Limiting the laser output power by inorganic nanoparticles

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Received November 15, 2005

Nonlinear absorption of solutions of inorganic nano-, submicron, and micron particles of various chemical composition, i.e., metal (Pt, Al), semiconductor (ITHO), and dielectric (ATO), has been measured at excitation by the Nd–YAG laser radiation (at 1064 and 532 nm wavelengths) of nanosecond duration. The limiting properties of the materials have been compared. Inexpensive and efficient nonlinear materials with Al as a basis are proposed for broadband limiters of laser radiation power.

Introduction

The intense development of laser instrumentation and laser technologies has raised a question on protection against the damaging action of laser radiation. In the first turn, this refers to the protection of eye and optical sensors.[1]

Various materials having different mechanisms of nonlinear attenuation are used to limit the power of laser radiation. The best characteristics are now obtained for optical limiters made from complex organic compounds.[2] They are characterized by high attenuation coefficient, high rate, and rather low threshold of operation. The mechanism of action of these limiters is re-absorption in the channel of singlet or triplet states or the two-photon and stepwise absorption.[3,4] The main disadvantages of these limiters are the spectrally selective action and the photodestruction of organic molecules during the irradiation.

Recently, the interest arose in the limiters made from inorganic nano-size materials. The first results showed the good promises of using nanoparticles as optical limiters. By now the nonlinear optical properties of various colloidal systems, containing metal, semiconductor, and dielectric particles of different size and chemical composition, have been studied. The studies have shown that the nonlinearity depends on the particle size and material.[5]

The mechanisms of optical limiting by nanoparticles are not fully understood yet. This is connected with a number of circumstances, for example, with the polydisperse composition of the systems, when particles of different size demonstrate different nonlinear mechanisms. Another reason is simultaneous action of different mechanisms of optical limiting, and the action of several mechanisms may by synergetic, amplifying each other.[6]

The aim of this work is to create stable dispersions of nanoparticles (NPs), submicron- and micron particles (MPs) of metals, semiconductors, and dielectrics, which can be used as optical limiters.

Production and stabilization of nano and submicron particles

Nano-sized platinum particles were synthesized by the reduction of hexachloroplatinum acid (H_2PtCl_6) by sodium tetrahydroborate in propylencarbonate (PC) in the presence of sodium citrate. As a result, the stable colloidal system of platinum nanoparticles in PC was produced. The aggregative stability is explained, in the first turn, by the presence of like charges in NPs, which prevents them from the formation of larger aggregates. The formation of such charges is connected with the adsorption of citrate ions on the NP surface.

Submicron and micron particles of semiconductors and dielectrics, such as antimony-doped tin oxide (ATO) and tin-doped indium hydroxide (ITHO), were synthesized separately by the sol-gel method in the Siberian Physical-Technical Institute by T.D. Malinovskaya and Yu.P. Egorov, who kindly placed them at our disposal. Ultrasonic processing was selected as a method of re-dispersion of the powder samples.

Aluminum MPs, coated with an aluminum oxide layer (about 1.5 nm), were synthesized by electric explosion. To stabilize ATO, ITHO, and Al particles, polyvinyl pyrrolidone (PVP) (MM = 55 000) was used. The PVP can adsorb on the surface of particles of various nature and keep their aggregative stability. It provides for the steric stabilization of NPs, what leads to the formation of a protecting barrier, a solid layer of solvate polymer chains, around a particle.

Linear absorption of media, containing NPs and MPs

Figure 1 shows the absorption spectra of solutions of platinum, aluminum, and antimony-doped tin oxide NPs.

Platinum particles have the smallest size (from 10 to 100 nm) among all the studied materials due to

0235-6880/06/02–03 117-04 $02.00

the technique used for their production. In the absorption spectrum (Fig. 1*a*), we can see characteristic absorption peaks at 270, 360, and 480 nm, which belong to the complex platinum ion (270 nm) and to the products of reaction (360 and 480 nm). This shows that in PC, in contrast to water, the reaction of reduction does not complete even upon heating. The plasmon absorption peak of platinum nanoparticles lies nearby 215 nm and is absent in the spectrum.[7]

