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Observation of stimulated Raman scattering in CVD-diamond

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We report the first experimental observation of nonlinear laser effect – stimulated Raman scattering (SRS) in the man-made diamond grown from the gaseous phase by chemical vapor deposition (CVD) technique. The multiple Stokes and anti-Stokes generation in the visible and near-IR was excited under nanosecond and picosecond pumping in a 350 μ thick plate. All the registered Raman induced lasing wavelengths were identified. We classify the CVD-diamond as a promising $\chi^{(3)}$-active material for Raman laser converters in a record wide spectral range.

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1. In the last decade the use of the stimulated Raman scattering (SRS) phenomenon in crystalline materials to shift the wavelengths of laser emission is becoming more widespread in solid-state laser physics (see, e.g. [1–4]). The SRS process allows to compress laser pulses, it can also improve the spatial quality of laser beams, etc. Modern laser applications require crystals providing a large Raman frequency shifts, considerably more than 1000 cm^{-1}. For the list of these SRS-active materials see Table 1. Natural diamonds are also included in the list. Recently, a big progress is achieved in synthesis of large area diamonds at low pressure using a chemical vapor deposition (CVD) technique [5]. The material is essentially polycrystalline with arbitrary oriented grains. In many respects the quality of CVD diamonds approaches to that of most pure natural diamonds. In contrast to natural stones the impurity and defect content in CVD diamond is quite reproducible and of low level.

This letter is devoted to reporting on the results of the first experimental observation of $\chi^{(3)}$-nonlinear laser effect, namely the high-order Stokes and anti-Stokes generation in CVD diamond thin plates under nano- and picosecond excitation in the visible and near IR.

2. Diamond belongs to the O_h^7 cubic space group with eight atoms per unit cell (two per primitive cell) giving to six phonon branches in the dispersion relation. At the center of Brillouin zone ($\mathbf{k} = 0$), the three optical branches are triply degenerate and the corresponding phonons belong to the F_{2g} irreducible representation. The first-order Raman spectrum contains one peak corresponding to the excitation of these optical phonons. Diamond consists of light mass of the C-atoms held together by strong covalent bonding and this combination produces many remarkable properties for laser physics, e.g. high thermal conductivity and relatively large energy of Raman-active mode $\approx 1332.5\,cm^{-1}$, which are promoting for SRS lasing. Some physical properties of natural and man-made diamonds that are known for us are listed in Table 2.

3. In the present work the transparent diamond film of $\approx 450\,\mu$ thickness was grown on a Si substrate in a microwave plasma assisted CVD reactor using CH_4/H_2 mixture as a source gas [6]. After the substrate has been etched off in acid, the film was laser cut to $6 \times 8\,mm^2$ samples, and mechanically polished to get plane parallel plates of $350\,\mu$ thickness. The major impurities were 75 ppm hydrogen and 1 ppm nitrogen (1ppm $= 1.76 \cdot 10^{17}\,cm^{-3}$) as determined from IR and UV absorption spectra, respectively [7]. Upon growth the grains, being chaotically oriented in the film plane, form columns with their axes directed perpendicular to surface. The columns with lateral size of about 40–100 μ are predominantly $\langle 110 \rangle$ oriented.

4. The SRS experiments with CVD diamond plate were performed at 300 K using a cavity-free single-pass excitation scheme and nano- and picosecond Nd^{3+}:$Y_3Al_5O_{12}$ lasers with an $\approx$ 30% efficient external frequency doublers as a pumping sources (see, e.g. [17,18]). Their generation with Gaussian beam profile at fundamental $\lambda_{f1} = 1.06415\,\mu$ (pump pulse duration $\tau_{p1} \approx 15$ ns and ≈ 110 ps, respectively) or SHG at $\lambda_{f2} = 0.53207\,\mu$ ($\tau_{p1} \approx 15$ ns and ≈ 80 ps, respectively) wavelength was focused onto the diamond plate by a lens with focal distance adjusted so that the SRS-lasing was maximum while avoiding the surface and volume optical damage of the sample. This was achieved when the waist beam diameter into diamond plate was 100–160 μ. These

