One more interesting property of the orthovanadate crystals is the presence of two intense vibrational lines in one of the polarized spontaneous Raman scattering configurations: the most intense one corresponds to the above mentioned high-frequency (ν$_1$) stretching mode, but the second line with a low frequency of ν$_2$~354–382 cm$^{-1}$ corresponds to O-V-O bending internal vibration of the crystal anionic group [11,12]. This is similar to polarized Raman spectra of scheelite-type crystals [13], but the crystalline structure is different leading to wider Raman lines in the orthovanadate crystals. This feature is interesting for the method of SRS pulse shortening down to an inverse width of the widest Raman line under synchronously pumped SRS with combined frequency shift [14]. This method comprises a cascade process of primary extracavity Raman conversion from pump radiation into a ν$_1$-shifted Stokes component and secondary intracavity Raman conversion from the ν$_1$-shifted Stokes component into the (ν$_1$ + ν$_2$)-shifted Stokes component with significant pulse shortening down to the inverse width of the widest ν$_2$ line. It was realized in a set of alkali-earth molybdate and tungstate crystals having a scheelite-type structure [14–17] where the ν$_2$ line is the widest because of an overlap of two symmetric bending (scissoring and twisting) modes (A$_g$ + B$_g$) of internal vibrations of the crystal anionic group [13]. In the SrMoO$_4$ and SrWO$_4$ crystals, the ν$_2$ line width is the widest among the scheelite-type crystals amounting Δν$_2$~10 cm$^{-1}$ that allowed to realize SRS pulse shortening down to 1/(πΔν$_2$)~1 ps [15,16]. Recently, using this method, the strongest 42-fold SRS pulse shortening down to 860 fs [18] has been achieved in a zircon-type GdVO$_4$ crystal because the ν$_2$ line is extremely wide (Δν$_2$ = 24 cm$^{-1}$), but the nature of its widening differs from that in scheelite-type crystals, and the minimal SRS pulse duration (860 fs) is longer than 1/(πΔν$_2$). In the present work, comparative investigation of SRS in YVO$_4$, GdVO$_4$, and Ca$_3$(VO$_4$)$_2$ crystals with a single and combined frequency shift on both Raman modes (stretching and bending) under synchronous picosecond pumping was carried out taking into account the crystalline and vibrational structure to answer the question how the nature of the bending Raman mode line widening affects the SRS pulse shortening.

