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Nonlinear refraction and nonlinear absorption of an aqueous colloidal solution of chalcogenide As_2S_3

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***Abstract*. Nonlinear optical characteristics of an aqueous colloidal solution of As_2S_3 are studied by the *Z*-scan technique at the wavelength 1064 of a 25-ns Nd : YAG laser. The measured values of the nonlinear refractive index and the third-order nonlinear susceptibility are found to be -2.8×10^{-11} and -4.7×10^{-12} CGSE units, respectively. The nonlinear absorption coefficient of the chalcogenide solution is found to be 1 cm GW^{-1}.**

Keywords: *laser ablation, chalocogenide As_2S_3, nonlinear optical characteristics.*

1. Introduction

One of the most urgent problems of laser physics and nonlinear optics involves the extension of the number of nonlinear media with a view to use them in various practical applications. The most prospective applications studied in recent years include the creation of optical switches, modulators, and optical limiters of laser radiation. Colloidal structures [1 – 3] offer considerable promise as prospective nonlinear media. Colloidal solutions were widely used owing to their quick response and a large nonlinearity coefficients. Earlier, we studied the nonlinear optical characteristics of various states of aggregation of colloidal solutions of metal (Ag, Au, Pt, Cu) particles and showed that they can be used as optical limiters of laser radiation of nanosecond as well as picosecond duration [4].

One of the most widely used methods of preparing aqueous colloidal solutions is the chemical method based on the dissolution of a substance in acid to obtain salts which are subsequently dissolved in water, as well as the method of sputtering of a substance in dielectrics. However, a number of problems are encountered while using these methods. The first method requires subsequent purification in order to remove the acidic residual ions as well as acids and salts that did not participate in the reaction or were not dissolved in water. The second method affects the oxidation of nanoparticles, thus affecting the experimental results. Hence, considerable attention has been paid in recent years to the quest and optimisation of the methods of obtaining colloidal nanostructures. Laser ablation is one of such techniques.

Laser ablation is quite efficient for preparing a number of nonlinear optical materials in the form of nanofilms or colloidal solutions of nanoparticles. This method is also very efficient for preparing pure nonoxidised particles of metals in various organic matrices. It was shown in Refs [5 – 7] that the aqueous colloidal solutions of metal and carbon nanoparticles prepared by the laser ablation method are highly stable and do not require any additional stabilisers. Such a method of preparing colloidal solutions of metals is comparatively inexpensive and can be implemented more easily than, for example, sputtering of metals in an arc discharge. The optical spectra of colloidal silver prepared by ablation using the Nd : YAG laser radiation and its harmonics ($\lambda = 1064$, 532 and 355 nm) were studied in Ref. [8] for focused and nonfocused radiation. The authors of Ref. [8] observed that the efficiency of formation of colloidal solution increased with the wavelength of the incident radiation in the case of focused radiation, while the opposite behaviour was observed for nonfocused radiation.

Another nonlinear-optical medium, semiconductors, is also interesting in view of its potential applications in connection with the above-mentioned problems. Numerous investigations [9 – 11] revealed the strong as well as weak aspects of practical applications of highly nonlinear semiconductors in laser physics. Further progress in this direction is envisaged in a combination of the positive properties of various media and in investigation of their various modifications. Thus, the amplification of the nanoparticle local field in colloidal suspensions [12, 13] and significant nonlinear optical susceptibility of semiconductor chalcogenide structures [14, 15] raise the hopes of discovering new interesting peculiarities of the combinations of these media.

In this work, the laser ablation technique is used for the first time to prepare an aqueous solution of the semiconductor As_2S_3. The results of the study of the nonlinear refractive index, nonlinear absorption coefficient and the third-order nonlinear susceptibility of this medium by the *Z*-scan technique are presented.

