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The Effect of the Size Factor of Nanodiamonds in Suspensions on Optical Power Limiting and Nonlinear Laser Light Scattering

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Abstract—The results of experimental studies of optical power limiting (OPL) and nonlinear light scattering (NLS) at a wavelength of 532 nm in suspensions of detonation-synthesis modified nanodiamonds (MNDs) with different grain-size compositions are described. It is found that, at the same nanoparticle concentration, OPL and NLS are more efficient in suspensions with large MNDs. It is shown that MND suspensions can exhibit a stable long-term operation as OPL in a field of laser pulses with a power density of 0.2 GW/cm^2 at a repetition frequency of 1 Hz.

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One of the intriguing features of the interaction between an intense laser emission and a material is optical power limiting (OPL) [1], which is of interest for developing devices to protect light-sensitive objects from the effects of high-power laser radiation, as well as for controlling the shape and duration of laser pulses. Optical power limiters based on nanocarbon materials, such as carbon black, graphite, carbon nanotubes (CNTs), onionlike carbon (OLC), and MNDs, can operate in a wide spectral range.

Many studies of OPL in suspensions of carbon black and CNTs have been reported (see, e.g., [2–6]). In general, suspensions of carbon black and single-walled CNTs prepared by simple ultrasonic dispersion are stable over time only for a few hours [2]. The preparation of stable (for many months) suspensions of multiwalled CNTs—for example, in water—requires a complex chemical treatment [6]. Meanwhile, to the best of our knowledge, there are only a few studies on OPL in suspensions of OLC and MNDs [7–9]. Aqueous suspensions of OLC are not stable over time; at high intensities of incident radiation at a wavelength of 1064 nm, OLC suspensions in dimethylformamide, which are stable over time, undergo irreversible bleaching to form a new substance with a high absolute value of diamagnetic susceptibility [10]. Our recent studies have also shown that aqueous suspensions of multiwalled CNTs that are stable over time are not resistant to multiple exposure to high-intensity laser pulses. At the same time, aqueous suspensions of MNDs [11], which exhibit the property of OPL, not only are stable over time, but also are resistant to multiple exposure to laser pulses with a high power density at a wavelength of 1064 nm [9]. The aim of this Letter is to study the effect of the size factor of MND particles suspended in water on OPL and NLS and the resistance of the suspensions to multiple exposure to laser pulses with a high power density at a wavelength of 532 nm.

The feedstock for preparing MNDs was a commercial detonation-synthesis nanodiamond powder produced by OOO Real-Dzerzhinsk (Russia). Modification was carried out via adding a solution of NaCl to the nanodiamond powder previously suspended in deionized water with the aid of sonication [12]. The modification led to a decrease in surface impurities and an increase in the colloidal stability of the nanoparticles and made it possible to use differential centrifugation. The end product of the modification and fractionation of the nanodiamonds was MND powders derived by drying the supernatants after differential centrifugation. Aqueous suspensions with a given concentration were prepared via simply adding a required volume of deionized water to a weighted portion of the MND powder. Samples 1, 2, and 3 with an average MND size of 320, 110, and 50 nm, respectively, were prepared for the studies. The measurements were carried out using the dynamic light scattering method.

During storage, the samples of aqueous suspensions of MNDs exhibited a high colloidal stability over time, which depended on particle size. Thus, a 3-wt % suspension with an average particle size of 50 nm does not form a precipitate within 3 years after its prepara-

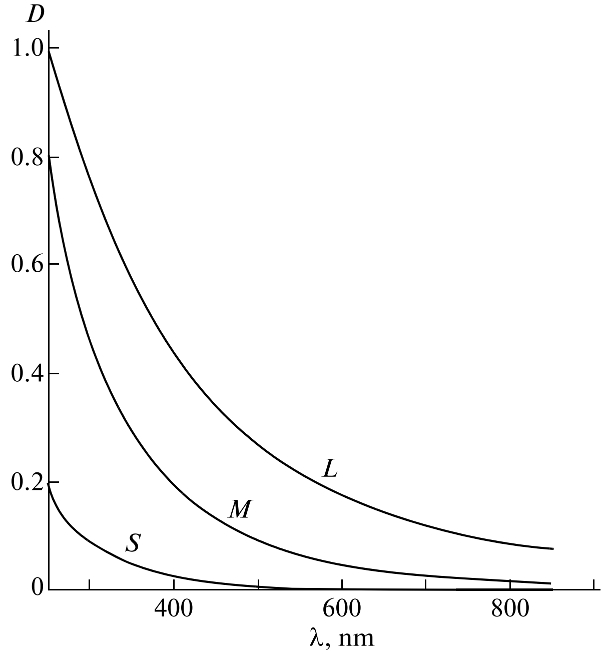

Fig. 1. Optical density of aqueous suspensions of MNDs with an average nanoparticle size of (S) 50, (M) 110, and (L) 320 nm against distilled water in a quartz cell with a thickness of 1.01 mm as a function of light wavelength.

tion. The absolute values of the zeta potential (colloidal stability index) of all three fractions of the MND suspensions are above 30 mV. This is indicative of a high electrostatic repulsive force between the particles, which prevents their aggregation [13].