2. Raman Crystals Characterization

Yttrium and gadolinium orthovanadate crystals (MVO$_4$ where M = Y or Gd) crystallize in the tetragonal zircon-type structure (I4$_1$/amd space group). Similarly to tetragonal scheelite-type crystals, they have vibrational structure with the most intense, high-frequency (stretching mode), narrow (Δν$_1$~3 cm$^{-1}$) Raman line (ν$_1$ = 889 cm$^{-1}$ for YVO$_4$ and ν$_1$ = 882 cm$^{-1}$ for GdVO$_4$) and the widest low-frequency (bending mode) Raman line (ν$_2$ = 376 cm$^{-1}$ for YVO$_4$ and ν$_2$ = 382 cm$^{-1}$ for GdVO$_4$). The zircon and scheelite structures containing tetrahedral anionic groups with strong covalent bond are similar in many respects. However, unlike the scheelite-type crystals, the ideal zircon structure (ZrSiO$_4$) has no overlap of two bending modes (A$_g$ and B$_g$) in the low-frequency ν$_2$ Raman line, but the ν$_2$ Raman line in YVO$_4$ and GdVO$_4$ has even stronger widening depending on temperature [19]. Figure 1 demonstrates decomposition of the ν$_2$ Raman line in the Raman spectra of YVO$_4$ and GdVO$_4$ crystals into two components, one of which (red dashed lines) is strongly dependent on temperature. It must be noted that this additional temperature-dependent component in the ν$_2$ Raman line (red dashed lines in Figure 1) is absent in the ideal zircon (ZrSiO$_4$) structure, and so it is caused by structural disordering in YVO$_4$ and GdVO$_4$. In work [19], it is explained by a thermally activated rotation of some tetrahedral anionic groups through 45° around their fourfold axis giving a partial zircon–scheelite phase transition. Thus, the additional component in the ν$_2$ Raman line can be identified as the scheelite-type internal vibration in these 45°-rotated anionic groups with an overlap of two bending modes (A$_g$ + B$_g$), and so, this scheelite-type component (red dashed lines in Figure 1) is wider than the ordinary zircon-type component (blue dotted lines in Figure 1) including only one (A$_g$) bending mode. This process is stronger in the GdVO$_4$ crystal with a larger cation, where the
scheelite-type and zircon-type component intensities are comparable already at room temperature. In GdVO$_4$ at 300 K (Figure 1e), we have the zircon-type component linewidth of $\Delta \nu_{21} = 10.4$ cm$^{-1}$ (the blue dotted line) and the scheelite-type component linewidth of $\Delta \nu_{22} = 17$ cm$^{-1}$ (the red dashed line) giving the full $\nu_2$ Raman line width of $\Delta \nu_2 = 24$ cm$^{-1}$ (black solid line) [18]. In YVO$_4$ at 300 K (Figure 1b), the additional scheelite-type component is low-intense yet, and therefore, the full $\nu_2$ Raman line width is only $\Delta \nu_2 = 11$ cm$^{-1}$ defined mainly by the zircon-type component. However, at increased temperature up to 600 K (Figure 1c), the scheelite-type component intensity becomes comparable with the zircon-type component intensity giving strong widening of the full $\nu_2$ Raman line up to $\sim 40$ cm$^{-1}$. In GdVO$_4$ at 600 K (Figure 1f) the scheelite-type component becomes significantly more intense than the zircon-type component, and therefore, the full $\nu_2$ Raman line width of $\sim 50$ cm$^{-1}$ is mainly defined by the scheelite-type component.

Both the stretching $\nu_1$ and bending $\nu_2$ Raman lines in YVO$_4$ and GdVO$_4$ are intense under excitation with polarization of light parallel to the crystal optical axis with scattering configuration $y(zz)y$. In this case, values of Raman scattering peak cross-section of the $\nu_1$ line differ each other only by 15% among these crystals at 300 K. For instance, the GdVO$_4$ crystal has Raman gain of 4.5 cm/GW under 1.06-$\mu$m excitation [3], while YVO$_4$ has a slightly higher gain of $\sim 5$ cm/GW.

