ISSN 1063-7850, Technical Physics Letters, 2015, Vol. 41, No. 12, pp. 1163–1166. © Pleiades Publishing, Ltd., 2015.
Original Russian Text © G.M. Mikheev, V.V. Vanyukov, T.N. Mogileva, A.P. Puzyr', V.S. Bondar', Y.P. Svirko, 2015, published in Pis'ma v Zhurnal Tekhnicheskoi Fiziki, 2015, Vol. 41, No. 24, pp. 9–16.

Saturable Absorption in Aqueous Suspensions of Detonation Nanodiamonds under Irradiation with Femtosecond Laser Pulses

G. M. Mikheev[a]*, V. V. Vanyukov[b], T. N. Mogileva[a], A. P. Puzyr'[c], V. S. Bondar'[c], and Y. P. Svirko[b]

[a] *Institute of Mechanics, Ural Branch, Russian Academy of Sciences, Izhevsk, 426067 Russia*
[b] *Institute of Photonics, University of Eastern Finland, 80101 Joensuu, Finland*
[c] *Institute of Biophysics, Siberian Branch, Russian Academy of Sciences, Krasnoyarsk, 660036 Russia*
**e-mail: mikheev@udman.ru*

Received June 11, 2015

Abstract—The phenomenon of saturable absorption has been observed in aqueous suspensions of detonation nanodiamonds (DNDs) with 34, 50, and 110 nm sized clusters of nanoparticles under irradiation with 795-nm laser pulses of 120-fs duration. The saturable absorption intensity has been studied as a function of the DND concentration in suspension. At a concentration of 2 wt % of DNDs with 50-nm average cluster size, the saturable absorption intensity amounts to 950 GW/cm^2.

DOI: 10.1134/S1063785015120263

Saturable absorption (SA) is a phenomenon whereby an optical medium exhibits a short-term decrease in the optical absorption of transmitted high-intensity light pulses, which is due to induced electron transitions between two energy levels. The SA effect is used for creating self-bleaching nonlinear optical filters (nonlinear saturable absorbers), which are employed in the cavities of lasers generating femto-, pico-, and nanosecond light pulses [1–4]. In the last decade, considerable effort has been devoted to the investigation of nonlinear optical properties of nanocarbon materials in view of their potential use in photonics and opto-electronics. In particular, SA in single-wall carbon nanotubes and graphene allows pico- and femtosecond laser pulses to be generated in a broad spectral range (see, e.g., [5, 6]). However, to the best of our knowledge, this effect has not been observed in detonation nanodiamonds (DNDs) representing a different form of nanocarbon.

The present work was aimed at studying the SA in aqueous DND suspensions irradiated by femtosecond laser pulses at a wavelength of 795 nm.

DNDs have been synthesized from carbon contained in high explosives. Specific features of this method of synthesis lead to the fact that the surface of primary diamond nanocrystals with average sizes of about 4–5 nm [7] contains a large amount of impurities, including nitrogen, silicon, oxygen, hydrogen, metals, and hydrocarbon fragments [8, 9]. In this work, commercial DNDs (Real-Dzerzhinsk Co., Russia) have been cleaned by adding NaCl solution to diamond nanoparticles suspended in deionized water with the aid of ultrasound. This processing leads to a decrease in the content of surface impurities in DNDs and an increase in their colloid stability, which makes possible the fractionation of nanoparticles by differential centrifugation of suspensions. The experiments were performed with aqueous DND suspensions containing clusters of nanoparticles with average sizes 34, 50, and 110 nm according to the results of dynamic light scattering measurements (Malvern Zetasizer Nano ZS).

