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OPTICAL PROPERTIES

Nonlinear Optical Properties of Gold Nanoparticles Dispersed in Different Optically Transparent Matrices

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Abstract—The nonlinear optical properties of gold nanoparticles dispersed in optically transparent matrices Al_2O_3, ZnO, and SiO_2 are investigated using the classical and off-axis techniques of the *Z*-scan method at a wavelength of 532 nm (radiation from a nanosecond Nd : YAG laser). The experimental data on the nonlinear refraction in composite materials are obtained. The nonlinear refractive indices and the light absorption coefficients are determined, and the real and imaginary parts of the third-order nonlinear susceptibility for the structures under investigation are calculated. It is demonstrated that, for the composite materials under consideration, the nonlinear properties of the medium under the chosen conditions of laser irradiation are predominantly determined by the Kerr effect and the contribution of this effect exceeds the contribution of the thermal lens.

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1. INTRODUCTION

Composite materials based on metal nanoparticles are of special interest for laser physics and optoelectronics owing to the ultrafast nonlinear optical response [1, 2] and the manifestation of the giant electronic Kerr effect [3–6]. A rather large number of works have been devoted to the investigation of the nonlinear optical properties of media containing gold nanoparticles. The dependences of the nonlinear optical properties of composite materials with metal nanoparticles have been studied as a function of their size and shape, specific features of the preparation of nanoparticles (ion implantation, magnetron sputtering, chemical methods of synthesis, etc.), and the laser radiation parameters (pulse duration, pulse rate, radiation wavelength). Special attention has been focused on the estimation of the degree of the influence of the dielectric and semiconductor matrices surrounding nanoparticles on the nonlinear optical properties of materials. Materials of various types (such as aqueous solutions [7–10]; amorphous substrates (silicate glasses) [3–5]; crystals $BaTiO_3$ [11], Al_2O_3 [12, 13], $LiNbO_3$ [14], TiO_2 [15], and others) have been used as matrices. The purpose of this work was to investigate the nonlinear optical properties of gold nanoparticles in the Al_2O_3, ZnO, and SiO_2 matrices.

For composite materials, the magnitude and the sign of the nonlinear refractive index γ are the most important characteristics associated with their practical application. The nonlinear refractive index can be positive in the case of self-focusing of laser radiation or negative in the case of self-defocusing. It is also evident that the characteristic values of the nonlinear refractive index γ depend not only on the individual properties of composite materials but also on the parameters of the laser radiation used.

There are different methods for investigating and determining the nonlinear optical characteristics of composite materials, including the phase conjugation; the degenerate four-wave mixing, which makes it possible to determine the magnitude of the third-order nonlinear susceptibility $|\chi^{(3)}|$ [16]; the nonlinear interferometry [17]; and the *Z*-scan method [18]. The last method enables one to determine the sign and the magnitude of the nonlinear refractive index irrespective of the degree of nonlinear absorption of light by the material [18]. Previously, Liao et al. [15] used the degenerate four-wave mixing technique in order to determine the magnitude of the third-order nonlinear susceptibility $|\chi^{(3)}|$ in the Al_2O_3 matrix with gold nanoparticles at wavelengths in the range of the surface plasmon resonance absorption of metal particles. In our work, the magnitudes and signs of the imaginary and real parts of the third-order nonlinear susceptibility $\chi^{(3)}$ of gold nanoparticles in different matrices, such as Al_2O_3, ZnO, and SiO_2, were determined using the *Z*-scan technique.

Table 1. Structural and optical characteristics of materials with gold nanoparticles

Matrix	Nanoparticle concentration, %	Thickness of the film with nanoparticles, nm	Average nanoparticle size, nm
Al_2O_3	8	117	3.1
SiO_2	8	141	2.6
ZnO	8.68	930	

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

Composite materials with gold nanoparticles were prepared by magnetron sputtering. The synthesis of nanoparticles in the used matrices is described in detail in [19] (Al_2O_3:Au), [20] (ZnO:Au), and [6] (SiO_2:Au). The structural characteristics of the sample under investigation according to the data of transmission electron microscopy are listed in Table 1. The analysis of the optical absorption spectra of the composite materials revealed the selective bands of the surface plasmon resonance of gold nanoparticles with maxima at λ = 525 nm for Al_2O_3, λ = 540 nm for ZnO, and λ = 500 nm for SiO_2.