2. Experimental

We used in experiments a *Q*-switched 1064-nm Nd : YAG laser. The laser emitted 25-ns pulses with a pulse repetition rate of 10 Hz. The technique described in Ref. [8] was used to prepare a colloidal semiconductor solution. The sample

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(chalcogenide glass As_2S_3) was placed in a quartz cell (of thickness 5 cm) containing distilled water. The laser radiation ($E = 50$ mJ) was focused by a lens of focal length $f = 25$ cm on the surface of As_2S_3 placed near the back wall of the cell to prevent the breakdown at the front wall. The sample was exposed to laser radiation for 15 minutes. As a result of laser ablation, the nanostructures of the chalcogenide As_2S_3 got into the aqueous medium, thus forming a colloidal solution.

The prepared solution had maximum absorption at 500 – 510 nm, compared to the maximum absorption in the initial sample at 525 nm. This circumstance (the blue shift of the absorption peak) was also mentioned in Ref. [16], where PbS films were studied whose absorption spectrum displayed a similar blue shift. The homogeneity of the solution remained unchanged over a period of one month, after which sedimentation occurred in the form of crystals whose colour was similar to that of the initial sample. Apparently, the ageing of the sample was associated with spontaneous clusterisation of nanoparticles of the semiconductor. More prolonged storage of the solution can be ensured by adding to the solution organic stabilisers based on gelatine or polyvinylpyrrolidone.

The nonlinear optical characteristics of the solution were studied by using the Z-scan technique [17]. A detailed description of the setup for measuring the nonlinear optical characteristics of various media by this method is given in Ref. [4]. As during the preparation of the solution, a 1064-nm, 25-ns Nd : YAG laser with a pulse repetition rate of 10 Hz was used. The radiation intensity at the focusing point was 3 GW cm^{-2}, which was lower than the optical-breakdown threshold in an aqueous solution of chalcogenide.

Laser radiation was focused by a lens of focal length 25 cm. Cells of thickness 1 mm containing the colloidal solution of chalcogenide were moved on a bench along the z axis, passing through the focusing region. The energy of individual laser pulses was measured with a calibrated FD-24K photodiode and recorded with a V4-17 digital voltmeter. The energy of laser radiation was measured with the help of calibrated neutral filters.

A diaphragm of diameter 1 mm was placed at a distance of 150 cm from the focusing region (the so-called limiting-diaphragm scheme) and transmitted $\sim 3\,\%$ of the laser radiation. The signal from a FD-24K photodiode placed behind the diaphragm was fed to a V4-17 digital voltmeter. To avoid the effect of instability of the output energy characteristics of the laser on the results of measurements, the signal recorded by this photodiode was normalised to the signal recorded by the reference photodiode. The limiting diaphragm scheme made it possible to determine both the magnitude and sign of the nonlinear refractive index n_2 of colloidal solutions of As_2S_3, as well as their third-order nonlinear susceptibility $\chi^{(3)}$.

To determine the nonlinear absorption coefficient β, the diaphragm was removed and the dependence of the transmission of the colloidal solution on the position of the cell relative to the focusing point of the radiation (open diaphragm scheme) was measured. The dependence of the transmission of the samples on the laser beam intensity was measured with a large detector placed at such a distance from the cell that all the radiation passing through the latter was detected. Thus, the decrease in the transmission of the cell containing the solution, measured in the open diaphragm scheme, was caused by nonlinear absorption in the cell.

3. Results and discussion

Fig. 1 shows the dependence of the normalised transmission T on the position of a 1-mm thick cell containing a colloidal solution of As_2S_3. This dependence characterises the self-defocusing of laser radiation in a medium with a negative refractive index n_2. The values of n_2 and $\chi^{(3)}$ obtained from the known relations in the Z-scan theory [18] were -2.8×10^{-11} and -4.7×10^{-12} CGSE units, respectively.

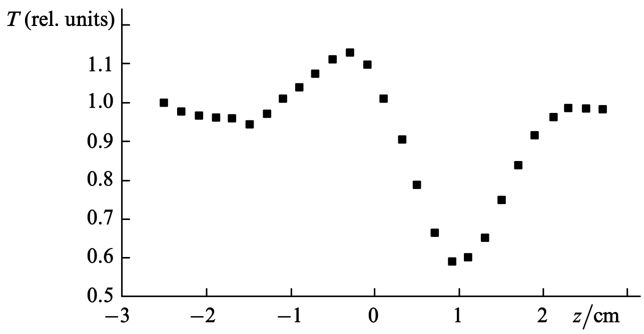

Figure 1. Dependence of the normalised transmission T of a 1-mm thick cell containing a colloidal solution of As_2S_3 in a limiting-diaphragm scheme on the position z of the cell.