Figure 1a shows typical particle size distribution in the DND fraction with an average size of 50 nm. Figure 1b presents the Raman spectra of the DND fraction with an average size of 34 nm measured at laser excitation at wavelengths of 633 and 473 nm. As can be seen, the spectra in both cases exhibit characteristic peaks at 1325–1329 cm^{-1} with the frequency shift which was determined by the excitation wavelength [10]. Previously, we have also reported [11] electron-microscopic images of DND particles. Aqueous suspensions of DNDs with preset concentrations were prepared by merely adding a necessary volume of deionized water to a weighed amount of nanodiamond powder. Values of zeta-potential below –30 mV, which are characteristic for aqueous DND suspensions [11, 12], are indicative of a force of high electrostatic repulsion that prevents nanoparticles and ensures their high colloidal stability in suspensions. It has been shown [12, 13] that aqueous DND suspensions are stable in time and resistant to periodic laser action at high power density.

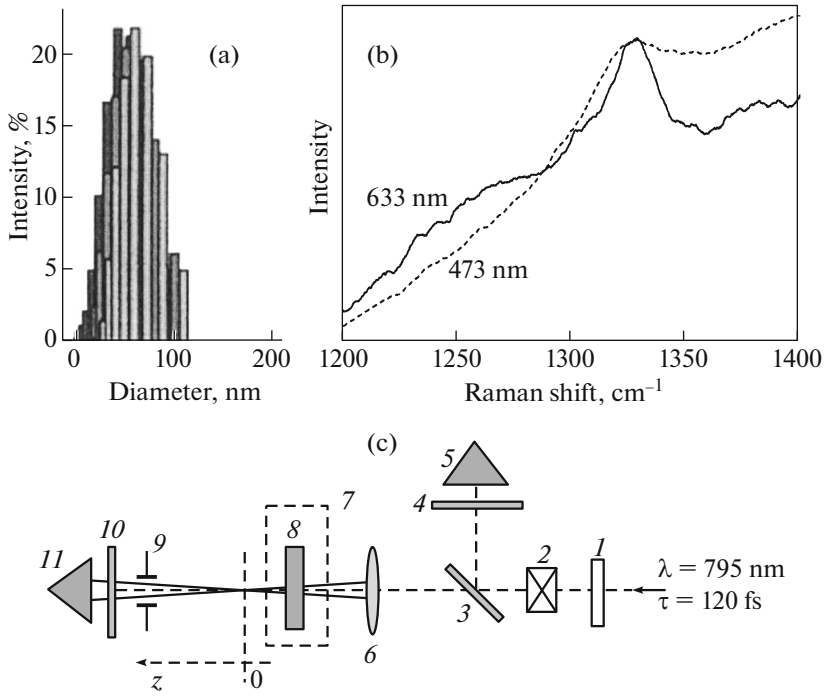

Fig. 1. (a) Typical particle size distribution in the DND fraction with an average size of 50 nm; (b) Raman spectra of the DND fraction with an average size of 34 nm measured on laser excitation at wavelengths of 633 and 473 nm; (c) sketch of the experimental setup for *z*-scan measurements: (*1*) half-wave plate, (*2*) polarizer, (*3*) beam divider plate, (*4*, *10*) neutral optical filters, (*5*, *11*) photodetectors, (*6*) focusing lens, (*7*) positioner table, (*8*) optical cell with suspension studied, and (*9*) open aperture.