The nonlinear optical characteristics of the composite materials were measured using radiation of an Nd^{3+}:YAG Q-switched laser (pulse duration, 7 ns; radiation wavelength, 532 nm; pulse rate, 10 Hz). The use of the classical and off-axis techniques of the *Z*-scan method for investigation of the nonlinear refraction and nonlinear absorption is thoroughly described in [21, 22]. A fast photodiode with a time response of 500 ps was used in the off-axis technique. The laser radiation intensities corresponded to the range 5×10^6–3×10^7 W/cm^2 and were lower than the optical breakdown threshold of the samples. Despite a rather strong optical absorption in the composite materials at a wavelength of 532 nm, no irreversible structural transformations upon laser irradiation (the possibility of appearing these changes was noted in [23, 24]) were observed in our study.

3. RESULTS AND DISCUSSION

The classical *Z*-scan technique with a limiting aperture [18] permits one to determine the sign and the magnitude of the nonlinear refractive index of the materials under investigation. The results of the experimental measurements of the normalized transmittance (i.e., the ratio of the radiation energy transmitted through the sample to the energy of incident radiation) of the samples are presented in Fig. 1. The order of the appearance of the minimum and the maximum of the normalized transmittance upon displacement of the samples along the *Z* scale through the focal point allows us to make the inference [18] that the nonlinear refractive index γ is positive and, correspondingly, the self-focusing of laser radiation is observed in the samples Al_2O_3:Au (Fig. 1, curve *a*) and SiO_2:Au (Fig. 1, curve *b*). However, the sample ZnO:Au (Fig. 1, curve *c*) has a negative nonlinear refractive index γ and, hence, is characterized by the self-defocusing effect. By using the *Z*-scan theory described in [18], we simulated the behavior of the normalized transmittance (Fig. 1, solid lines). According to the best agreement between the calculated curves and the experimental data, the values of the quantities γ and $\mathrm{Re}\chi^{(3)}$ [18] were determined for each composite material under consideration (Table 2). The observed differences between the optical nonlinearities of the composite materials can be explained by different positions of

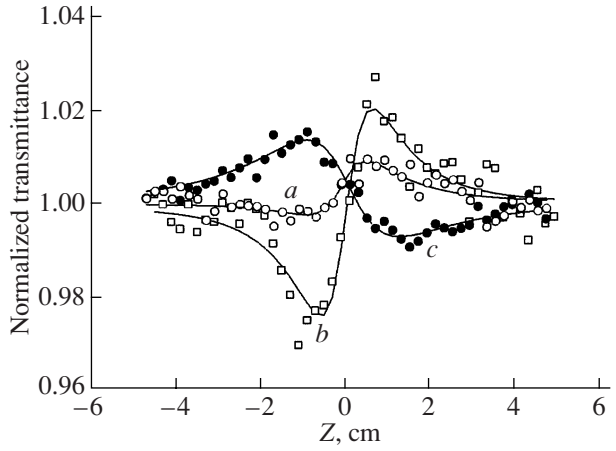

Fig. 1. Dependences of the normalized transmittance for the (*a*) Al_2O_3:Au, (*b*) SiO_2:Au, and (*c*) ZnO:Au samples in the scheme with a limiting aperture. Solid lines represent the theoretical dependences calculated in terms of the *Z*-scan theory described in [18]. I_0 = (*a*) 5.7, (*b*) 28.0, and (*c*) 8.0 MW cm^{-2}.

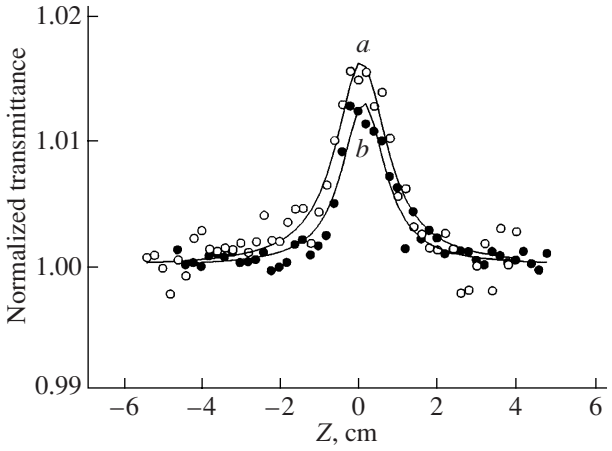

Fig. 2. Dependences of the normalized transmittance for the (*a*) Al_2O_3:Au and (*b*) SiO_2:Au samples in the scheme with an open aperture. Solid lines represent the theoretical dependences calculated in terms of the *Z*-scan theory described in [25]. I_0 = (*a*) 5.7 and (*b*) 28.0 MW cm^{-2}.

