Spectral dependence of nonlinear optical absorption of silica glass with copper nanoparticles

A N Golubev1, S I Nikitin1, M A Smirnov1 and A L Stepanov1,2

1Kazan Federal University, Kremlevskaya 18, Kazan, Russia
2Zavoisky Physical-Technical Inst. of RAS, Sibirsky Trakt 10/7, Kazan, Russia

E-mail: golubevandrei@yandex.ru

Abstract. The nonlinear optical properties of silica glass with copper nanoparticles synthesized by ion implantation were investigated by z-scan method in nanosecond time scale. The reverse saturation absorption (RSA) at the wavelength range of 450-540 nm and saturation absorption (SA) at 550-585 nm were observed. It was supposed that the two-photon electron absorption from bound of d-states determined the RSA effect and the SA is due to saturation of plasmon excitation.

1. Introduction
Looking for new photonic materials and the design of ultrafast optical devices with these materials are determining the progress of modern optoelectronics. Composite materials based on optical transparent dielectrics with metal nanoparticles (MNPs) are prospective for this purpose. Such composites can be used for light signal controlling in dielectric waveguides as ultrafast nonlinear optical switchers, light modulators and optical limiters [1]. Additionally to application aims there are still some fundamental questions in nature of nonlinear optical effects in spite of numerous studies of the composites with MNPs. The development of optimal methods for MNP synthesis to produce composites with controlled optical properties is also the actual technological task.

Two decades ago ion implantation as a method for MNP synthesis in dielectrics was suggested for fabrication of novel nonlinear optical materials. The first paper devoted to investigation of nonlinear optical properties of dielectric materials with ion-synthesized MNPs was published in 1991 [2]. In this work the Au nanoparticles in SiO2 glass were studied. At 532 nm wavelength, which is near of plasmon absorption maximum of Au nanoparticles (λmax=525 nm), the giant value of \(\chi^3\) ~ 10⁻⁷ esu was observed. The same order of the real part of \(\chi^3\) in soda-lime silicate glass with implanted Cu nanoparticles - \(Re(\chi^3)=1.3·10^{-7}\) esu was detected at 532 nm [3]. These values measured with nanosecond laser pulses are five orders higher than one for the standard nonlinear material CS2 with \(Re(\chi^3)\sim 10^{-12}\) esu. Researches of nonlinear optical properties of materials with MNPs were continued on Cu:SiO2, Ag:SiO2 and Au:SiO2 for different spectral areas in picosecond time scale [4-8].

In general the nonlinear optical properties of dielectrics with MNPs dependent on many parameters: nanoparticles size, size distribution and shape, concentration, dielectric environment etc. For different synthesis conditions of MNPs composites based on same SiO2 matrix can demonstrate none equivalent nonlinear optical properties. For example, in the work [9] it was shown that in SiO2 glass containing Cu nanoparticles fabricated by ion-exchange process after thermal annealing at 500-650°C reveals different kind of nonlinear absorptions (nonlinear absorption was measured with z-scan technique for the laser pulse duration of 7 ns at 532 nm). Thermal annealing at 500°C initiates the SA
of the composite whereas after treatment at 600 and 650 °C the RSA was detected. The SA in the sample was changed to RSA at higher laser intensities also. Such changes of nonlinear absorption were also observed for SiO₂ with implanted Cu nanoparticles for picosecond laser pulses (55 ps) at the same wavelength [8]. Thus, nonlinear optical properties of dielectrics with MNPs are determined not only by chemical compositions but also by a selected synthesis method and by an arrangement of nanoparticle structure in the samples. This happened because technological processes of MNP synthesis are not still known well.

The aim of present article is to study of nonlinear absorption of composite such as SiO₂ glass with ion-implanted Cu nanoparticles in wide spectral area around plasmon resonance absorption in nanosecond pulse laser regime.

2. Experimental method

Composite material on basis of silica glass with copper nanoparticles was synthesized by ion implantation using Wikham accelerator (Sussex University, UK). Implantation was performed by one-charged Cu+ ions with energy of 160 keV, dose of 8·10¹⁶ ion/cm² and current density of 10 µA/cm². Thickness of layer with MNPs was about 100 nm and average particle size was ~ 5 nm [10].

Transmission spectra of Cu:SiO₂ sample and virgin glass (figure 1) were measured using dual-beam spectrophotometer SPECORD M40 in 200-900 nm wavelengths range. Registered absorption band at 560 nm of the implanted glass (figure 1) corresponds to surface plasmon resonance in copper nanoparticles [11].

