Optical limiting in nanodiamond suspension: shortening of the laser pulses

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Abstract. Optical limiting (OL) in an aqueous suspension of nanodiamonds (NDs) with an average nanoparticle size of 20 nm is studied and the results are presented. NDs are obtained by grinding the micron-sized diamond powders manufactured by static high-pressure, high-temperature (HPHT) synthesis. The experiments are performed by the z-scanning technique with a closed aperture. The temporal parameters of nanosecond laser pulses at 1064 nm passing through the suspension in the OL mode are measured. It is found that the closer the cuvette with suspension to the laser beam waist, the shorter both the trailing edge of the laser pulses passing through the suspension and the laser pulse duration. The smooth control capability of the pulse duration in the range from 22 to 15 ns is demonstrated.

1. Introduction
Optical limiting is a phenomenon in which the power of a laser beam passing through an optical medium is nonlinearly attenuated. The physical mechanisms leading to OL can be two-photon (multiphoton) absorption, free-carrier absorption, inverse saturable absorption, nonlinear light scattering, nonlinear refraction, etc. [1, 2]. In the nanosecond range of laser pulses, OL was observed in suspensions of carbon-black [3], carbon nanotubes [4–7], onion-like carbon [8, 9], graphene [10, 11], and detonation nanodiamonds (DNDs) [12–14]. Recently, we have carried out studies of the nonlinear optical properties of aqueous suspensions of single-digit DNDs and have found a saturable absorption that transforms into OL at high laser influence [15]. However, the studies of OL in HPHT NDs suspensions with larger primary crystallites sizes have not been previously carried out. It is known that OL is accompanied by a change of the temporal shape of the transmitted laser pulses. The OL in the carbon nanotube (CNT) suspension due to nonlinear scattering of light by vapor bubbles leads to the shortening of the laser pulse duration [16]. The shortening of the pulse duration is due to the preferential scattering of the trailing edge of the laser pulse. The OL due to two-photon absorption leads to strong absorption of laser power at the top of the laser pulse. As a result, the duration of the laser pulse passing through the nonlinear medium increases. Therefore, it is important to study the temporal shape of laser pulses to reveal the mechanism of the OL in the aqueous suspension of HPHT NDs.

In this paper, we demonstrated that by scanning a cell with HPHT ND aqueous suspension along the axis of a focused laser beam, it is possible to smoothly control the duration of nanosecond laser pulses at 1064 nm. The shortening of the duration of light pulses occurs due to the shortening of the trailing edge of laser pulses passing through the suspension.
2. Experiments

NDs purchased from Van Moppes, Ltd were produced by grinding the micron-sized diamond powder manufactured by static high-pressure, high-temperature synthesis in hydraulic presses. To ensure the formation of a stable HPHT ND suspension in water the sample was chemically treated in acidic environment, resulting in zeta potential of -45 mV. Obtained ND suspension had been stable for a long time (more than 3 years). Examination of the nanoparticles on an electron microscope confirmed that the most of the particles were of 20 nm in diameter.

To characterize the HPHT ND particles by Raman spectroscopy, the appropriate aqueous HPHT suspension was used. The sample was deposited onto the glass substrate and dried at room temperature. Raman spectra were measured with Horiba Jobin Yvon HR 800 Raman spectrometer at 632.8 nm excitation. In order to prevent NDs from graphitization and blackening the input laser intensity was set below 10 kW/cm² [17–19]. From Figure 1, one can see that Raman spectra of HPHT ND clusters have a clear nanodiamond band at approximately 1330 cm⁻¹. This value exactly coincides with the Raman shift for nanodiamond films synthesized by chemical vapor deposition (CVD) [20], but is 2 cm⁻¹ less than for bulk crystalline diamond [21].