Immediately prior to the experiment on recording the OPL and NLS, an aliquot of a concentrated suspension was diluted with distilled water to a concentration of 0.03 wt %. Suspensions with an average nanoparticle cluster size of (S) 50, (M) 110, and (L) 320 nm and optical cells with a working thickness of 1.06 mm were used in the experiments. The linear transmission coefficient of the S, M, and L suspensions was 0.87, 0.73, and 0.54, respectively, at a wavelength of 532 nm. The optical densities of the resulting suspensions against distilled water as a function of wavelength in a range of 250–900 nm are shown in Fig. 1. The resulting dependences are similar and exhibit an increase in the optical density with decreasing light wavelength.

The experiments were carried out at a laser wavelength of 532 nm. The laser pulse duration was $\tau = 17$ ns. A lens with a focal length of 100 mm was used to focus the beam. The laser-beam waist diameter was about 0.07 mm. Energies of laser pulses incident on the cell ε_{in} and transmitted through it ε_{out} were measured using calibrated photodetectors connected to an automated multichannel recording system operating in conjunction with a PC. To study the relationship between OPL and NLS, an additional photodetector was used; it registers energy ε_d of laser pulses scattered at right angles to the optical axis of the incident laser beam in accordance with the experimental arrangement described in [6]. All the experiments were conducted for laser light polarized in a vertical plane.

In the experiments, the values of ε_{in}, ε_{out}, and ε_d in a broad variation range of incident laser pulse energy ε_{in} were recorded and stored. Figure 2a depicts resulting input–output energy density dependences $P_{out}(P_{in})$ for a cell filled with distilled water (DW curve) and the S, M, and L suspensions under study. It is evident that dependence $P_{out}(P_{in})$ corresponding to the distilled water is represented by a straight line passing through the origin of coordinates with a slope to the axis of abscissas of 0.9. Dependences $P_{out}(P_{in})$ derived for the MND suspensions (S, M, and L curves) clearly show the occurrence of an OPL effect. At low values of P_{in}, an increase in the light flux at the input of the cell with the above suspensions leads to a respective increase in P_{out} with proportionality coefficients P_{out}/P_{in} equal to linear transmission coefficients of $T_0^S = 0.87$, $T_0^M = 0.73$, and $T_0^L = 0.54$ for the S, M, and L suspensions, respectively. However, with a further increase in P_{in}, the proportional increase in the output waveform ceases and P_{out} stabilizes at a certain level P_{out}^{lim}, which weakly depends on P_{in}. The S, M, and L curves show that the value of P_{out}^{lim} is determined by the characteristic size of MNDs, and, the larger the characteristic nanoparticle size in the suspension, the lower the level of P_{out}^{lim}. It is also noteworthy that the dependences of ε_d on P_{in} derived for suspensions with different characteristic size of MNDs exhibit an opposite behavior. The larger the characteristic size of MNDs, the higher the level of right-angle scattered radiation at any fixed value of P_{in} (Fig. 2b).

The experimental results presented in Fig. 2a make it possible to obtain dependences of transmission coefficients T of the studied suspensions on incident radiation energy density P_{in}. These dependences normalized to the respective linear transmission coefficients make it possible to determine the threshold values of $P_{in} = P^{thr}$ at which the linear transmission coefficients halve. The found OPL threshold values P_{thr}^S, P_{thr}^M, and P_{thr}^L for samples of the S, M, and L suspensions were 4.5, 1.2, and 1.1 J/cm^2, respectively.

