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NONLINEAR OPTICAL PHENOMENA

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Nonlinear absorption of visible light in silicate glasses doped with copper nanoparticles

R.A. Ganeev, A.I. Ryasnyanskii, A.L. Stepanov, T. Usmanov

***Abstract*. The nonlinear absorption of light by silicate glasses doped with copper nanoparticles is studied. Two-photon and saturated absorptions were observed simultaneously and interpreted. The measured two-photon absorption coefficient was 6×10^{-6} cm W^{-1} and the saturation intensity was 4.3×10^{8} W cm^{-2}.**

Keywords: *nonlinear absorption, nanoparticles, two-photon absorption.*

1. Introduction

The nonlinear-optical properties of metal nanoparticles attract great attention because they are promising for applications in optoelectronics [1 – 3]. The study of the optical properties of silver [4, 5], gold [3, 5], cobalt [6], platinum [7], and copper [4, 5, 8 – 12] nanoparticles doped into dielectric matrices are of most interest. Copper nanoparticles exhibit the giant third-order nonlinear susceptibility achieving $10^{-9} - 10^{-7}$ CGSE units [8, 9]. Modern technologies using ion implantation make it possible to fabricate glass matrices doped with nanoparticles at concentrations providing good nonlinear-optical properties of the matrices. Such composition structures with the high Kerr susceptibility in the picosecond range can find applications in ultrafast optical switches and limiters [4].

The *z*-scan method is a convenient tool for studying the nonlinear-optical properties of materials [13]. This method was used to study the dependences of the nonlinear refractive index [11], third-order nonlinear susceptibility and the time response to an external perturbation [10, 12] on the characteristic size of nanoparticles and the conditions of their synthesis [4, 5, 9]. In such composition materials, nonlinear processes can occur, which are caused by absorption saturation manifested in an increase in the transparency of a material irradiated by a high-power laser and by two-photon absorption resulting in a decrease in the material transparency in the field of an intense wave [3, 4]. These processes determine significantly the optical properties of dielectrics containing metal nanoparticles and, hence, are important for practical applications.

In this paper, we present the result of our study of the properties of nonlinear absorption in the visible range (at 532 nm) near the maximum of linear absorption of light caused by the surface plasma resonance in copper nanoparticles [1] embedded into a silicate glass by ion implantation.

2. Experimental

The nonlinear-optical absorption of light by copper nanoparticles was measured using a *z*-scan setup described in detail in Ref. [14]. We used 532-nm, 55-ps, 0.3-mJ second-harmonic pulses from a Nd : YAG laser. To avoid the influence of heating on the experimental results, the pulse repetition rate did not exceed 2 Hz. The laser power density on samples was $5 \times 10^{8} - 3 \times 10^{10}$ W cm^{-2}. Note that at higher densities the optical breakdown occurred.

As a composition material, we used a SiO_2 silicate glass (Heraeus, Germany), which did not exhibit nonlinear-optical properties. A substrate was made in the form of a 2×2-cm plate of thickness 1 mm. Cu^{+} ions in an ion beam were implanted at a pressure of 10^{-5} Torr and at the energy of 50 keV. The implantation dose was 8.0×10^{16} ion cm^{-2} and the current density in the ion beam was 10 μA cm^{-2}. The average size of copper nanoparticles synthesised in the $SiO_2 - Cu$ glass was estimated by the method of X-ray reflectometry in the regime of angular dispersion mode [15]. Composition samples were analysed by small-angle X-ray scattering. The average size of copper nanoparticles measured by this method was 3.5 – 4.5 nm. The penetration depth of copper nanoparticles in glasses did not exceed 60 nm [16]. The transmission spectra of samples were recorded with a Lambda-19 Perkin Elmer spectrophotometer in the region from 300 to 1100 nm. The formation of copper nanoparticles is confirmed by the appearance of the absorption bands in the region between 550 and 600 nm in the transmission spectra of implanted glasses (Fig. 1), which are related to the surface plasma resonance in copper nanoparticles [1].

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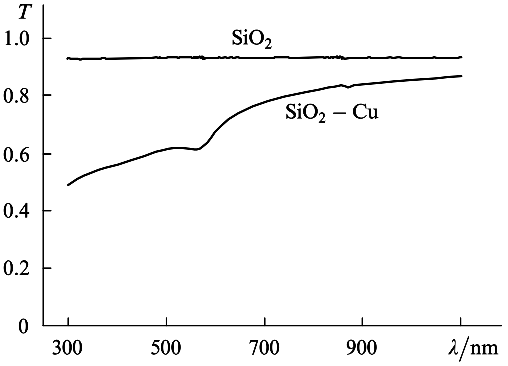

Figure 1. Transmission spectra of the SiO_2 glass before and after implantation of Cu.