The physical factors responsible for self-defocusing may be the nonlinearities caused by the high-frequency Kerr effect or the thermal-lens effect. Consider first the contribution of the Kerr effect. In the three-level model, the nonlinear susceptibility relation determining the sign of the Kerr nonlinearity under conditions away from resonance [19] has the form

$$\chi_{\rm K}^{(3)}(\omega) \approx \sum_{n,m,j} \frac{Nd_{jn}^2 d_{nm}^2}{(\omega_{hj} - \omega)^2} \frac{\omega_{mj} - 2\omega}{(\omega_{mj} - 2\omega)^2 + \Gamma_{mj}^2}, \qquad (1)$$

where N is the concentration of particles; d_{jn} is the dipole moment of transition at the frequency ω_{nj}; and Γ_{mj} is the homogeneous half-width of the transition. Note that Γ_{mj} in the vicinity of the two-photon resonance may be considerably different from the natural half-width.

Taking into account that the radiation wavelength differs from the resonance wavelength (505 nm), the sign of the nonlinearity will be determined by the sign of detuning from the two-photon resonance of As_2S_3 nanoparticles. In the case under consideration, this sign will be positive, i.e., self-focusing should occur, whereas self-defocusing was observed in the experiment.

Another possible nonlinearity mechanism is the thermal effect based on heat transport from semiconductor particles to the surrounding dielectric (water in our case). Thermal effect appears in a medium due to propagation of an elastic wave, and the order of magnitude of the time over which the steady state density distribution sets in is determined by the ratio $\tau = r/\upsilon_{\rm s}$ of the beam radius r to the velocity $\upsilon_{\rm s}$ of sound in the dielectric. For the conditions of our experiment ($r = 50$ μm, $\lambda = 1064$ nm, $\upsilon_{\rm s} \sim 1500$ m s^{-1}), we obtain $\tau \sim 33$ ns, i.e., the thermal lens formed in this case must affect the radiation propagation during the pulse (25 ns).

Note that the formation of a thermal lens also requires a sufficient absorption in the medium. The coefficient α of linear absorption calculated by us was found to be 1.05 cm^{-1}. Effects associated with nonlinear absorption (two-photon effects, reverse saturation absorption, etc.) may be manifested during the propagation of high-intensity laser radiation. This is confirmed by the asymmetry of the dependence $T(z)$ in the limiting-diaphragm scheme (Fig. 1). To confirm the presence of nonlinear absorption, we investigated the process experimentally. Fig. 2 shows the dependence of normalised transmission on the position of the cell in the open-diaphragm scheme. One can see that this dependence is characteristic of nonlinear absorption.

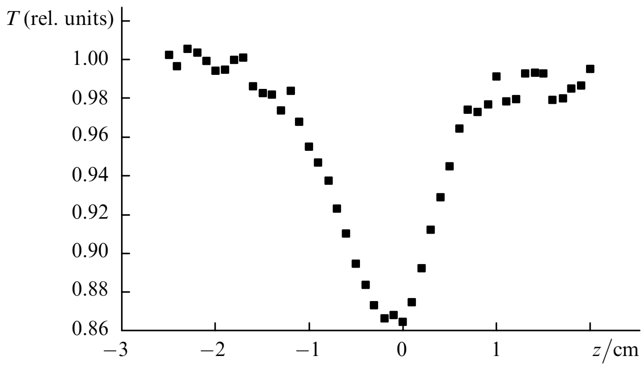

Figure 2. Dependence of the normalised transmission T of a 1-mm thick cell containing a colloidal solution of As_2S_3 in an open-diaphragm scheme on the position z of the cell.