Table 2. Nonlinear optical characteristics of materials with gold nanoparticles

Matrix	γ, 10^{-9} cm^2 W^{-1}	$\mathrm{Re}\chi^{(3)}$, 10^{-7} esu	β, 10^{-3} cm W^{-1}	$\mathrm{Im}\chi^{(3)}$, 10^{-7} esu	$\lvert\chi^{(3)}\rvert$, 10^{-7} esu	$\lvert\chi_m^{(3)}\rvert$, 10^{-8} esu
Al_2O_3	7.62	5.03	–1.31	–5.33	7.33	6.25
SiO_2	2.97	1.38	–0.12	–0.067	1.38	2.7
ZnO	–1.31	–1.47			1.47	2.46

the maxima associated with the surface plasmon resonance of gold nanoparticles in the matrices under consideration with respect to the laser radiation wavelength.

The classical *Z*-scan technique without limiting aperture provides a means for investigating the nonlinear absorption in composite materials irrespective of the manifestation of the nonlinear refraction [18]. The experimental dependences of the normalized transmittance for the Al_2O_3:Au and SiO_2:Au samples are plotted in Fig. 2. The solid lines represent the theoretical curves obtained using the theory described in [25]. The shape of the normalized transmittance curves indicates that the nonlinear absorption coefficient β for these materials is negative [25], which is characteristic of the saturated absorption. No nonlinear absorption was revealed for the ZnO:Au sample. With the use of the theory described in [25], we calculated the values of the nonlinear absorption coefficient β and the imaginary part $\mathrm{Im}\chi^{(3)}$ (Table 2). When analyzing the nonlinear optical properties of composite materials, it is necessary to take into account the optical nonlinearities of the matrix containing nanoparticles. As regards the Al_2O_3, ZnO, and SiO_2 matrices without metal nanoparticles, no nonlinear refraction and nonlinear absorption were observed for the laser radiation parameters used in our work. According to the data available in the literature, the nonlinear refractive index γ at a wavelength of 532 nm is equal to 3.3×10^{-16} cm^2 W^{-1} for Al_2O_3 [26], -9×10^{-15} cm^2 W^{-1} for ZnO [27], and 2.24×10^{-16} cm^2 W^{-1} for SiO_2 [28]. It can be seen that these values are considerably smaller than the nonlinear refractive indices γ for the composite materials with metal nanoparticles.

When estimating the optical nonlinearities for layers with metal nanoparticles and matrices onto which these layers are deposited, the effective thicknesses of the components should be taken into account. The contribution of a particular material is determined by the quantity characterizing the phase shift in the pulse at the focus due to the nonlinear refraction ($\Delta\Phi_0 = k\gamma I_0 L_{\mathrm{eff}}$, where k is the wave vector and L_{eff} is the effective thickness of the sample) [18]. In turn, the parameter $\Delta\Phi_0$ determines the amplitude of the dependence of the normalized transmittance (Fig. 2). For example, at the same wavelength and the same radiation intensity, the film (containing nanoparticles) with the thickness $L_{\mathrm{eff}} = 100$ nm and the nonlinear refractive index $\gamma = 1 \times 10^{-10}$ cm^2 W^{-1} is responsible for the phase shift in the pulse and, correspondingly, the amplitude of the normalized transmittance (Fig. 2) identical to those produced by the matrix with the thickness $L_{\mathrm{eff}} = 10$ cm and the nonlinear refractive index $\gamma = 1 \times 10^{-16}$ cm^2 W^{-1}. In our case, the samples represented the matrices with thicknesses of 1.0 mm for ZnO, 2.0 mm for SiO_2, and 2.5 mm for Al_2O_3 and the thicknesses of the films deposited onto these matrices varied from 100 to 1000 nm. The calculated estimates show that the values of the parameter $\Delta\Phi_0$ for the layers with nanoparticles exceed those for the matrices by more than two orders of magnitude.