![Figure 1. Raman spectrum of the HPHT NDs obtained upon excitation by light at a wavelength of 632.8 nm.](image1)

Figure 2 shows the optical density spectrum of the 1 wt % aqueous HPHT ND suspension placed in an optical cuvette with a thickness of 1 mm. The absorption spectrum was measured with a Perkin ELMER

![Figure 2. The optical density of the 1 wt % aqueous HPHT ND suspension in the 1 mm path length optical cuvette and photograph of the 1 mm cuvettes with the (right) suspension and (left) distilled water (inset).](image2)
LAMBDA 650 double-beam UV/Vis spectrophotometer relative to the same cuvette filled with distilled water. It is seen that in the range of 400-900 nm the optical density of the suspension decreases monotonically with wavelength increase. Such a spectrum of optical density in the visible and near infrared ranges is characteristic for suspensions of carbon nanotubes, onion-like carbon and DNDs [8, 9, 13, 16, 22, 23]. Photographs of the 1 mm cuvettes with the suspension and distilled water are shown in Figure 2 (see inset). Linear transmittance of the 1 mm thick 1 wt % HPHT ND suspension at 1064 nm laser wavelength was 62.9 %. Experiments were carried out using a z-scan technique with a close aperture z-scan system [24] according to the optical scheme shown in Figure 3. In the experiments we used passive Q-switch YAG: Nd³⁺ - laser, which generates TEM₀₀ mode single-frequency radiation [18]. The τ₀ pulse duration of the laser, operated at λ = 1064 nm, was 22.1 ns.

![Figure 3. Schematics of the experimental setup.](image)

The laser beam was focused by a lens (Lens 1) with a focal length of 150 mm. The diameter of the laser beam 2w₀ in the beam waist (z = 0) was 114 μm. For the Gaussian beam w²(z) = w₀²[1+z²/z₀²], where z₀ = πw₀²/λ is true. The 1 mm cell with the suspension was located on a one-coordinate motor stage. An aperture was used to select the scattered radiation from the transmitted laser beam. It was located in the focal plane of the output lens (Lens 2). The focal length of the output lens was 100 mm. At the position of the cuvette far from the waist of the focused beam, the laser radiation passed through the diaphragm completely. The laser pulses passed through the aperture and then, after attenuation by neutral filters, passed through the milk glass and entered the fast speed SIR-5 photodetector (ThorLab) with a rise time less than 60 ps. The electrical pulses generated at the output of the photodetector were recorded by a broadband TDS7704B digital oscilloscope (TEKTRONIX). The amplitude and the temporal shape of output laser pulses were studied as a function of the cuvette position z/z₀ along the focused laser beam axis. The duration of the input and output laser pulses τᵉₑ was defined with respect to the ratio 0.5 of its maximum. The temporal evolution of the laser pulses was characterized by measurement of the rise time τᵉᵣ𝑒 and fall time τᵉᵓ, which were defined with respect to 0.1 and 0.9 of the pulse amplitude.

3. Results and discussion
Figures 4a shows oscillograms (normalized to the maximum value) of the output laser pulses at various values of z/z₀, where z₀ = πw₀²/λ, z₀ = 9.6 mm (z₀ is Rayleigh length). One can see that the less the z/z₀, the smaller the transmitted laser pulse amplitude (Figure 4b). This indicates that OL occurs. One can also observe that the less the z/z₀, the shorter the output laser pulse duration (Figures 4c). As a result, the duration of the laser pulse decreases from 22 to 15 ns. The pulse duration can be approximated by the formula \( \tau_{out} = \tau₀\left[1 - a\exp\left(-\left(\frac{z}{z₀}\right)^2 / 2b^2\right)\right] \), where \( a = 0.35, b = 0.84 \). It can also be observed that the decrease of the amplitude is accompanied by the decrease of the pulse duration (Figures 4b, c). Figure 4d shows the fall time of the output laser pulse as a function of z/z₀.
From this figure, as well as from the oscillograms presented in Figure 4a, it follows that the shortening of the transmitted pulses duration occurs due to the output laser pulse trailing edge being cut off. This means that the OL in HPHT ND suspensions does not arise due to the two-photon absorption, but due to the cumulative effect, leading to a nonlinear light scattering. As shown in Figure 4b, the dependence of the transmitted laser pulse on $z/z_0$ is not symmetric with respect to the point $z/z_0 = 0$. This means that nonlinear refraction also occurs along with nonlinear scattering in the suspension.

![Figure 4. (a) Oscillograms of the output laser pulse at fixed input pulse energy for different $z/z_0$; the transmitted laser pulse (b) amplitude, (c) duration and (d) fall time as a function of $z/z_0$.](image)

Thus the obtained results show that the OL in the HPHT ND suspension is due to nonlinear scattering and nonlinear refraction of light.

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