The Ca$_3$(VO$_4$)$_2$ crystal crystallizes in the whitlockite-type structure ($R\bar{3}c$ space group), which is a distorted variant (displacement of calcium and oxygen atoms from their ideal positions with random distribution of vacancies) of the ideal palmierite (K$_2$Pb(SO$_4$)$_2$) structure ($R\bar{3}m$ space group) [20,21]. Disordering of the nonequivalent oxygen atoms with different local coordination spheres leads to an overlap of many vibrational modes that would otherwise be split in the case when the vacancies were ordered (in the ideal palmierite structure) [21]. It results in the partial coupling of the internal modes of the tetrahedral (VO$_4$)$^{2-}$ anion vibrations with the strongest broadening of the stretching and bending Raman lines at room temperature demonstrated in Figure 2. It must be noted that in the polarized Raman spectra (Figure 2), both the stretching ($\nu_1 = 854$ cm$^{-1}$) and bending ($\nu_2 = 354$ cm$^{-1}$) Raman lines in the Ca$_3$(VO$_4$)$_2$ crystal are intense in scattering configuration $y(xx)y$ in contrast to the YVO$_4$ and GdVO$_4$ crystals, where it was in scattering configuration $y(zz)y$. Both values of the line width amount $\sim 50$ cm$^{-1}$. The Ca$_3$(VO$_4$)$_2$ crystal has Raman gain of about 1.6 cm/GW under 1.06-$\mu$m excitation, which is 2.4 times lower than that in the KGd(WO$_4$)$_2$ [4] and in YVO$_4$ and GdVO$_4$ crystals.
The YVO₄ and GdVO₄ crystal optical axis (c) was oriented horizontally for pumping by E⊥c enabling to access the maximum intensities of the ν₁ and ν₂ Raman lines [11]. The Ca₃(VO₄)₂ crystal optical axis (c) was oriented vertically for pumping by E∥c enabling to access the maximum intensities of the v₁ and v₂ Raman lines (see Figure 2). For optimal mode matching between the pump beam and the Raman laser cavity mode, the pump beam was focused into the crystal by a spherical lens (f = 100 mm). The external bow-tie ring cavity of the Raman laser system was compensated for astigmatism and consisted of two concave high-reflective (HR) mirrors PM and M1 having identical radius of curvature of 100 mm, a flat HR mirror M2 (HR@1169–1174 nm), and a flat output coupler OC. We tested two output couplers noted as OC1 and OC2. OC1 (R = 87–88%@1169–1174 nm, R = 80%@1220–1228 nm) was used for oscillation at the ν₁-shifted first Stokes SRS wavelength of λₙ₁ = (λ₀⁻¹−ν₁)⁻¹. OC2 (R = HR@1169–1174 nm, R = 95%@1220 nm, and R = 90%@1228 nm) was used for oscillation at the unusual cascade SRS wavelength of λ₁₂ = [λ₀⁻¹ − (ν₁ + ν₂)]⁻¹ with a combined (ν₁ + ν₂) Raman shift. Both output couplers had high transmittance at the second (ν₁ + ν₂)-shifted Stokes component (HT@1299–1311 nm).

The generated Stokes components were separated by long-pass filter with the cut-on wavelength of 1200 nm (Thorlabs FEL 1200). The radiation spectra were measured by OceanOptics NIR512 spectrometer (wavelength range 850–1700 nm, FWHM resolution ~3 nm). The average power was measured with a Standa 11PMK-15SH5 power meter; pulse energy was determined by calculation of

![Figure 2. Polarized Raman spectra of Ca₃(VO₄)₂ at room temperature.](image-url)
average power, repetition rate, and duty factor of QCW pumping. The output pulses were measured by a laboratory designed non-collinear second harmonic generation (SHG) autocorrelator based on a LiIO$_3$ crystal. For pulse duration calculation, we assumed a Gaussian shape of the measured autocorrelation curves.

**Figure 3.** The experimental setup of the synchronously pumped extracavity crystalline Raman laser.

### 4. Perfect Synchronization Case

The output characteristics of SRS radiation were significantly dependent on the synchronization condition that was adjusted by precise translation of the mirror $M_2$. In the case of perfect synchronization of the pump pulses repetition period with the Raman laser cavity round-trip time, the lowest SRS oscillation thresholds and the highest slope efficiencies were achieved. Table 1 summarizes the SRS generation characteristics in the perfect synchronization case.

**Table 1.** The SRS characteristics in the YVO$_4$, GdVO$_4$, and Ca$_3$(VO$_4$)$_2$ Raman lasers with OC1 and OC2, where $\lambda$ is a generated wavelength, $\eta$ is a slope efficiency, and $E_p$ is an output pulse energy.