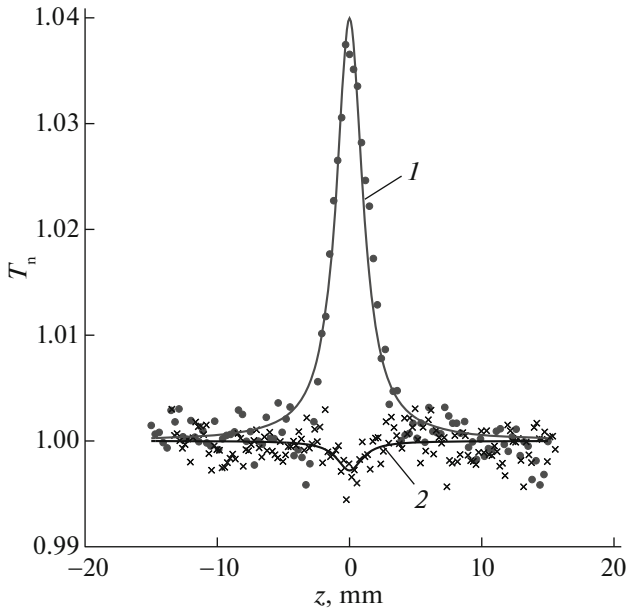

Fig. 2. Experimental plots of normalized nonlinear transmission T_n of focused laser radiation vs. coordinate z relative to the beam waist ($z = 0$) for (points) aqueous DND suspension with 2 wt % concentration of nanoparticles and (crosses) distilled water measured at laser pulse energy $E_{in} = 100$ nJ. Curves *1* and *2* show the approximations of experimental data by formula (2) for the suspension and by a model of four-photon absorption for distilled water, respectively.

The phenomenon of SA in aqueous DND suspensions has been studied using the well-known open-aperture *z*-scan technique [14]. The suspensions were irradiated at $\lambda = 795$ nm by Quantronix Integra-C laser with pulse duration $\tau = 120$ fs and a pulse repetition frequency of 1 kHz. The laser pulse energy E_{in} monitored by photodetector *5* was varied within 10–200 nJ by half-wave plate *1* and polarizer *2* positioned at the entrance of the *z*-scan system (Fig. 1c). The laser beam for *z*-scanning was focused by lens *6* with a focal distance of 75 mm. The laser beam radius at the focal point was $w_0 = 17.3$ μm as measured by a CCD camera (DCC1545M, Thor-Labs Inc.). Nonlinear transmission coefficient T of a DND suspension in a quartz cell of thickness $h = 1$ mm was determined as a function of coordinate z relative to the waist of the focused laser beam: $T = E_{out}/E_{in}$, where E_{out} is the laser pulse energy at the cell output measured by photodetector *11* (Fig. 1c). The $T(z)$ values were averaged over 900 laser pulses at a *z*-scan step of 0.3 mm.

Figure 2 (curve *1*) presents an experimental normalized plot of $T_n(z) = T(z)/T_0$ for the DND suspension with an average clusters size of nanoparticles of 50 nm at concentration $C = 2$ wt % measured using laser pulses with $E_{in} = 100$ nJ. Here, T_0 is the linear transmission coefficient. Figure 2 (curve *2*) also shows the experimental dependence obtained for the

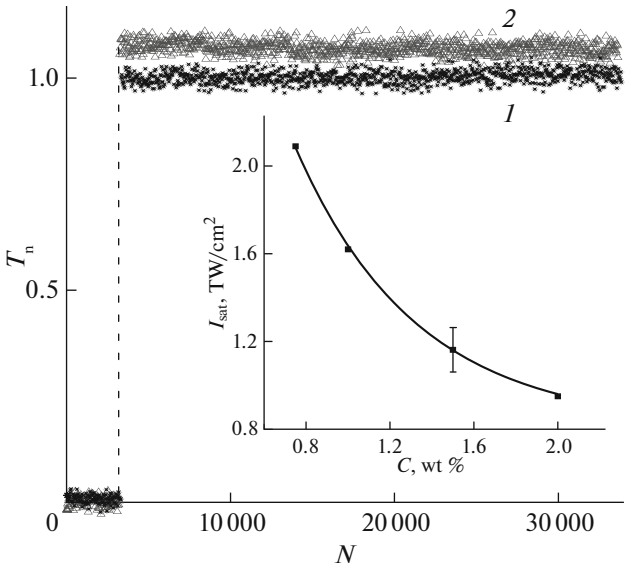

Fig. 3. Plots of normalized nonlinear transmission T_n of the aqueous DND suspension with concentration 2 wt % vs. number N of laser with energy $E_{in} = 100$ nJ measured in the optical cell positioned at $z = 15$ mm (*1*, asterisks) and $z = 0$ (*2*, triangles); vertical dashed line corresponds to the moment of removal of a nontransparent screen situated in front of the cell. The inset shows a plot of saturable absorption intensity I_{sat} vs. concentration C of diamond nanoparticles in the aqueous suspension.

same cell with distilled water. The dependence of $T_n(z)$ for the DND suspension shows that the approach to $z = 0$ is accompanied by the development of SA. The symmetry of the $T_n(z)$ curve relative to point $z = 0$ indicates that bleaching of the optical medium is reversible. Therefore, the growth in T_n near $z = 0$ is not caused by the irreversible light-induced transparency that was observed, e.g., in suspensions of onion-like carbon nanoparticles [15] and multiwall carbon nanotubes in dimethylformamide [16] under the action of the nanosecond pulses of laser radiation.