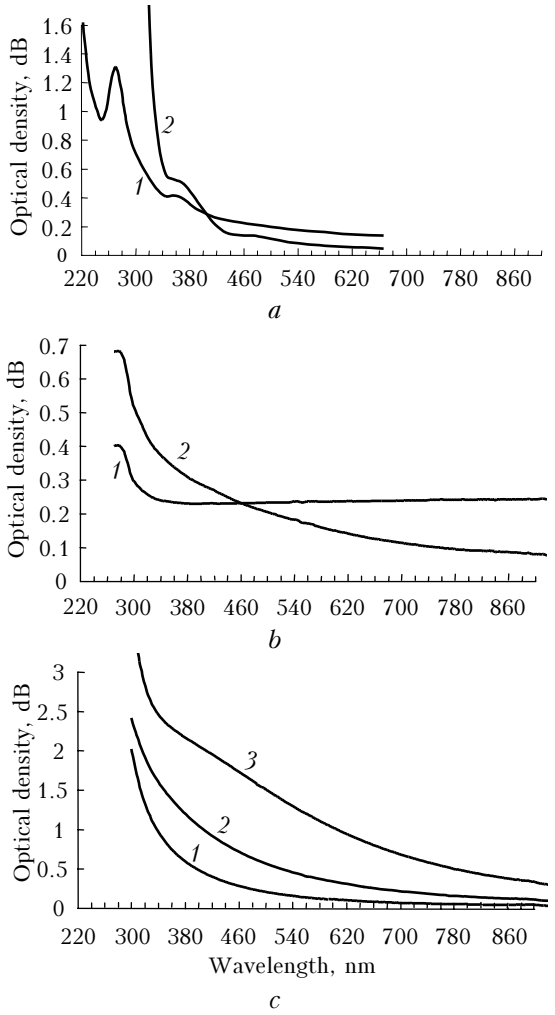

Fig. 1. Absorption spectra of dispersions with NPs: (*a*) platinum, particle size: up to 10 nm (*1*), up to 100 nm (*2*); (*b*) aluminum, particle size: up to 600 nm (*1*), from 2600 nm (*2*); (*c*) ATO, particles size: from 200 to 400 nm (*1*), from 200 to 400 nm (with micron-sized particles up to 2% of the mass) (*2*), from 400 to 1050 nm (with micron-sized particles up to 10% of the mass) (*3*).

Aluminum and ATO powders, produced by the sol-gel and electric combustion methods, contain particles of larger size. To decrease their size variability, the fractioning of particles was carried out by sedimentation and centrifugation of initial dispersions in ethyl alcohol. The absorption spectra of the solutions, containing aluminum and ATO particles, are shown in Figs. 1*b* and *c*. It should be noted that ATO dispersions include not only particles of the size mentioned above, but the larger ones as well. Thus, the hydrodynamic analysis has shown that the studied ATO dispersions included insignificant amount of particles with the size of 40 and even 100 to 110 μm.

The general regularities observed in the dispersions studied are the decrease of their optical density with the increase of the wavelength of exciting radiation. The long-wavelength absorption also decreases with the decreasing particle size. This is connected with the weaker influence of Rayleigh scattering by small (smaller than the wavelength of the exciting radiation) particles.

Nonlinear absorption of nano and submicron particles

The nonlinear absorption of colloid dispersions was studied using a setup, shown in Fig. 2. A pulsed Nd–YAG laser radiation (at 1064 or 532 nm, wavelength, 15 ns duration, and 100 mJ pulse energy) was focused by a spherical lens $F = 500$ mm onto a 5-mm long cell with the solution studied. The transmitted radiation was recorded with an ED-100A pyroelectric detector, whose diameter of 5 mm was twice as large as the beam diameter. The maximum power density of the radiation incident on the solution was 300 MW/cm^2; the radiation was attenuated by nonselective filters.

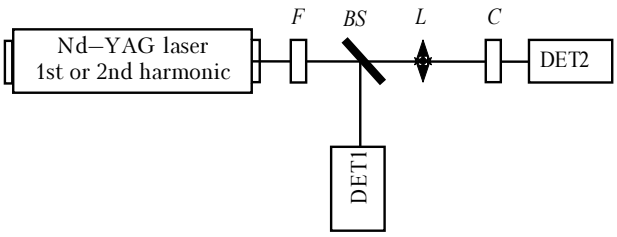

Fig. 2. Schematic of the experimental setup for investigation of the dependence of the medium transmittance on the power density of the exciting radiation: neutral-density filters *F*, beam-splitting plate *BS*, lens *L*, cell with the studied solution *C*, ED-100A pyroelectric detectors DET1, 2.

Figures 3 and 4 show the results of investigation of the dispersion transmittance as a function of the power density of laser radiation incident on the medium. The dispersions with platinum NPs demonstrate the strongest attenuation.