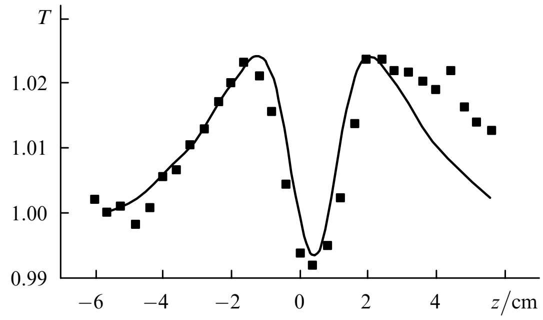

Figure 2. Dependence of the normalised transmission T on the position of the $SiO_2 - Cu$ glass sample in the open-aperture scheme for the laser power density of 5.35×10^9 W cm^{-2} (solid curve is calculations, squares are experimental data).

3. Results and discussion

Figure 2 shows the experimental dependence of the normalised transmission $T(z)$ on the position of a $SiO_2 - Cu$ sample with respect to the focus of a lens in a scheme with an open aperture for the laser power density equal to 5.35×10^9 W cm^{-2}.

The open-aperture scheme allows one to study the imaginary part of the complex nonlinear third-order susceptibility responsible for nonlinear processes related to saturated and two-photon absorption. In particular, when only two-photon absorption is present, the dependence $T(z)$ observed during the moving of a sample along the focal plane of the beam along the z axis behaves as follows. When the sample is located far from the focus, the laser radiation intensity is relatively small, and only linear absorption is observed. In this case, the normalised transmission is close to unity. When the sample approaches the focus, the intensity of focused laser light increases and transmission in the sample decreases, achieving its minimum in the focus. The movement of the sample along the z axis behind the focus leads to a decrease in two-photon absorption and an increase in transmission. As a result, a characteristic dependence $T(z)$ appears in the form of an upset bell located near the lens focus. If saturated absorption appears when the sample approaches the lens focus, transmission in the sample increases, unlike the case of two-photon absorption. The dependence $T(z)$ will again have the form of a bell, however, in a normal position. Therefore, the form of the curve $T(z)$ shows the sign of nonlinear absorption.

By analysing a system of metal nanoparticles by the method of degenerate four-wave frequency mixing, the authors of Refs [17, 18] assumed that, if the laser frequency is close to the frequency of the surface plasma resonance of nanoparticles in the case of one-photon resonance, then the nonlinear absorption is negative. At the same time, we cannot make from the dependence observed in our experiment (Fig. 2) an unambiguous conclusion about the manifestation of only two-photon absorption or saturated absorption. One can see from Fig. 2 that the normalised transmission is close to unity far from the focus, and the function $T(z)$ increases when the sample approaches the focus, indicating to the presence of saturated absorption. However, the value of $T(z)$ drastically decreases when the sample further approaches the focus and the close vicinity of the focus, which demonstrates the influence of two-photon absorption. Therefore, the type of the dependence $T(z)$ shows that nonlinear absorptions of the opposite signs are present simultaneously.

In the general case of the presence of two nonlinear absorptions of opposite signs in a material, the absorption coefficient α can be written in the form [19]

$$\alpha = \alpha_{\rm NA} + \alpha_{\rm TA}, \tag{1}$$

where $\alpha_{\rm SA}$ and $\alpha_{\rm TA}$ are the saturated and two-photon absorption coefficients, respectively, each of the coefficients containing the linear absorption coefficient α_0.

The saturated absorption coefficient can written in the form [20]

$$\alpha(I)_{\rm NA} = \alpha_0 \frac{1}{1 + I/I_{\rm abs}}, \tag{2}$$

where $I_{\rm abs}$ and I are the saturation intensity and the incident radiation intensity, respectively. The absorption coefficient α_0 was obtained by measuring the linear absorption at 532 nm and was ~ 62000 cm^{-1}. In the absence of nanoparticles, the absorption coefficient of the glass was ~ 0.5 cm^{-1}.

The dependence of $\alpha_{\rm TA}$ on I can be written in the form

$$\alpha_{\rm TA}(I) = \alpha_0 + \beta I, \tag{3}$$

where β is the two-photon absorption coefficient.