This conclusion is also evidenced by the absence of changes in the dependences of T_n on number N of pulses (Fig. 3) transmitted through the cell with DND suspension positioned at the beam waist ($z = 0$) and far from this point (e.g., at $z = 15$ mm). As can be seen from Fig. 3, the T_n values in both cases remain constant to within fluctuations of the detection system. This result implies that a DND suspension occurring at the laser beam waist exhibits SA rather than irreversible light-induced transparency. Additional experiments showed that SA also took place in DND suspensions with average clusters sizes 34 and 110 nm. Figure 2 (curve *2*) reveals an extremely weak nonlinear absorption for $E_{in} = 100$ nJ by distilled water at the laser beam waist, which leads to a very small decrease in $T_n(z)$. This effect can be explained by the four-photon absorption that arises in water in the field of high-power femtosecond laser pulses.

Taking into account the possibility of four-photon absorption in water by analogy with [17], optical absorption coefficient α in aqueous DND suspensions can be expressed as follows:

$$\alpha = \alpha_0 \frac{1}{1 + I/I_{sat}} + \beta I^3, \qquad (1)$$

where α_0 is the coefficient of linear absorption dependent on the DND concentration and laser wavelength; $I_{in} = E_{in}/(\tau \times S(z))$, $S(z) = \pi w^2(z)$, $w(z)$ is the laser beam radius at distance z from the waist ($z = 0$) of the focused laser beam; I_{sat} is the saturable absorption intensity that determines the SA nonlinearity; and β is the nonlinear absorption coefficient which characterizes four-photon absorption in water [18]. For a Gaussian beam, $w^2(z) = \omega_0^2[1 + (\lambda z/\pi w_0^2)^2]$ is rightly. Neglecting the small four-photon absorption ($\beta = 0$) in distilled water (Fig. 2, curve *2*) and with allowance for the well-known expression of transmission $T(z)$ as a function of α (see, e.g., [19]), formula (1) yields the following relation for the normalized transmission coefficient:

$$T_n(z) = \exp\left[\alpha_0 h\left(1 - \frac{1}{1 + I(z)/I_{sat}}\right)\right]. \qquad (2)$$

Linear absorption coefficient α_0 for this formula was determined from the absorption spectra of suspensions studied.

Based on the above considerations, the experimental plots of $T_n(z)$ obtained for various E_{in} and different DND concentrations C were approximated using a single parameter I_{sat} dependent on C. The plot of saturable absorption intensity I_{sat} versus concentration C is shown in the inset to Fig. 3. As can be seen, an increase in C leads to a monotonic decrease in I_{sat}. Note that the value of I_{sat} for the DND suspension with concentration $C = 2$ wt % in a 1-mm-thick cell is about 160 times as large as the value reported for a graphene bilayer at 780 nm [20]. From this it follows that the SA effect in aqueous DND suspensions is much weaker than that in graphene.

Thus, we have discovered SA in aqueous DND suspensions irradiated by femtosecond laser pulses at 795 nm. In an impurity-free diamond crystal, the optical absorption is absent due to a large bandgap (5.4 eV). However, aqueous DND suspensions are semitransparent and their extinction monotonically decreases with increasing wavelength of the incident light. This behavior is determined by the scattering of light, the cross section of which decreases with increasing wavelength of incident radiation, and by the optical absorption that is caused by the presence of a graphite-like layer [21–23] and dimer chains on the surface of diamond nanoparticles [24]. According to [24], a DND suspension exhibits an absorption

band in the region of 1–2 eV with a maximum at 1.5 eV, which almost coincides with the photon energy (1.56 eV) of the laser radiation employed. This probably explains the SA effect observed in aqueous DND suspensions.