The nonlinear nature of scattered radiation is clearly shown in the dependences of $\eta = \varepsilon_d/P_{in}$ on P_{in} (inset in Fig. 2b). The dependences are derived from the experimental results shown in Fig. 2b and plotted on a logarithmic scale along the axis of abscissas. It is evident that, at $P_{in} \longrightarrow 0$, the ε_d/P_{in} ratio tends to a constant value of η_0, which depends on the suspension under study. The larger the characteristic size of

MNDs, the higher the value of η_0. In other words, this means that the linear scattering cross section increases with increasing particle sizes in the suspension. The dependences of η on P_{in} for the M and L suspensions are well approximated by a function that includes the sum of two exponential terms:

$$\eta = \eta_0 + \eta_1[1 - \exp(-\eta_2 P_{in})] + \eta_3[1 - \exp(-\eta_4 P_{in})],$$

where η_0, η_1, η_2, and η_4 are some dimensional coefficients that depend on the average size of the nanoparticles that constitute the suspension. The resulting formula is indicative of a complex mechanism of nonlinear scattering in MND suspensions.

Precipitation of particles, a decrease in the size of CNTs [5], or chemical reactions between the nanocarbon particles of the suspension and the molecules of the liquid [8, 10] can occur in a high-power laser radiation field. To detect these phenomena in MND suspensions, the cell with the studied S, M, and L samples was placed at the beam waist and sequentially exposed to 8000 laser pulses at a frequency of 1 Hz. The laser pulse energy in the experiment was 134 ± 20 μJ. Under these conditions, all the three suspensions under study exhibited an OPL behavior. In each experiment, the laser pulses were incident on the same area of the cell. The suspension in the cell was not stirred. The laser exposure duration was more than 133 min.

In the experiments, the values of $T = \varepsilon_{out}/\varepsilon_{in}$ and $\varepsilon_d/\varepsilon_{in}$ were determined for each laser burst. Figure 3 depicts dependences T and $\varepsilon_d/\varepsilon_{in}$ on number N of laser bursts, which were derived via averaging the measured values of 50 laser bursts. It is evident from Fig. 3 that the nonlinear transmission coefficient of the L suspension after exposure to 8000 laser bursts remains unchanged within experimental error. After laser treatment, these coefficients for the S and M suspensions increase by 20 and 8% of their initial values, respectively. It is noteworthy that a significant increase in the nonlinear transmission coefficient of the S suspension is accompanied by a respective decrease in the energy of right-angle scattered laser pulses (Fig. 3b, S curve).

The results suggest that the action of laser radiation on the S and M MND suspensions is accompanied by a decrease in the particle aggregate size. The sizes of nanodiamond aggregates in suspensions can decrease under the action of laser radiation owing to the chemical reaction between water and nondiamond forms of carbon that bind the primary nanodiamond particles ($C + H_2O \longrightarrow CO + H_2$) [14]. The chemical reaction between carbon and oxygen adsorbed on the surface of nanodiamond particles [15] or dissolved in water can also occur in the laser action field.

Thus, the NLS waveform that occurs under OPL in aqueous suspensions of MNDs biexponentially depends on energy density. As the average nanoparticle size increases, the threshold power of OPL in MND suspensions decreases and the NLS intensity increases. Suspensions of MNDs with an average size of 320 nm can withstand a periodic exposure to laser pulses with a power density of 0.2 GW/cm² for a long time without changing their nonlinear optical properties. The studies show that aqueous suspensions of