Therefore, we can make the inference that the contribution of the metal nanoparticles to the total optical nonlinearity of the composite materials is dominant. The magnitudes of the third-order nonlinear susceptibility $|\chi^{(3)}|$ (Table 2) were calculated from the values of $\mathrm{Im}\chi^{(3)}$ and $\mathrm{Re}\chi^{(3)}$.

Now, we consider the specific features of the nonlinear refraction in the materials with metal nanoparticles under investigation. It should be noted that the contribution to the nonlinear refractive index of composite materials can be made by the thermal effect due to the energy transfer from nanoparticles heated by laser radiation to the surrounding transparent matrix, which results in a change in the density of the matrix [29]. The characteristic time t it takes for this process to manifest itself is determined by the ratio between the laser beam radius w_0 at the lens focus in the *Z*-scan setup and the sound velocity v in the matrix containing nanoparticles. Taking into account the experimental conditions ($w_0 = 35$ μm for Al_2O_3:Au and SiO_2:Au and $w_0 = 45$ μm for ZnO:Au) and the sound velocities v in the matrices under investigation ($v = 6700$ m s^{-1} for Al_2O_3, 6590 m s^{-1} for ZnO [31], and 5939 m s^{-1} for SiO_2 [32]), the aforementioned characteristic times were determined to be 5.2, 5.8, and 5.9 ns, respectively.[1] These durations t of the processes appear to be rather close to the pulse duration ($\tau = 7$ ns) of the laser used in our experiments. This circumstance suggests that the thermal effect should be taken into account in consideration of the nature of the nonlinear refraction in the composite materials under investigation. Moreover, it should be

[1] The value of the longitudinal sound velocity in amorphous Al_2O_3 synthesized by rf sputtering was measured by B. Perrin and coworkers [30].

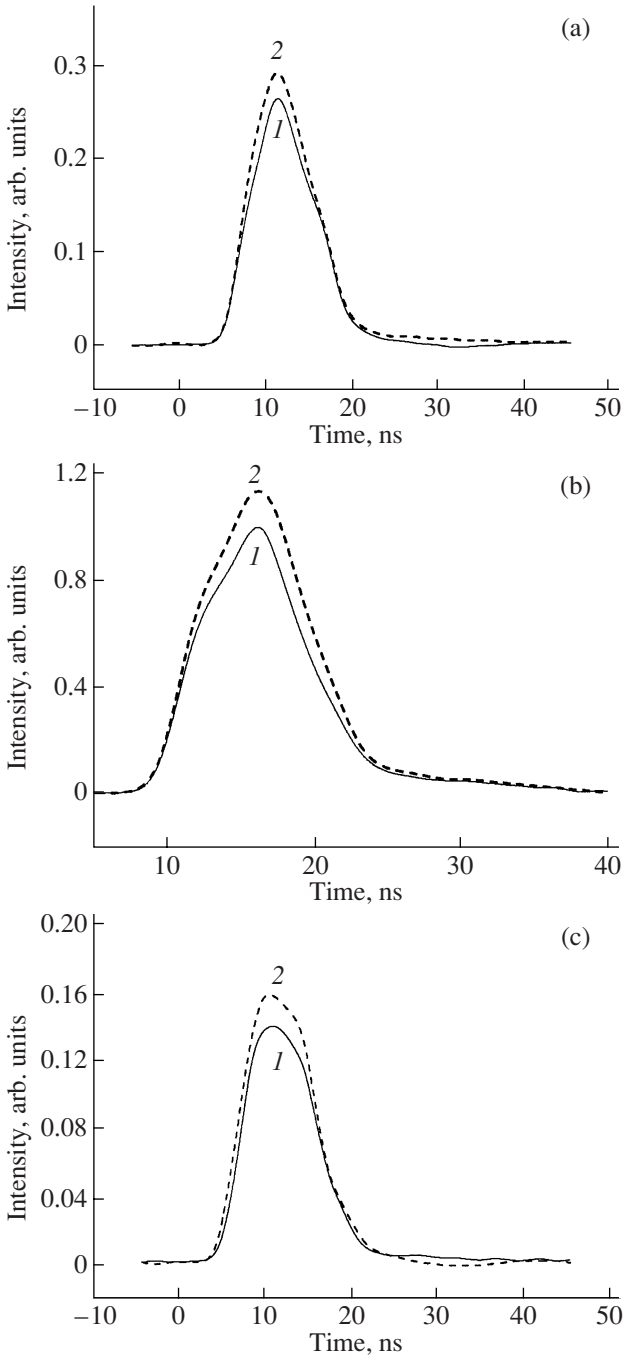

Fig. 3. Temporal profiles of (*1*) the incident laser pulses and (*2*) the pulses transmitted through the samples in measurements with an aperture displaced from the optical axis for the (a) Al_2O_3:Au, (b) SiO_2:Au, and (c) ZnO:Au composite materials.

noted that there can arise a cumulative thermal effect with the use of laser pulses at high rates (several kilohertz or megahertz [33]). However, the use of the low pulse rate (10 Hz) in our work permits us to eliminate the cumulative thermal effect from consideration.