Therefore, the general expression for the absorption coefficient in the presence of two-photon and saturated absorption takes the form

$$\alpha(I) = \alpha_0 + \alpha_0 \frac{1}{1 + I/I_{\rm abs}} + \beta I. \tag{4}$$

The best fit of the experimental data was obtained for $\beta = 6 \times 10^{-6}$ cm W^{-1} and the saturation intensity $I_{\rm abs} = 4.3 \times 10^8$ W cm^{-2} (solid curve in Fig. 2). Note for comparison that nonlinear absorption in a silicate glass containing copper nanoparticles was observed (the surface plasmon resonance wavelength was 565 nm) in Ref. [8] using 6-ns pulsed dye laser tunable in the range from 570 to 600 nm. The measured coefficient β was varied in the range $(0.1 - 1) \times 10^{-6}$ cm W^{-1}, i.e., it was an order of magnitude lower than that obtained in our paper.

Note that saturated absorption (2) is characterised by the saturation intensity $I_{\rm abs}$. The typical ratio of the laser power density $I = 5.35 \times 10^9$ W cm^{-2} used in our experiments to $I_{\rm abs} = 4.3 \times 10^8$ W cm^{-2} for the glass studied in our paper was 12.5. Because the ratio $I/I_{\rm abs}$ greatly exceeds unity, we see that strong optical saturation is observed. This suggests that glasses doped with metal nanoparticles are promising as elements for mode locking.

Figure 3 shows the dependences $T(z)$ calculated for values of β varied from 2.5×10^{-6} to 8.4×10^{-6} cm W^{-1}, the other parameters, α_0, $I_{\rm abs}$, and I, being fixed. This range of β was chosen to observe the simultaneous influence of nonlinear absorptions of the opposite signs (if $\beta > 8.4 \times 10^{-6}$ cm W^{-1}, then two-photon absorption dominates, whereas saturated absorption dominates when $\beta < 2.5 \times 10^{-6}$ cm W^{-1}). When the two-photon absorption coefficient is small ($\beta = 2.5 \times 10^{-6}$ cm W^{-1}), the nonlinear process is completely determined by saturated absorption, whereas for the values of β in the range $(4-6) \times 10^{-6}$ cm W^{-1}, the superposition of the two nonlinear processes of the opposite signs is observed.

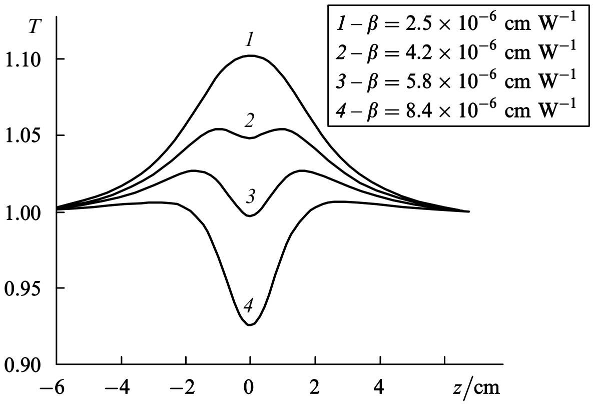

Figure 3. Dependences of the normalised transmission T of the $SiO_2 - Cu$ glass sample on its position z calculated for different values of β.

Consider the possible reasons for nonlinear absorption in a medium containing metal nanoparticles. Laser radiation in the spectral region of the surface plasma resonance of nanoparticles is absorbed directly by the nanoparticles, provided the matrix is transparent in this spectral region. A part of the energy absorbed by noble metal nanoparticles is spent to excite the d electrons to the conduction band, while the remaining part is absorbed in the case of the surface plasmon resonance during interband transitions of conduction electrons. At the same time, conditions appear for the production of hot electrons [21]. It is the contribution of hot electrons to the third-order nonlinear susceptibility of copper nanoparticles that was considered in Ref. [22] as dominating when the laser frequency was close to the surface plasma resonance of copper nanoparticles. It is possible that the properties of two-photon and saturated absorption observed in our paper are also caused by the contribution from hot electrons. However, at present there is no generally accepted point of view in the literature about the role of nonlinear mechanisms in the optical properties of metal nanoparticles.