The nonlinear absorption coefficient β is defined by the relations [18]

$$\beta = \frac{q_0}{I_0 L_{\text{eff}}} \quad (2)$$

and

$$T_0 = q_0^{-1} \ln(1 + q_0), \quad (3)$$

where T_0 is the minimum normalised transmission in the open-diaphragm scheme; q_0 is a dimensionless parameter determined by the characteristics of the focused radiation; I_0 is the radiation intensity in the focal plane; and L_{eff} is the effective length of the nonlinear medium defined by the relation $L_{\text{eff}} = [1-\exp(-\alpha L)]/\alpha$, L being the length of the medium.

The nonlinear absorption coefficient β calculated from expressions (2) and (3) was 1 cm GW^{-1}. For an intensity of 3 GW cm^{-2}, nonlinear absorption makes a significant contribution to the surplus absorption in the medium. As a result, the thermal effect dominates during the self-action of laser radiation.

Therefore, a thermal lens was formed in our case due to linear and nonlinear absorption. The authors of Ref. [20] also explained the formation of a thermal lens in organic solvents (toluene, ethanol, etc.) by a combined action of linear and nonlinear absorption. We cannot draw any conclusions about mechanisms contributing to the nonlinear absorption because no information is available on the two-photon transition cross sections and the lifetimes of transitions describing the reverse saturation absorption in a solution of As_2S_3 nanoparticles in the five-level model. Further experimental studies are planned to find an answer to this question.

An important factor describing the self-action of laser radiation (self-focusing or self-defocusing) in the field of a thermal lens in solutions is the parameter $M = (1/C\rho) \times (dn/dt)$, which is equal to -1.04×10^{-4} cm^3 cal^{-1} for water. Here, C is the heat capacity of water, ρ is the density of the solvent, n is the refractive index of the colloidal solution, and t is the temperature. The parameter M is vital for determining the variation Δn of the refractive index and characterises the relation between Δn and the energy ΔE absorbed in a unit volume of the medium: $\Delta n = M\Delta E$. A numerical analysis of this relation was performed in Ref. [21] for an aqueous solution of silver nanoparticles in a nanosecond radiation field. The authors of Ref. [21] showed that thermal effects lead to self-defocusing in such aqueous solutions. Thus, in the case considered by us, the induced thermal lens responsible for self-defocusing of nanosecond radiation is the dominating mechanism behind a change in the refractive index.

Because the variations of the output signal in a limiting-diaphragm scheme are caused by variations in the fraction of the radiation passing through an aperture with a transmission coefficient $\sim 3\,\%$, only one-sixth of the focal spot can play a significant role in the process of self-defocusing. Thus, self-defocusing processes start playing a significant role just after 6 ns following the beginning of the pulse propagation through the medium. These estimates of self-defocusing were confirmed in experiments with colloidal metals [4].

Note that the nonlinearities of the structures investigated in this work may be enhanced significantly. In our opinion, this requires a more detailed analysis of the process of clusterisation, i.e., the formation of fractal aggregates whose size can be controlled by introducing substances with stabilising properties. An analysis of clusterisation is also important for controlling the volume concentration of nanoparticles in a solution. This parameter determines the magnitude of the third-order nonlinear susceptibility. While this problem can be treated as solved for colloidal solutions of metals by now, a lot remains to be done for the semiconductor solutions. Note that the increase in nonlinearity with increasing volume fraction of the substance was proved theoretically in Ref. [22] for semiconductor nanoparticles in films. However, this question remains open for solutions.

4. Conclusions

Thus, in the course of investigations of the aqueous colloidal solution of the chalcogenide As_2S_3 prepared by the laser ablation technique, the refractive index ($n_2 = -2.8 \times 10^{-11}$ CGSE units), third-order nonlinear susceptibility ($\chi^{(3)} = -4.7 \times 10^{-12}$ CGSE units) and the nonlinear absorption coefficient ($\beta = 1$ cm GW^{-1}) have been measured. It is shown that the main process responsible for the self-action of laser radiation is the thermal process caused by a combined effect of linear and nonlinear absorption, which leads to self-defocusing of nanosecond radiation in aqueous solutions of As_2S_3.

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