Additional information on the nonlinear refraction in the materials with nanoparticles was obtained using the off-axis *Z*-scan technique. This experimental technique differs from the classical technique of the *Z*-scan method with the limiting aperture in that the position of the aperture was displaced perpendicular to the optical axis of the setup (by 5 mm in our work). The given technique allows us to estimate the time and spatial resolutions of the normalized transmittance measured at different aperture positions (in the optical axis and upon displacement) [29]. In this case, the sample is placed in the range with a minimum transmittance on the *Z* scale and the temporal profiles of the incident pulse and the pulse transmitted through the sample are measured in the experiment. Previously, Mehendale et al. [29] performed the corresponding experiment with colloidal gold and revealed that the shape and the amplitude of the pulse after transmission through the sample are changed as compared to those measured in the absence of the sample. Figure 3 shows the oscillograms of the incident pulse (curve *1*) and the pulse transmitted through the sample (curve *2*), which were measured for the aperture displaced with respect to the optical axis for samples located in the range $Z = +0.5$ cm for the Al_2O_3:Au sample (Fig. 1, curve *a*), $Z = +0.7$ cm for the SiO_2:Au sample (Fig. 1, curve *b*), and $Z = -0.9$ cm for the ZnO:Au sample (Fig. 1, curve *c*). It can be seen from these oscillograms that the incident pulses and the pulses transmitted through the samples under investigation differ in the amplitude; however, no time shift between the pulses is observed. This circumstance enables us to made the inference that the thermal effect is insignificant and that the effect of the electronic nonlinearities is dominant.

Let $\chi_m^{(3)}$ be the third-order nonlinear susceptibility of gold nanoparticles. Then, the nonlinear susceptibility of the composite material can be written in the following form [16]:

$$\chi^{(3)} = p|f^2|f^2\chi_m^{(3)}, \quad (1)$$

where p is the volume fraction of metal nanoparticles in the composite material (the filling factor), from which the nanoparticles consist, and f is the local-field factor defined by the relationship

$$f = \frac{3\varepsilon_d}{\varepsilon_m + 2\varepsilon_d}. \quad (2)$$

Here, ε_d and ε_m are the permittivities of the matrix and the metal, respectively. Relationship (2) can be used to describe the properties of composite materials with a low content of metal nanoparticles [34]. Earlier, it was demonstrated that, as the volume fraction p in the composite material increases, the local-field factor f differs from the value determined using relationship (2). However, this difference is insignificant for SiO_2:Au at $p =$

8% [34], as well as for the samples Al_2O_3:Au, SiO_2:Au (Table 1, $p = 8\%$), and ZnO:Au (Table 1, $p = 8.68\%$) under consideration. By using expressions (1) and (2), it is possible to calculate the magnitude of the third-order nonlinear susceptibility $|\chi^{(3)}|$ for the composite materials at a wavelength of 532 nm (Table 2). It should be noted that the calculated values of the quantity $\chi_m^{(3)}$ are in good agreement with the data obtained on the third-order nonlinear susceptibility $\chi_m^{(3)}$ by other authors (5×10^{-8} esu [16], $2–4 \times 10^{-8}$ esu for H_2O:Au [35]).

4. CONCLUSIONS

Thus, the nonlinear optical characteristics of different materials (Al_2O_3, SiO_2, ZnO) containing gold nanoparticles were investigated by the *Z*-scan method. The real and imaginary parts of the third-order nonlinear susceptibility were measured at a wavelength of 532 nm. The inference was made that the differences between the optical nonlinearities of different composite materials are most likely associated with the position of the surface plasmon resonance of gold particles in the matrices used. The use of the off axis *Z*-scan technique allowed us to draw the conclusion that the contribution of the electronic optical nonlinearities is dominant and the thermal effects are almost absent.

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