<table>
<thead>
<tr>
<th>Crystals</th>
<th>$\nu_1$-Shifted Stokes Component (OC1)</th>
<th>$\nu_1 + \nu_2$-Shifted Stokes Component (OC2)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda$ [nm]</td>
<td>$\eta$ [%]</td>
</tr>
<tr>
<td>YVO$_4$</td>
<td>1174</td>
<td>27.4</td>
</tr>
<tr>
<td>GdVO$_4$</td>
<td>1173</td>
<td>24.7</td>
</tr>
<tr>
<td>Ca$_3$(VO$_4$)$_2$</td>
<td>1169</td>
<td>14.3</td>
</tr>
</tbody>
</table>

Measured output spectra of these lasers with the output coupler OC2 are presented in Figure 4 (in the case of OC1, the $(\nu_1 + \nu_2)$-shifted Stokes component in the output spectra was absent). The measured wavelengths of the $\nu_1$-shifted and $(\nu_1 + \nu_2)$-shifted Stokes SRS components (see Table 1 and Figure 4) are in a good agreement with the calculated values of $\lambda_1 = (\lambda_0^{-1} - \nu_1)^{-1}$ and $\lambda_{12} = [\lambda_0^{-1} - (\nu_1 + \nu_2)]^{-1}$, respectively.

**Figure 4.** Laser output radiation spectra of the (a) YVO$_4$, (b) GdVO$_4$, and (c) Ca$_3$(VO$_4$)$_2$ Raman lasers with OC2.
Figure 5 demonstrates the output–input energy characteristics in the perfect synchronization case for the YVO$_4$, GdVO$_4$, and Ca$_3$(VO$_4$)$_2$ Raman lasers with the output couplers OC1 and OC2.

In the case of OC1, as is shown in Figure 5a,c,e, a single $\nu_1$-shifted Stokes component was generated with high slope efficiency for all the active crystals. The single-Stokes SRS generation threshold was achieved at the input pulse energies of 128, 133, and 188 nJ for the YVO$_4$, GdVO$_4$, and Ca$_3$(VO$_4$)$_2$ active crystals, respectively. These values correlate with the row of their Raman gains. The slope efficiencies were 27.4, 24.7, and 14.3%, respectively. At the maximal input pump pulse energy of 330 nJ, the output pulse energies reached 54, 49, and 21 nJ (optical-to-optical efficiencies of 16.4, 14.8, and 6.4%) for YVO$_4$, GdVO$_4$, and Ca$_3$(VO$_4$)$_2$, respectively. The SRS oscillation in the YVO$_4$ Raman laser was more efficient due to a higher Raman gain.

In the case of OC2, as is shown in Figure 5b,d,f, the Raman laser generated not only the first $\nu_1$-shifted Stokes component but also the component with the combined ($\nu_1 + \nu_2$) Raman shift. The SRS

Figure 5. Dependencies of the output SRS pulse energy on the input pump pulse energy in the (a,b) YVO$_4$, (c,d) GdVO$_4$, and (e,f) Ca$_3$(VO$_4$)$_2$ Raman lasers with (a,c,e) OC1 and (b,d,f) OC2.
generation threshold of this additional Stokes component was achieved at the input pulse energies of 141, 146, and 201 nJ for the YVO₄, GdVO₄, and Ca₃(VO₄)₂ active crystals, respectively. It can be seen that slope efficiency for the first Stokes component ($\nu_1$-shifted) was low (1.2, 1.4, and 1.3% for YVO₄, GdVO₄, and Ca₃(VO₄)₂) in comparison with 2.2–4.8 times higher slope efficiency for the ($\nu_1 + \nu_2$)-shifted Stokes component (5.8, 5.0, and 2.8% for YVO₄, GdVO₄, and Ca₃(VO₄)₂). This is a result of using OC2 that has higher transmission (5%) around 1220 nm for realization of nonlinear cavity dumping of the Raman laser [22]. As a result, at the maximal input pump pulse energy of 330 nJ, we achieved the top output energies of 11, 10, and 4 nJ in the ($\nu_1 + \nu_2$)-shifted Stokes component for YVO₄, GdVO₄, and Ca₃(VO₄)₂, respectively.

5. Cavity Length Detuning for the Strongest Pulse Shortening

For the purpose of obtaining the maximal SRS pulse shortening, we realized the Raman laser cavity length detuning relative to the perfect synchronization case (zero detuning). Figure 6 presents the measured dependencies of the output pulse duration and energy on the cavity length detuning for the YVO₄, GdVO₄, and Ca₃(VO₄)₂ Raman lasers with the output coupler OC2 under maximal pump pulse energy of 330 nJ.