Acknowledgments. We are grateful to K.G. Mikheev (Laboratory of Laser Methods of Investigation, Institute of Mechanics, Izhevsk) for measuring Raman spectra of DND suspensions.

This study was supported by the Russian Foundation for Basic Research (project no. 13-02-96016_r_ural_a) and the Academy of Finland (grant no. 288547).

REFERENCES

1. H. W. Mocker and R. J. Collins, Appl. Phys. Lett. **7**, 270 (1965).
2. N. Sarukura, Y. Ishida, T. Yanagawa, and H. Nakano, Appl. Phys. Lett. **57**, 229 (1990).
3. M. I. Demchuk, V. P. Mikhailov, A. M. Prokhorov, et al., Kvantovaya Elektron. **10**, 1051 (1983).
4. G. M. Mikheev, D. I. Maleev, and T. N. Mogileva, Kvantovaya Elektron. **19**, 45 (1992).
5. T. Hasan, Z. Sun, F. Wang, et al., Adv. Mater. **21**, 3874 (2009).
6. Z. Sun, T. Hasan, and A. C. Ferrari, Phys. E **44**, 1082 (2012).
7. V. N. Mochalin, O. Shenderova, D. Ho, and Y. Gogotsi, Nature Nanotechnol. **7**, 11 (2011).
8. V. S. Bondar' and A. P. Puzyr', Phys. Solid State **46** (4), 716 (2004).
9. J. M. Say, C. van Vreden, D. J. Reilly, et al., Biophys. Rev. **3**, 171 (2011).
10. G. M. Mikheev, K. G. Mikheev, T. N. Mogileva, et al., Quantum Electron. **44**, 1 (2014).
11. V. Vanyukov, T. Mogileva, G. Mikheev, et al., Appl. Opt. **52**, 4123 (2013).
12. G. M. Mikheev, A. P. Puzyr', V. V. Vanyukov, T. N. Mogileva, and V. S. Bondar' Tech. Phys. Lett. **39** (3), 229 (2013).
13. G. M. Mikheev, A. P. Puzyr', V. V. Vanyukov, K. V. Purtov, T. N. Mogileva, and V. S. Bondar', Tech. Phys. Lett. **36** (4), 358 (2010).
14. M. R. Ferdinandus, M. Reichert, T. R. Ensley, et al., Opt. Mater. Express **2**, 1776 (2012).
15. G. M. Mikheev, V. L. Kuznetsov, D. L. Bulatov, et al., Quantum Electron. **39**, 342 (2009).
16. G. M. Mikheev, V. L. Kuznetsov, K. G. Mikheev, T. N. Mogileva, M. A. Shuvaeva, and S. I. Moseenkov, Tech. Phys. Lett. **39** (4), 337 (2013).
17. R. A. Ganeev, A. I. Ryasnyanskii, A. L. Stepanov, and T. Usmanov, Quantum Electron. **33**, 1081 (2003).
18. H. Shim, M. Liu, C. Hwangbo, and G. I. Stegeman, Opt. Lett. **23**, 430 (1998).
19. W. D. Tan, C. Y. Su, R. J. Knize, et al., Appl. Phys. Lett. **96** (1), 031106 (2010).
20. H. Yang, X. Feng, Q. Wang, et al., Nano Lett. **11**, 2622 (2011).
21. T. Hamilton, E. Z. Kurmaev, S. N. Shamin, et al., Diamond Relat. Mater. **16**, 350 (2007).
22. A. P. Puzyr, A. E. Burov, G. E. Selyutin, et al., Tribol. Trans. **55**, 149 (2012).
23. V. L. Kuznetsov, S. I. Moseenkov, K. V. Elumeeva, et al., Phys. Stat. Solidi **248**, 2572 (2011).
24. A. E. Aleksenskii, A. Ya. Vul', S. V. Konyakhin, K. V. Reich, L. V. Sharonova, and E. D. Eidel'man, Phys. Solid State **54** (3), 578 (2012).

Translated by P. Pozdeev