Figures 3*a* and *b* depict the transmittance of the platinum dispersions of different size as functions of the power density of the exciting radiation at the wavelengths of 532 and 1064 nm. The dispersion with finer particles is characterized by stronger nonlinear absorption. At the excitation wavelength of 532 nm, for the dispersion of particles with the size up to 10 nm and the initial transmittance of 82% at the excitation power density of 100 MW/cm^2, the attenuation coefficient KO_W, equal to the ratio of the linear transmittance at the excitation wavelength to

the transmittance at the given power density KO_{100}, amounts to 2.7, while at the maximum power density of 270 MW/cm^2 $KO_{270} = 5$. As the transmittance decreases to 50%, $KO_{270} = 6$, and when it is 38%, $KO_{270} = 8.2$. At the wavelength of 1064 nm, the attenuation is less significant: $KO_{120} = 2$ at the initial transmittance of 94% and the excitation power density of 120 MW/cm^2.

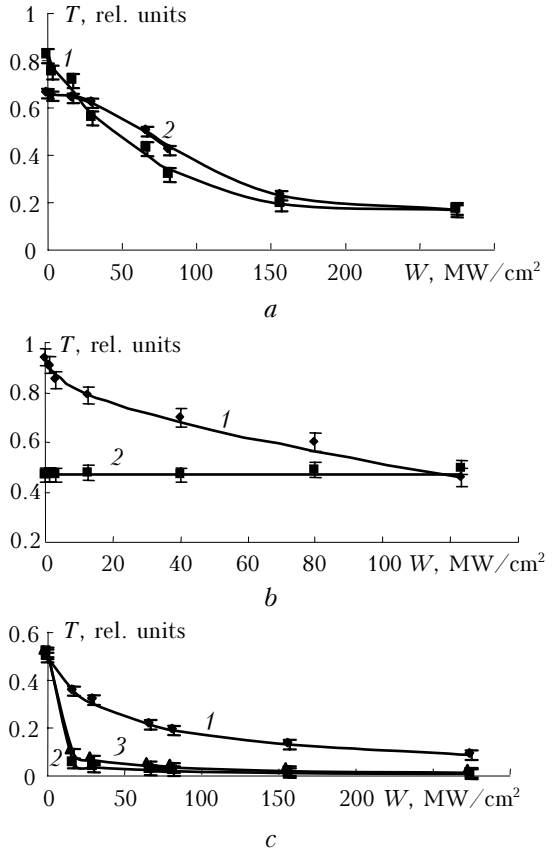

Fig. 3. Transmittance of the studied platinum-based nonlinear media as a function of the excitation power density: (*a*) excitation at 532 nm, NPs with the size up to 10 nm (*1*) and 100 nm (*2*); (*b*) excitation at 1064 nm, NPs with the size up to 10 nm (*1*) and 100 nm (*2*); (*c*) excitation at 532 nm, NPs with the size up to 10 nm (*1*), PC792 dye (*2*), and 1:1 mixture of the media *1* and *2* (*3*).

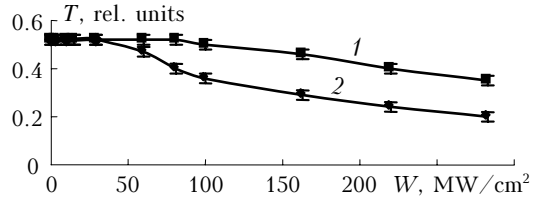

Fig. 4. Transmittance of the studied ATO-based nonlinear media as a function of the excitation power density. Excitation at 532 nm, particle size: from 200 to 400 nm (*1*); from 400 to 1050 nm (including micron-sized particles up to 10% of the mass) (*2*).

For platinum particles with the size up to 100 nm, the nonlinear absorption is much weaker. Thus, at the excitation wavelength of 532 nm, the excitation power density of 270 MW/cm^2, and the initial transmittance of 66%, $KO_{270} = 3.9$ (for particles smaller than 10 nm at $T_0 = 82\%$, $KO_{270} = 5$). Platinum particles with the size up to 100 nm (Fig. 3*b*) do not limit the radiation with the wavelength of 1064 nm (the measurements were conducted up to the power density of 120 MW/cm^2).

Figure 3*c* shows the transmittance of the platinum NPs dispersion (up to 10 nm) as a function of the excitation power density in comparison with the solution of the polymethine dye, which limits the laser radiation power by the mechanism of the inverse saturated absorption (reabsorption in the channel of singlet states) studied earlier.[2,8] The initial transmittance in both cases was 50%.

It can be seen from Fig. 3*c* that the dye has higher nonlinear absorption, especially, in the region of low intensities. As the excitation power density increases, this difference decreases, because the dye absorption begins to saturate. The media based on inorganic nanoparticles can be used along with the solutions of organic dyes. The dyes, having low threshold, can operate at low pump intensity, while NPs can be used at high intensities, what can significantly widen the dynamic range of an optical limiter.