![Figure 1. Transmission spectrum of silica glass (a) and silica glass with copper nanoparticles (b).](image)

For measurement of nonlinear optical absorption the z-scan method was applied [12]. The z-scan setup is presented in figure 2. In experiments Solar LS LX325 Ti:Sapphire and dye lasers were used. These lasers were pumped with second harmonic of Nd:YAG Solar LS LQ829 laser and second or third harmonics of Nd:YAG Solar LS LQ129, respectively. After some modifications of the lasers the laser beams have the almost Gaussian profile. Laser pulse widths on half-height were measured using the high-speed photodetector and they were equals to 3-6 ns for dye laser, 12 ns for Nd:YAG and 10-30 ns for Ti:Sapphire laser.

Laser beam was focused by lens with a focal length of 18 cm. Spots radii in beam waist were 10-15 µm. Sample was mounted on motorized translation stage. Signals from photodiodes were digitized using 14-bit ADC. Value of normalized transmission T(z) was defined as ratio of the amplitude of the signals from photodiode 2 to photodiode 1 and was averaged by 300-500 pulses at the each sample
position z. Obtained dependences of $T(z)$ are plotted as functions of sample position z respect to the focus of lens. For elimination thermal effects pulse repetition rate was not exceed 10 Hz.

![Figure 2. Experimental z-scan setup.](image)

3. Results and discussion
The study of the nonlinear optical properties of the silica glass with copper nanoparticles was done in the broad spectral range from 450 to 585 nm. In dependence on a laser wavelength the Cu:SiO$_2$ sample demonstrates the RSA or the SA. In figure 3 results of the $T(z)$ measurements of the sample for two wavelengths – 510 and 560 nm are presented. At these wavelengths the values of the nonlinear RSA (figure 3a) and SA (figure 3b) are maximal. It is important to point out, that the shape of $T(z)$ like presented on figure 3a can be caused by optical damage of the sample, which appears as a result of the overheating with following destruction of MNPs under laser irradiation. In this case a decreasing $T(z)$ near the lens focus will be induced by increasing of scattered laser emission on the optically destructed region. When the laser beam diameter becomes comparable with this destructed region contribution to $T(z)$ is most significant. However, it was measured that laser damage threshold of nanoparticles in the our setup was around 4 $\mu$J. Therefore all measurements were done at smaller laser energy.

![Figure 3. The measured normalized transmission - open circle of Cu:SiO$_2$ as function of sample position at z for different wavelengths $\lambda_s$: a. - reverse saturable absorption at 510 nm and b. - saturable absorption at 560 nm. Fitting was done using equation (5) – solid line.](image)
Absorption coefficient in the case of only the RSA is written by
\[ \alpha_{RSA}(I) = \alpha_i + \beta I. \]  
(1)
The SA can be presented as
\[ \alpha_{SA}(I) = \frac{\alpha_2}{1 + I/I_s}, \]  
(2)
where \( \alpha_i \) – the linear absorption coefficients, \( I \) – the laser intensity, \( I_s \) – the saturation intensity and the nonlinear absorption coefficient \( \beta_i > 0 \). In an approximation of the small nonlinearity \( (I \ll I_s) \), which was realized in present experiments, the coefficient of the SA (2) will be
\[ \alpha_{SA}(I) = \alpha_2 - \alpha_2 I/I_s = \alpha_2 + \beta_2 I, \]  
where \( \beta_2 = -\alpha_2/I_s < 0 \).  
(3)
Thus in the case of small nonlinearity the expressions of nonlinear absorption coefficients for RSA and SA are similar but they differ with sign of the \( \beta_i \).

Taking into account equations (1) and (3), in the general case the \( T(z) \) in z-scan method can be obtained by solving equation [12]:
\[ \frac{dI}{dz} = -(\alpha + \beta I)I, \]  
(4)
where \( z' \) - propagation depth in the sample, \( \alpha \) and \( \beta \) – are linear and nonlinear absorption coefficients taking into account the all possible transitions, respectively. For Gaussian beam the dependence \( T(z) \) is given by expression:
\[ T(z) = 1 - \frac{I_0 L_{eff} \beta}{1 + z^2/z_0^2}, \]  
(5)
where \( I_0' \) - maximum intensity of the laser beam on its axis in the waist, \( L_{eff} \) – effective thickness of layer with MNPs, \( L_{eff} = (1-e^{-aL})/\alpha \) \( (L \approx 100 \text{ nm for the present sample}) \); \( z_0 \) – diffraction length. Also in such approximation it is possible to write:
\[ I_0 L_{eff} = \frac{(1-e^{-aL})E}{\alpha \pi^{1/2} 2^{1/2} \omega_0^2 \tau}, \]  
(6)
where \( E \) – laser pulse energy, \( \tau \) – laser pulse duration, \( \omega_0 \) – size of the laser beam waist.