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Table 1

Crystal[1)]	Space group	Nonlinearity (class)	ω_{SRS} (cm^{-1}) [2)]	References
Inorganic crystals				
$LiHCOO{\cdot}H_2O$	$C_{2\nu}^9$	$\chi^{(2)}+\chi^{(3)}$ (polar)	≈ 1372	[8]
Natural diamond [3)]	O_h^7	$\chi^{(3)}$	≈ 1332	[9, 10]
CVD-diamond [4)]	O_h^7	$\chi^{(3)}$	1332.5 ± 0.8	this work
$CaCO_3$ (calcite)	D_{3d}^6	$\chi^{(3)}$	≈ 1086	[9, 11, 12]
$Sr(NO_3)_2$	T_h^6	$\chi^{(3)}$	≈ 1057	[13]
$Y(HCOO)_3 \cdot 2H_2O$	D_2^4	$\chi^{(2)}+\chi^{(3)}$	$\approx 1395, \approx 1377, \approx 2895$	[14]
$Ba(NO_3)_2$	T_h^6	$\chi^{(3)}$	≈ 1049	[15, 16]
Organic crystals				
$C_{12}H_{22}O_{11}$ (sugar, sucrose)	C_2^2	$\chi^{(2)}+\chi^{(3)}$ (polar)	≈ 2960	[17]
$C_{15}H_{19}N_3O_2$ (AANP)	$C_{2\nu}^9$	$\chi^{(2)}+\chi^{(3)}$ (polar)	≈ 1280	[18]
$C_{16}H_{15}N_3O_4$ (MNBA)	C_s^4	$\chi^{(2)}+\chi^{(3)}$ (polar)	≈ 1587	[19]
Metal-organic crystal				
$C_{14}H_{26}N_8O_{13}Zr$ (GuZn-III)	D_2^5	$\chi^{(2)}+\chi^{(3)}$	≈ 1008, ≈ 2940	[20]

[1)] Some of these crystal are already commercial materials.
[2)] Room-temperature data.
[3)] Natural diamond crystals of type IIA with a thickness of about 2 mm.
[4)] Man-made polycrystalline diamond.

Table 2

Space group	$O_h^7 - Fm\bar{3}d$ (No.227)
Unit cell parameter (Å)	$a_o = 3.56676$
Site symmetry of atoms	C_1
Formula units per cell	$Z = 8$ [1)]
Density ($g.cm^{-3}$)	$d \approx 3.51$
Melting point (°C)	> 3400
Debye temperature (K)	≈ 1860
Band gap (eV)	≈ 5.4
Optical transparency range (μ)	$\approx 0.225-3.8$; $5.5-\infty$ (Till radio frequencies.)
Dielectric constant	$\varepsilon \approx 5.7$ (For $f =$ up to 10^{11} Hz.)
Refractive index (Sellmeier equation) (λ in μ)	$n^2 = 1 + \frac{4.3356\lambda^2}{\lambda^2 - 0.0256} + \frac{0.3306\lambda^2}{\lambda^2 - 0.030625}$
$dn/dT(10^{-6}\,K^{-1})$	≈ 10 (For $\lambda = 0.587\,\mu$.)
Nonlinear refractive index ($10^{-13}\,cm^3 \cdot erg$). (At $\lambda = 0.545\,\mu$ and laser pulse duration $\tau_p = 4$ ns.)	$n^2 \approx 7.2$
Thermal conductivity ($W \cdot cm^{-1}\,K^{-1}$) (For our polycrystalline CVD-diamond.)	≈ 18
Thermal expansion coefficient ($10^{-6}\,K^{-1}$)	≈ 1
Elastic constants (10^{11} N m^2)	$C_{11} = 10.40$; $C_{12} = 1.70$; $C_{44} = 5.50$
Elastooptic coefficients. (At $\lambda = 0.540-0.589\,\mu$.)	$p_{11} = -0.278$; $p_{12} = 0.123$; $p_{44} = -0.161$; $p_{11} - p_{12} = -0.385$
Energy of SRS-active vibration mode (cm^{-1})	$\omega_{SRS} = 1332.5 \pm 0.8$
Linewidth (FWHM) of the Raman-shifted line in first-order spontaneous Raman scattering spectra (cm^{-1})	$\Delta\nu_R \approx 2.5$ (For our polycrystalline CVD-diamond.) $\Delta\nu_R$ for natural diamonds ranges from 1.65 to 2.7 (see, e.g. [21, 22]).
Phonon spectrum extension (cm^{-1}) [2)]	≈ 1333