It is evident from Figure 6a,c,e that the detuning range, where the SRS generation was observed, was short (from 0 up to +50 μm) at the positive cavity length detuning, while the detuning range was significantly wider at the negative detuning (from 0 down to −200 μm). There is a similarity with other synchronously pumped Raman lasers [14–18,23–28], and it is explained by non-efficient interaction between the SRS and pump pulses where only the front edge of the SRS pulse is amplified at positive detuning. Nevertheless, positive cavity length detuning has allowed us to achieve the strongest SRS pulse shortening, as shown in Figure 6b,d,f.

It can also be observed from Figure 6b,d,f that the $\nu_1$-shifted Stokes pulses (at 1174, 1173, and 1169 nm) have been shortened only slightly from pump pulse $t_p = 36$ ps to $t_S = 21–22$ ps at the positive cavity length detuning of +50 μm. However, the ($\nu_1 + \nu_2$)-shifted Stokes pulses (at 1228, 1228, and 1220 nm) went through strong self-shortening from negative to positive cavity length detuning and pulse duration remained below 7 ps. The strongest pulse shortening down to $t_S = 1.19 ± 0.06$ ps for YVO₄, $t_S = 0.86 ± 0.03$ ps for GdVO₄, and $t_S = 1.18 ± 0.24$ ps for Ca₃(VO₄)₂ was achieved at the positive cavity length detuning of +50 μm.

Strong pulse shortening can be explained by the theory of ultra-short SRS pulse formation at intracavity pumping [29] that predicted the shortened SRS pulse duration close to a dephasing time of a Raman mode equal to an inverse half-width of the homogeneously broadened Raman line. We should take into account that generation of the strongly shortened ($\nu_1 + \nu_2$)-shifted SRS pulses in the extracavity Raman laser took place on the bending ($\nu_2$) Raman line under intracavity pumping by the $\nu_1$-shifted SRS radiation.

For the YVO₄ crystal with the homogeneously broadened bending Raman line with a linewidth of $\Delta \nu_2 = 11$ cm⁻¹ at room temperature (Figure 1b), the measured SRS pulse duration ($t_S = 1.2$ ps) was really close to the inverse half-width of the bending Raman line ($1/(\pi \Delta \nu_2 c) = 0.96$ ps). Similar results of the strongest pulse shortening were recently achieved for synchronously pumped SRS in scheelite-type crystals with homogeneously broadened Raman lines [14–18].

However, for the GdVO₄ crystal having wider bending line width of $\Delta \nu_2 = 24$ cm⁻¹ at room temperature (Figure 1e), the measured SRS pulse duration ($t_S = 0.86$ ps) was longer than $1/(\pi \Delta \nu_2 c) = 0.44$ ps. However, the bending Raman line in GdVO₄ consists of two homogeneously broadened spectral components (Figure 1e) corresponding to the zircon-type and scheelite-type structures with linewidths of $\Delta \nu_{21} = 10.4$ cm⁻¹ and $\Delta \nu_{22} = 17$ cm⁻¹, respectively. We can conclude that, the pulse duration is determined not by the total spectral width of the bending Raman line, but by that of the homogeneously broadened component. It can be both the zircon-type and scheelite-type components, because the SRS pulse duration is almost in the middle between the corresponding values of dephasing time of $1/(\pi \Delta \nu_{21} c) = 1.02$ ps and $1/(\pi \Delta \nu_{22} c) = 0.62$ ps, respectively. Taking into account all the previous
results [14–17], we have never observed SRS pulse duration shorter than dephasing time of the homogeneously broadened bending Raman mode, and so the present result of 860 fs is more likely caused by the scheelite-type bending mode having a shorter dephasing time (0.62 ps).