A simultaneous manifestation of saturated and two-photon absorption was earlier observed in Ref. [23] in organic compounds irradiated by 532-nm, 88-ps second-harmonic pulses from a Nd : YAG laser. The authors of paper [23] interpreted their experimental results with the help of a three-level model and considered the electronic transitions upon absorption from excited levels, i.e., they considered the effect of excited states on nonlinear processes. The authors of Ref. [24] observed a superposition of saturated absorption and inverse saturated absorption in a solution containing gold nanoparticles irradiated by 532-nm, 35-ps laser pulses. Unfortunately, the nonlinear mechanisms of experimental effects observed in Ref. [24] were not identified. The manifestation of only two-photon absorption or saturated absorption was also observed for copper – silver alloy nanoparticles embedded by ion implantation into a silicate glass [25]. The presence of one or another absorption depended on the fraction of each of the metals in the composition of nanoparticles. However, nonlinear absorptions of the opposite signs were not observed simultaneously in this paper. The reasons for the change in the sign of nonlinear absorption were not explained as well.

The dynamics of the contributions of two-photon and saturated absorption depending on the laser radiation intensity in the lens focus is as follows. At low radiation intensities, only two-photon absorption is observed. As the radiation intensity increases, saturated absorption appears, which later dominates. As an example, Fig. 4 shows the dependence $T(z)$ obtained in the open-aperture scheme (for convenience, only a part of a complete symmetric curve obtained upon the z-scan is presented) for the incident radiation intensity equal to 2.5×10^{10} W cm^{-2}, which is five times greater than the radiation intensity used in the previous experiment (Fig. 2). One can see from Fig. 4 that saturated absorption dominates over the entire length of the z axis. Note that similar results can be obtained using the limiting-aperture scheme. For example, for the laser power density equal to 2.5×10^9 W cm^{-2} (i.e., half the value in Fig. 2), two-photon absorption affects the shape of the curve $T(z)$, which is typical of a medium with the negative nonlinear refraction index [13], i.e., with the transmission peak observed before the focus and the hole after the focus (Fig. 5). This result should be expected according to the analysis describing the sequence of manifestations of different absorption processes with increasing radiation intensity. Note that we found earlier the negative value of n_2 in the $SiO_2 - Cu$ glass at a wavelength of 1064 nm [26].

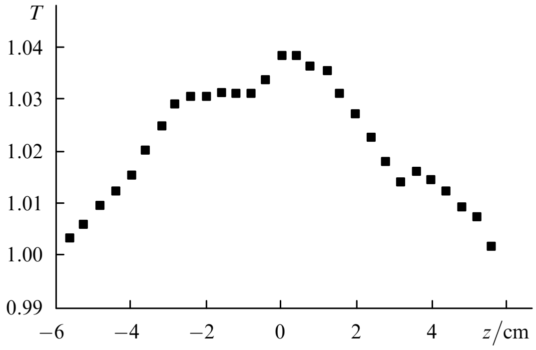

Figure 4. Dependence of the normalised transmission T of the $SiO_2 - Cu$ glass sample on its position z in the open-aperture scheme for the incident laser power density of 2.5×10^{10} W cm^{-2}.

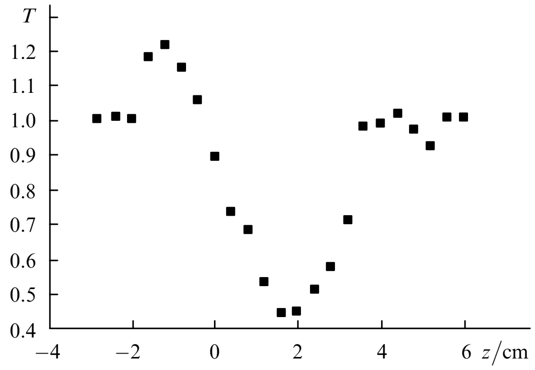

Figure 5. Dependence of the normalised transmission T of the $SiO_2 - Cu$ glass sample on its position z in the limiting-aperture scheme for the incident laser power density of 2.5×10^9 W cm^{-2}.

4. Conclusions

We have simultaneously observed and studied two-photon and saturated absorption in a glass doped with copper nanoparticles irradiated by a laser at 532 nm. As the laser power density increases ($I \geqslant 2.5 \times 10^{10}$ W cm^{-2}), saturated absorption becomes dominant and determines the propagation of radiation in the composite glass. The saturation intensity and two-photon absorption coefficient are estimated in model calculations as 4.3×10^8 W cm^{-2} and 6×10^{-6} W cm^{-1}, respectively.