[1)] Primitive (Bravais) cell contains two formula units $N^{Br} = 2$.
[2)] From first-order spontaneous Raman scattering spectra.

excitation conditions provided well the steady-state $\chi^{(3)}$-generation regime, because, for the studied CVD diamond $\tau_p \gg T_2 = 1/\pi\Delta\nu_R \approx 4.2$ ps (here T_2 and $\Delta\nu_R$ are the phonon relaxation time and the linewidth

Table 3

Nanosecond pumping		Picosecond pumping		Line attribution
Wavelength (μ)	Line	Wavelength (μ)	Line	
Pumping at $\lambda_{f1} = 1.06415\,\mu$				
		0.7466	ASt_3	$\omega_{f1} + 3\omega_{SRS}$
		0.8290	ASt_2	$\omega_{f1} + 2\omega_{SRS}$
0.9320	ASt_1	0.9320	ASt_1	$\omega_{f1} + \omega_{SRS}$
1.06415 (≈ 1.3) [1)]	λ_{f1}	1.06415 (≈ 2.5) [1)]	λ_{f1}	ω_{f1}
1.2400	St_1	1.2400	St_1	$\omega_{f1} - \omega_{SRS}$
1.4854	St_2			$\omega_{f1} - 2\omega_{SRS}$
Pumping at $\lambda_{f2} = 0.53207\,\mu$				
		0.4660	ASt_2	$\omega_{f2} + 2\omega_{SRS}$
0.4968	ASt_1	0.4968	ASt_1	$\omega_{f2} + \omega_{SRS}$
0.53207 (≈ 0.3) [1)]	λ_{f2}	0.53207 (≈ 0.7) [1)]	λ_{f2}	ω_{f2}
0.5727	St_1	0.5727	St_1	$\omega_{f2} - \omega_{SRS}$
		0.6200	St_2	$\omega_{f2} - 2\omega_{SRS}$

[1)] Pump power density (in parentheses) given in GW cm^{-2}.

of corresponding peak in spontaneous Raman scattering spectrum, respectively. The spectral composition of Stokes and anti-Stokes lasing in the visible and near-IR under maximum possible pump density power was measured with grating monochromators equipped with appropriate detectors (Si-CCD, InSb-diode, ets.). The generated SRS wavelengths observed are summarized in Table 3, which contains room-temperature Stokes and anti-Stokes generation wavelengths in CVD-diamond ($350\,\mu$ thick plate) with natural abundance of isotopic (carbon) composition connected with its SRS-active vibration mode $\omega_{SRS} = 1332.5\,\mathrm{cm}^{-1}$ under nano- and picosecond Nd^{3+}:$Y_3Al_5O_{12}$-laser excitation at $\lambda_{f1} = 1.06415\,\mu$ and $\lambda_{f2} = 0.53207\,\mu$ (SHG) fundamental wavelengths.

5. For rough estimation of the steady-state Raman gain coefficient $g_{ssR}^{St_1}$ in the near-IR we applied a simple comparative method using the well known relation (see, e.g. [23]) $g_{ssR}^{St_1} I_{thr} l_{SRS} = 25{-}30$ (where I_{thr} is the threshold pump intensity l_{SRS}, is the SRS-active length of sample) and based on a measurement of the pumping threshold for the first Stokes generation component in our $\approx 350\,\mu$ CVD diamond ($\lambda_{St1} = 1.2400\,\mu$, see Table 3) and in a reference $\approx 500\,\mu$ $C_{15}H_{19}N_3O_2$ (AANP) crystal ($\lambda_{St1} = 1.2320\,\mu$m [18]) under the same excitation conditions. We observed that the threshold for the first Stokes nanosecond lasing of the diamond thresold was about 40% less than for the AANP plate. This means that the coefficient $g_{ssR}^{St_1}$ is no less than $8\,\mathrm{cm} \cdot \mathrm{GW}^{-1}$. The SRS conversion efficiency into all Stokes and anti-Stokes components in the examined diamond sample, even grown in not optimized conditions, reached the value of about 30% at pump power density of approximately $2.5\,\mathrm{GW} \cdot \mathrm{cm}^{-2}$ under picosecond excitation at $\lambda_{f2} = 0.53207\,\mu$m wavelength.