It was mentioned above that for the Cu:SiO\textsubscript{2} sample the SA and the RSA were observed at different wavelengths at same laser energy. It means that the absorption coefficient consists of the two parts corresponding to the SA and the RSA and the contributions from these parts depend on wavelength. Using linear coefficient \( \alpha \) obtained from transmission measurements (figure 1) the nonlinear part of the absorption coefficient (\( \beta \)) was estimated by fitting with the expression (5). Collected data for different wavelength are presented in figure 5.

As seen from figure 4 the kind of the nonlinear absorption in Cu:SiO\textsubscript{2} sample depends on wavelength: the RSA prevails in spectral range of 450-540 nm, inverse situation was observed at 550 – 585 nm where the main contribution is from the SA. The SA dominates for spectral area where the linear absorption is determined mainly by the surface plasmon resonance in copper nanoparticles (figure 4). The RSA was observed when the linear absorption is described by electron excitations from the \( d \)-zone of copper particles.
In literature the several mechanisms of the optical nonlinearity of the MNPs were assumed [13, 14], which are determined due to intraband, interband electron transition or free carrier absorption. Obtained in present experiment results evidence that different kind absorptions are responsible for the nonlinear effects of Cu:SiO$_2$ sample. The spectral dependence of nonlinear coefficient $\beta$ allows to suppose that the mechanism responsible for the RAS at 450-480 nm wavelengths is the two-photon absorption which is determined by electron transitions from the bound $d$-states to conduction band of copper nanoparticles. On the other hand, the SA effect is based on saturation of the plasmon excitation in MNPs. For deeper understanding of the proposed mechanisms the time-resolved measurements of the nonlinear absorption are planning to be done.

4. Conclusion
In nanosecond time scale of laser irradiation in a spectral area near surface plasmon resonance absorption band of copper nanoparticles in silica glass the RSA in range of 450-540 nm and the SA in range of 550-585 nm were observed for the first time. It was supposed that the RSA is determined by two-photon absorption due to electron transitions from bound of $d$-states to conduction band of copper nanoparticles and the SA effect is due to saturation of plasmon excitation.

Acknowledgments
This work was supported in part by the Ministry of Education and Science of the Russian Federation (No. 02.740.11.0797) and the Russian Foundation for Basic Research (No. 11-02-90420-Ukr).

5. References
[1] Haglund Jr 1974 Quantum-dot composites for nonlinear optical applications Optics of small particles, interfaces and surfaces ed. R Hummel and P Wissmann (London: CRC Press) chapter 2 pp 192-224
[2] Fukumi K, Chayahara A and Kadono K 1991 Japan. J. Appl. Phys. 30 L742-L744
[3] Tsuji H, Kido S, Gotoh Y and Ishikawa J 2000 Rev. Sci. Instr. 2000 71 804-806
[4] Haglund Jr, Magruder R, Morgan S, Henderson D, Weller R, Yang L and Zuur R 1992 Nucl. Instr. Meth. Phys. Res. 65 405-411
[5] Haglund Jr, Yang L, Magruder H, Wittig J, Becker K, and Zuur R 1993 Opt. Lett. 18 373-375
[6] Magruder R, Yang Li, Haglund Jr, White C, Yang L, Dorsinville R and Alfano R 1993 Appl. Phys. Lett. 62 1730-1733
[7] Ganeev R, Ryasnyansky A, Stepanov A and Usmanov T 2004 Phys. Stat. Sol. B. 241 935-944
[8] Ganeev R, Ryasnyansky A, Stepanov A and Usmanov T 2004 Phys. Stat. Sol. B. 241 R1-R4-944
[9] Karthikeyan B, Anija M, Sandeep S, Nadeer M and Philip R 2008 Opt. Comm. 281 2933-37
[10] Stepanov A, Valeev V, Nuzhdin V and Faizrakhmanov I 2009 Phys. Solid. State 2009 51 1912-18
[11] Kreibig U and Volmer M 1995 Optical properties of metal clusters (Berlin: Springer)
[12] Sheik-Bahae M, Said A, Wei T, Hagan D and Stryland E 1990 IEEE J. Quant. El. 26 760-769
[13] Hache F, Ricard D and Girard C 1988 Phys. Rev. B 38 7990–96
[14] Hache F, Ricard D, Flytzanis C and Kreibig U 1988 Appl. Phys. A 47 347–357