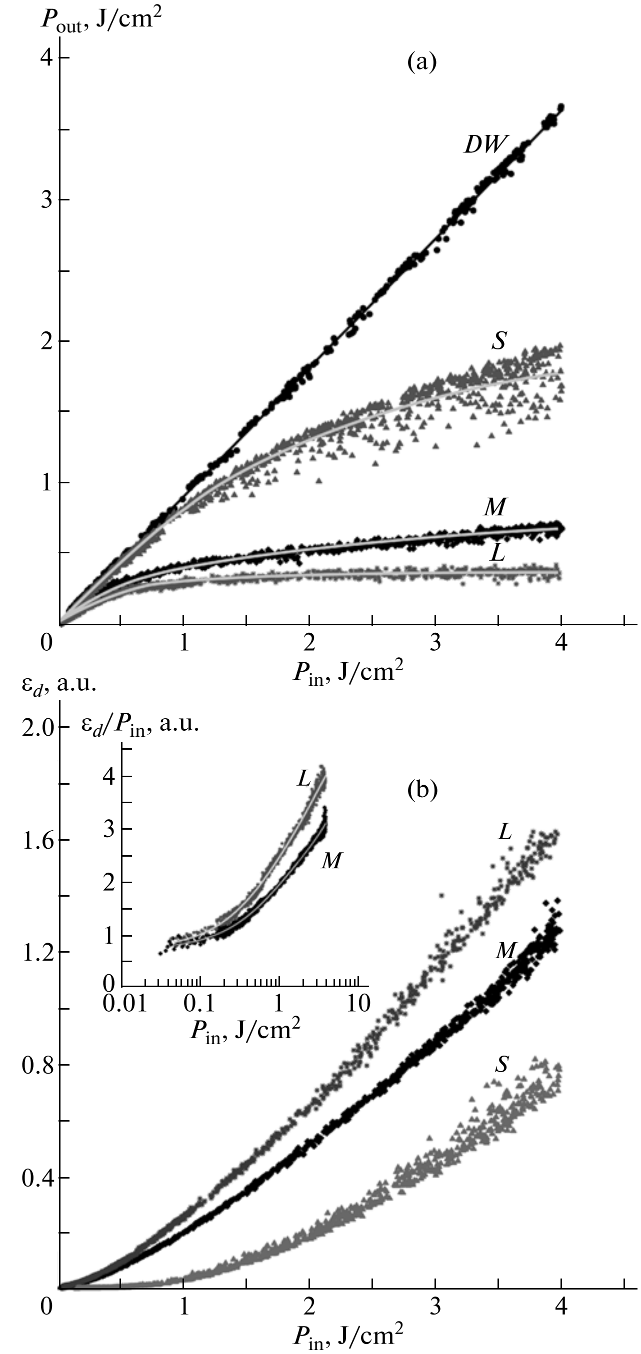

Fig. 2. Dependences of (a) transmitted energy density P_{out} and (b) scattered pulse energy ε_d on energy density P_{in} of incident laser pulses for the S, M, and L suspensions and DW distilled water; the inset shows the dependences of ε_d/P_{in} on P_{in} for the L and M suspensions plotted on a logarithmic scale along the axis of abscissas.

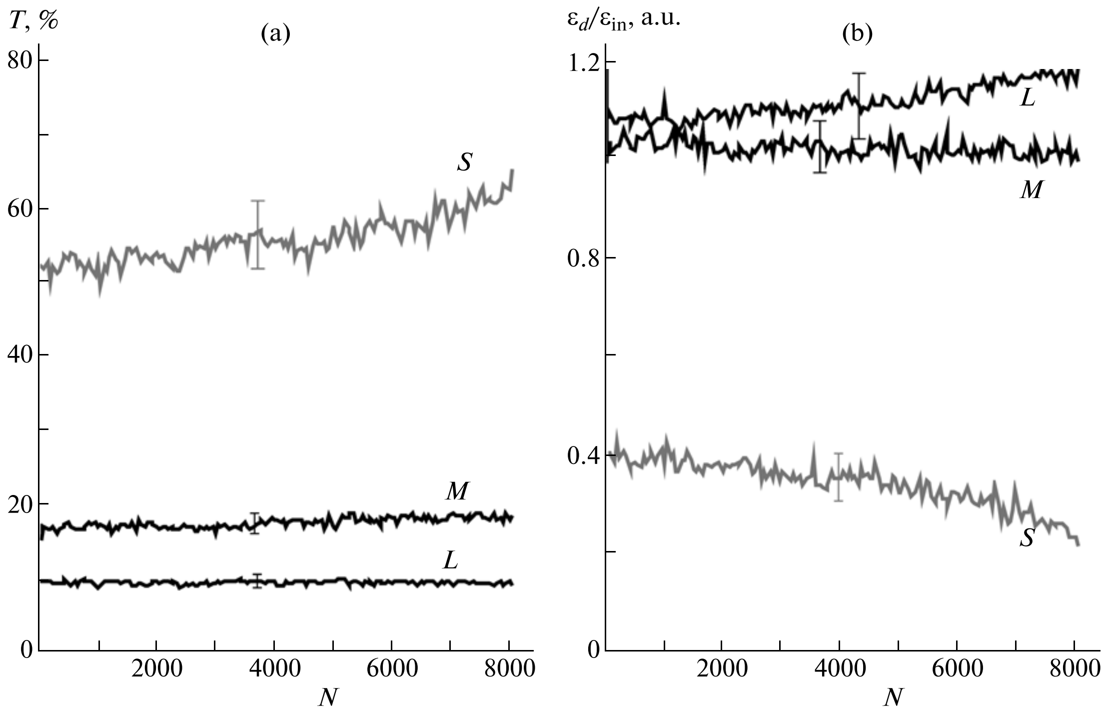

Fig. 3. Dependences of (a) nonlinear transmittance T and (b) the energy of scattered pulses normalized to the energy of incident laser pulses $\varepsilon_d/\varepsilon_{in}$ on the number N of laser bursts for the S, M, and L MND suspensions. The vertical bars show the standard deviations of the experimental data from the average values.

MNDs are a promising material for limiting the laser beams with a high power density.

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