6. In conclusion, we have discovered $\chi^{(3)}$-nonlinear laser potential for CVD diamonds. Due to continuous progress in CVD diamond technology large size (diameter $> 100\,$mm, thickness $> 2\,$mm), and even ultrapure CVD diamond single crystal [24] become available. From these considerations we believe that new generation of CVD diamonds in near future can hold a leading position among all known $\chi^{(3)}$-active crystalline materials for Raman laser converters.

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1. M. J. Weber, *Handbook of Lasers*, CRC Press, Boca Raton, 2001.
2. A. A. Kaminskii, *Crystalline Lasers: Physical Processes and Operating Schemes*, CRC Press, Boca Raton, 1996.
3. *Optical Materials - Special issue*, Eds. T. T. Basiev and R. C. Powell, **11**, March 1999.
4. G. A. Pasmanik, Laser Focus Word **35**, 137 (1999).

5. *Handbook of Industrial Diamonds and Diamonds Films*, Eds. M. Prelas at al., Marcel Dekker, New York, 1997.
6. V. G. Ralchenko, A. A. Smolin, V. I. Konov et al., Diamond Relat. Mater. **6**, 417 (1997).
7. S. V. Nistor, M. Stefan, V. Ralchenko et al., J. Appl. Phys. **87**, 8741 (2000).
8. K. K. Lai, W. Schusslbauer, H. Silberbauer et al., Phys. Rev. **B42**, 5834 (1990).
9. G. Eckhard, D. P. Bortfeld, and M. Geller, Appl. Phys. Lett. **3**, 137 (1963).
10. A. K. McQuillan, W. R. L. Clements, and B. P. Stoicheff, Phys. Rev. **A1**, 628 (1970).
11. R. Chiao and B. P. Stoicheff, Phys. Rev. Lett. **12**, 290 (1964).
12. V. A. Chirkov, V. S. Gorelik, G. V. Peregudov, and M. M. Sushinskii, JETP Lett. **10**, 416 (1969).
13. A. A. Kaminskii, J. Hulliger, H. Eichler et al., Dokl. Phys. **44**, 69 (1999).
14. A. A. Kaminskii, L. Bohaty, P. Becker et al., Phys. Status Solidi **(a)202**, N1 (2004).
15. A. S. Eremenko, S. N. Karpukhin, and A. I. Stepanov, Sov. J.Quantum Electron. **10**, 113 (1986).
16. P. G. Zverev, J. T. Murreay, R. C. Powell et al., Opt. Commun. 97, 59 (1993).
17. A. A. Kaminskii, Crystalogr. Rep. **48**, 295 (2003).
18. A. A. Kaminskii, T. Kaino, T. Taima et al., Jpn. J. Appl. Phys. **41**, L603 (2002).
19. A. A. Kaminskii, J. Hulliger, and H. J. Eichler, Phys. Status Solidi **(a)186**, R19 (2001).
20. A. A. Kaminskii, E. Haussuhl, J. Hulliger et al., Phys. Status Solidi **(a)193**, 167 (2002).
21. S. A. Solin and A. K. Ramdas, Phys. Rev. **B1**, 1687 (1970).
22. T. T. Basiev, A. A. Sobol, P. G. Zverev et al., Appl. Opt. **38**, 594. (1999).
23. W. Kaiser and M. Maier, *Laser Handbook*, Eds. F. T. Arecchi and E. O. Schulz-Dubois, North-Holland, Amsterdam, 1972, p. 1077; Y. R. Shen, *The Principles of Nonlinear Optics*, Wiley, New York,1984.
24. J. Isberg, J. Hammersberg, E. Johansson et al., Science **297**, 1670 (2002).