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References

1. Kreibig U., Vollmer M. *Optical Properties of Metal Clusters* (Berlin: Springer, 1993) p. 533.
2. Ricard D., Roussignol P., Flytzanis C. *Opt. Lett.*, **10**, 511 (1995).
3. Kyoung M., Lee M. *Bull. Korean Chem. Soc.*, **21**, 26 (2000).
4. Uchida K., Kaneko S., Omi S., Hata C., Tanji H., Asahara Y., Ikushima A.J., Tokizaki T., Nakamura A. *J. Opt. Soc. Am. B*, **11**, 1236 (1994).
5. Ila D., Williams E.K., Sarkisov S., Smith C.C., Poker D.B., Hensley D.K. *Nucl. Instr. Met. B*, **141**, 289 (1998).
6. Cattaruza E., Gonella F., Mattei G., Mazzoldi P., Gatteschi D., Sangregorio C., Falconieri M., Salvetti G., Battaglin G. *Appl. Phys. Lett.*, **73**, 1176 (1998).
7. Qu S., Song Y., Liu H., Wang Y., Gao Y., Liu S., Zhang X., Li Y., Zhu D. *Opt. Commun.*, **203**, 283 (2002).
8. Haglund R.F. Jr., Yang L., Magruder T.H. III, Witting J.E., Becker K., Zuhr R.A. *Opt. Lett.*, **18**, 373 (1993).
9. Yang L., Becker K., Smith F.M., Magruder T.H. III, Haglund R.F. Jr., Yang L., Dorsinville R., Alfano R.R., Zuhr R.A. *J. Opt. Soc. Am. B*, **11**, 457 (1994).
10. Tokizaki T., Nakamura A., Kaneko S., Uchida K., Omi S., Tanji H., Asahara Y. *Appl. Phys. Lett.*, **65**, 941 (1994).
11. Battaglin G., Calvelli P., Cattaruza E., Gonella F., Polloni R., Mattei G., Mazzoldi P. *Appl. Phys. Lett.*, **78**, 3953 (2001).
12. Olivares J., Requejo-Isidro J., del Coso R., de Nalda R., Solis J., Afonso C.N., Stepanov A.L., Hole D., Townsend P.D., Naudon A. *J. Appl. Phys.*, **90**, 1064 (2001).
13. Sheik-Bahae M., Said A.A., Wei T., Hagan D.J., Van Stryland E.W. *IEEE J. Quantum Electron.*, **26**, 760 (1990).
14. Ganeev R.A., Ryasnyanskii A.I., Kamalov Sh.R., Kodirov M.K., Usmanov T. *Zh. Tekhn. Fiz.*, **72**, 95 (2002).
15. Nadon A., Thaiaudiere D. *J. Appl. Cryst.*, **30**, 882 (1997).
16. Stepanov A.L., Hole D.E. *Recent Res. Devel. Appl. Phys.*, **5**, 1 (2002).
17. Yu B., Yin G., Zhu C., Gan F. *Opt. Mater.*, **11**, 17 (1998).
18. Hamanaka Y., Hayashi N., Nakamura A., Omi S. *J. Luminescence*, **87**, 859 (2000).
19. Sheik-Bahae M., Hutchings D.C., Hagan D.J., Van Stryland E.W. *IEEE J. Quantum Electron.*, **27**, 1296 (1991).
20. Yang L., Dorsinville R., Wang Q.Z., Ye P.X., Alfano R.R., Zamboni R., Taliani C. *Opt. Lett.*, **17**, 323 (1992).
21. Hache F., Ricard D., Flytzanis C., Kreibig U. *Appl. Phys. A*, **47**, 347 (1988).
22. Eesley G.L. *Phys. Rev. B*, **33**, 2144 (1986).
23. Rangel-Rojo R., Stranges L., Kar A.K., Mendes-Rojas M.A., Watson W.H. *Opt. Commun.*, **203**, 385 (2002).
24. Philip R., Kumar G.R., Sandhyarani N., Pradeep T. *Phys. Rev. B*, **62**, 13160 (2001).
25. Magruder R.H. III, Osborne D.H. Jr., Zuhr R.A. *J. Non.-Cryst. Sol.*, **176**, 299 (1994).
26. Ganeev R.A., Ryasnyanskii A.I., Stepanov A.L., Kodirov M.K., Usmanov T. *Opt. Spektrosk.*, **95**, 832 (2002).