Figure 3*c* (curve *3*) shows the results for the 1:1 mixture of the dye solution and the platinum NPs dispersion.

It seems promising to study the nonlinear absorption of such systems at the excitation power density higher than 300 MW/cm^2, since in this case the multiphoton absorption of nanoparticles will be present in addition to the processes of nonlinear scattering at NPs. It is also interesting to study the case that dye molecules are adsorbed on the surface of stabilized NPs.

Figure 4 shows the dependence $T(W)$ for ATO dispersions. The particles have the size from 200 nm and larger. Here we can see the dependence different to that in platinum NPs, i.e., the medium with larger particles limits laser radiation better than the medium with smaller particles does. In the general case, the limiting effect of the ATO dispersions is lower than that of the platinum dispersions. Thus, for ATO with the initial transmittance of 52%, $KO_{280} = 1.5$ for particles with the size from 200 to 400 nm and $KO_{280} = 2.6$ for particles larger than 400 nm.

The dependence, similar to that in platinum NPs, of the limiting capability of the medium on the particle size is also observed, i.e., aluminum particles of smaller size (below 600 nm) limit laser radiation better than particles with the size greater than 2600 nm (Fig. 5). The best results, as compared to other media studied, were obtained for the dispersions with aluminum. At the excitation power density of 100 MW/cm^2, $KO_{100} = 4$ for particles with the size greater than 2600 nm and $KO_{100} = 5$ for particles with the size smaller than 600 nm. At the excitation power density of 220 MW/cm^2, KO_{220} achieves, respectively, 8.4 and 10, which approaches

the results obtained for limiters made from solutions of organic dyes.[2]

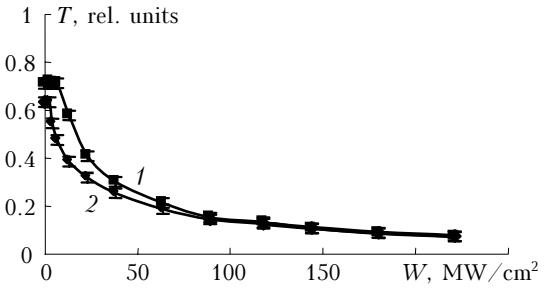

Fig. 5. Transmittance of the studied aluminum-based nonlinear media as a function of the excitation power density. Excitation at 532 nm, particle size: up to 600 nm (*1*), from 2600 nm (*2*).

The dispersions with ITHO MPs (size distribution similar to that of ATO) have virtually no limiting effect at the wavelength of 532 nm up to the excitation power density of 300 MW/cm^2.

Conclusions

1. It has been found that the nonlinear absorption of semiconductor MPs is weaker than that of platinum and aluminum. Aluminum nanoparticles have the best limiting properties. It has been shown that the nonlinear optical properties depend on the particle size and on the nature of the nanocrystal material. For metal nanoparticles, the nonlinear absorption decreased as the particle size increased, while for the semiconductor ATO particles the dependence was opposite. The dielectric ITHO MPs do not limit the power of the Nd–YAG laser second harmonic radiation.

2. When particles have the size much smaller than the wavelength of visible radiation (from one to several tens of nanometers), the ordinary Rayleigh scattering on them is almost absent and the medium resembles true solutions in its optical properties. In this case, the primary limiting mechanism is, likely, the inter-band phonon absorption, which lies in the blue and near-UV spectral regions for the materials under study as a result of two-photon or stepwise transitions (through impurity levels) in the field of intense light. This mechanism should be more pronounced for finer particles, since their amount in the medium is much larger at the same linear absorption. This mechanism can, probably, take place in our case for platinum nanoparticles and, partially, for aluminum.

The primary multiphoton absorption causes local inhomogeneities of the refractive index and small-size thermal inhomogeneities in the medium, which then increase the limiting effect. At the time of attenuation of the laser radiation, the giant amount of heat is released into the medium, more than 1 J/cm^3. This leads to the solution boiling up (this effect is seen visually in the experiment) and to adhesion or fragmentation of NPs. Therefore, it is desirable to increase the optical path in the medium by decreasing the particle concentration. For larger particles (hundreds nanometers), the main mechanism of laser radiation attenuation is, likely, the nonlinear scattering of various nature.

3. In the investigation carried out, we have developed inexpensive media of aluminum MPs with high radiation limiting properties, which can be used to limit laser radiation power.

Acknowledgments

This work was supported, in part, by the Russian Foundation for Basic Research (Grant No. 04–02–16515-a), the Ministry of Education and Science of the RF (Project No. 15459 and the State Contract No. 2.442.11.7085), and Russian–American BRHE Program (Projects No. Y2–P16–01 and No. Y2–P16–06).

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