Despite the widest (~50 cm$^{-1}$) Raman lines in Ca$_3$(VO$_4$)$_2$, the shortened SRS pulse ($t_S = 1.2$ ps) was significantly longer than the inverse half-width of the bending Raman line of $1/(\pi\Delta\nu c) = 0.21$ ps. It can be explained by inhomogeneous broadening of Raman lines in Ca$_3$(VO$_4$)$_2$ because of its structural disordering. Using the shortest generated SRS pulse duration, we can estimate the homogeneous broadening of the inhomogeneously broadened bending Raman line of Ca$_3$(VO$_4$)$_2$ as $1/(\pi t_S c) \approx 9$ cm$^{-1}$.

![Figure 6](image-url) Dependencies of (a,c,e) the output pulse energy and (b,d,f) the output pulse duration on the cavity length detuning for the (a,b) YVO$_4$, (c,d) GdVO$_4$, and (e,f) Ca$_3$(VO$_4$)$_2$ Raman laser with the output coupler OC2 under pumping with the maximal pulse energy of 330 nJ.

Figure 6. Dependencies of (a,c,e) the output pulse energy and (b,d,f) the output pulse duration on the cavity length detuning for the (a,b) YVO$_4$, (c,d) GdVO$_4$, and (e,f) Ca$_3$(VO$_4$)$_2$ Raman laser with the output coupler OC2 under pumping with the maximal pulse energy of 330 nJ.
6. Conclusions

We have presented a comparative investigation of synchronously pumped SRS in the YVO₄, GdVO₄, and Ca₃(VO₄)₂ orthovanadate crystals at both long ($\nu_1$) and short ($\nu_2$) Raman shifts. It was found that among these crystals, GdVO₄ is the most suitable for SRS generation on both the $\nu_1$ stretching and $\nu_2$ bending modes of internal anionic group vibrations with the strongest SRS pulse shortening under synchronous picosecond pumping. It is as a result of GdVO₄’s widest linewidth ($\Delta\nu_{22} = 17\text{ cm}^{-1}$) of the homogeneously broadened scheelite-type component of the bending $\nu_2$ Raman line. This property led to the strongest SRS pulse shortening down to the dephasing time $1/(\pi\Delta\nu_{22}c)$ of the widest (scheelite-type) Raman mode at the secondary intracavity short-shifted SRS conversion. It allowed us to achieve SRS pulses with sub-picosecond duration under tens-of-picoseconds pumping due to the strongest 42-fold pulse shortening. Using the Ca₃(VO₄)₂ crystal with essentially wider Raman lines (~50 cm⁻¹) did not allow us to generate SRS pulses shorter than 1 ps. It can be explained by inhomogeneous broadening of the Raman lines in Ca₃(VO₄)₂ because of its structural disordering. Using the measured SRS pulse duration, the homogeneous broadening of the inhomogeneously broadened bending Raman line of Ca₃(VO₄)₂ was estimated to be ~9 cm⁻¹. Among the orthovanadate crystals, the YVO₄ crystal with the highest Raman gain and with homogeneously broadened Raman lines allowed us to realize the most efficient SRS lasing and SRS pulse shortening truly down to inverse the half-width of the bending Raman line.

Author Contributions: Conceptualization, S.N.S.; Formal analysis, M.F. and S.N.S.; Investigation, M.F., S.N.S., M.J., D.V., V.E.S., L.I.I., E.E.D., D.P.T. and I.S.V.; Methodology, M.F. and S.N.S.; Resources, V.E.S., L.I., E.E.D. and I.S.V.; Supervision, P.G.Z. and V.K.; Validation, P.G.Z. and V.K.; Visualization, M.F. and D.P.T.; Writing—original draft, M.F. and S.N.S.; Writing—review & editing, M.F., S.N.S., M.J., D.V., P.G.Z. and V.K. All authors have read and agreed to the published version of the manuscript.

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