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The theory of heterogeneous dielectric nanostructures with non-typical low-threshold nonlinearity



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ABSTRACT

The recently discovered, ultralow-threshold, nonlinear refraction of low-intensity laser radiation in dielectric nanostructures has an atypical dependence on radiation intensity in the pulsed and continuous modes. In this study, we present a theoretical explanation. The theory suggests that the nonlinearity is photoinduced in nature, rather than thermal, and depends directly on the nanoparticle electronic structure and the relationship between permittivities of the dielectric matrix and the nanoparticles.

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1. Introduction

Over the last 20 years, significant scientific attention has been paid to nanostructures and nanocomposites based on nanoparticles of semiconductor materials ($1 \text{ eV} < E_{\text{gap}} < 3 \text{ eV}$). This response occurs in the visible and infrared region of the electromagnetic spectrum and reaches a maximum then decreases to zero with increasing intensity [1–5]. The dielectric nanostructures show other unexpected nonlinear optical properties. The non-linear interaction of the high-intensity radiation of different frequencies results in the generation of harmonics in conventional dielectric media. In the case of the propagation of the low-intensity radiation of different frequencies in the dielectric nanostructures, the nonlinear interaction is manifested in the dependence of the light beam intensity on the intensity of another collinearly propagating light beam [6]. The two-frequency interaction observed in the nanostructures does not prevent the generation of harmonics, but this process requires radiation intensities four orders of magnitude higher.

The study of nonlinear optical properties of dielectric nanostructures containing nanoscale objects of different chemical natures, shapes and sizes has shown that the existence of a low-threshold optical response is due to a number of conditions. The

first is the presence of defect levels in the band gap of nanoparticles' charge carriers, which is manifested in the form of absorption bands in the nanoparticles' transmission spectrum [1,2,7–9]. Second, the radiation forming the nonlinear response of the nanostructure must have a frequency lying within the absorption band [1,2]. Third, the size and shape of the nanoparticles have to lead to the formation of a wide range of exciton states due to the quantum size effect [10–14]. Fourth, the matrix permittivity must be less than that of the nanoparticle material because the chemical nature of the matrix material significantly affects the formation of long-lived exciton states [2,7,15]. Fifth, the value of the electric dipole moments induced by electron phototransition should be substantially larger than the dipole moments in the bulk material, which allows for observation of the optical nonlinearity of nanostructures with a low concentration of nanoparticles under low-intensity optical fields.

The theoretical description of the observed effects [16–18] is based on the fact that the occurrence of non-typical optical nonlinearity requires the existence of defect levels and a broad band of exciton states in the energy band gap of charge carriers. The radiation causes electron transition from the defect to the exciton levels, thereby creating the photo-induced population difference. This process is accompanied by the appearance of the nanoparticle electric dipole moment, whose module depends nonlinearly on the intensity and the light wavelength. The theory conclusions and theoretical modelling of the transmission spectrum and the behaviour of the nonlinear refractive index are similar to the experimental results [2]. It follows from the theory that the nature of the nonlinearity is determined not only by the behaviour of the

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photo-induced dipole moment module in an external field but also by the nanoparticle's orientation along the vector E . However, this orientation has a minor contribution to the nonlinearity, so the observed nonlinear optical response can occur in the case of unpolarized light and solid nanostructures, which is in agreement with the experiment. This chapter is an original quantitative study of the nonlinear refraction and absorption of continuous low-intensity laser radiation in different heterogeneous dielectric nanostructures and compares these data with theoretical results. In addition, the theory of nonlinear light transmission by dielectric nanostructures is discussed.

2. Preface

The theoretical description of the physical and optical properties of heterogeneous nanocomposites containing nanoparticles is a complex problem. It seems impossible to calculate correctly the physical characteristics of an individual nanoparticle as a system consisting of a great number of particles obeying the quantum mechanics laws. Attempts to apply the methods of solid state physics to describe the nanoparticles' properties run into problems because it is not possible to disregard the effects caused by surface defects, as well as crystal lattice defects. The optical properties of a quantum mechanical system are associated with the features of the energy spectrum of the charge carriers (electrons and holes).

The optical and electric properties of nanoparticles have significant differences compared to bulk samples due to the features of the energy spectra. These differences are caused by three effects. First, the band gaps of nanoparticle charge carriers contain the allowed energies zone, and the energy structure is defined by the high density of the surface structural defects and the irregular shape of the nanoparticles. Second, the excitons and discrete energy spectra are formed below and into the conduction band due to the small nanoparticle size and size-quantization effect, respectively. In turn, the size quantization effect is caused by spatial confinement of the charge carriers' wave functions. Third, the electric dipole moments of the electronic transitions in such quasi-zero dimensional systems can be larger than that of the bulk sample. The formation of the above states is of threshold character, and the threshold depends on the nanoparticle dimensions. Specifically, for a spherical nanoparticle (with permittivity ε_2) dispersed in a medium (ε_1), such states can be formed if the nanoparticle radius α is smaller than some critical radius α_c :

$$\alpha \leq \alpha_c = 6|\beta|^{-1} \alpha_{e,h} \quad (1)$$

where

$$\frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + \varepsilon_2} \quad (2)$$

Here, $\alpha_{e,h}$ is the Bohr radius of the charge carriers in the nanoparticle material [19].

Some properties of the quantum states' spectrum can be clarified by studying the nanocomposites' transmittance spectra. As a rule, experimental studies are concerned with the transmittance spectra of nanoparticles' arrays embedded in a solid matrix or deposited on a transparent material surface. In this case, the electronic structure of nanoparticles is substantially influenced by the matrix material and the interaction between nanoparticles. Because of these effects, it is not possible to consider the transmittance spectra as the spectra of no photonics of heterogeneous dielectric nanostructures interacting nanoparticles' arrays. Nanocomposites containing low concentrations of nanoparticles almost satisfy the condition due to the lack of the above interactions;

however, to study the optical properties of such composites, one cannot take into account the effects of the optical field on the distribution of the particles through the degrees of freedom. In this case, given the low-intensity radiation, the optical field effect on the coordinates of a gravity centre of a nanoparticle can be disregarded, which cannot be said for the distribution of particles throughout the rotational degrees of freedom.

There is no well-known theoretical approach taking into account the characteristics of the nanoparticle dimensions, the orientation of nanoparticles in the external field of laser radiation, and the dependences of the scattering and absorption cross-sections on the propagating radiation intensity. In this context, it is necessary to develop a theoretical model of the scattering and absorption cross-sections in dielectric nanocomposites with the abovementioned features of such systems.

In this study, we suggest a semiphenomenological model of the optical transmittance of the array of non-interacting, small-sized ($\alpha < \alpha_c$), dielectric nanoparticles embedded in the dielectric matrix. We show that the basic mechanisms of the low-threshold effects of nonlinear scattering and the absorption of laser radiation in the HDN are: the photo induction of electric dipole moments of nanoparticles in the external optical field and the orientation of nanoparticles along the polarization direction of this field. In addition, we discuss the behaviour of the HDN transmittance in the central frequency vicinity of the absorption band and the dependence of the band depth on the radiation intensity.

3. Theoretical approach

We consider the HDN consisting of a low concentration (the number of nanoparticles N per unit volume) of dielectric nanoparticles embedded in an isotropic transparent dielectric matrix with a small coefficient of viscosity and linear optical properties within the visible spectral range. In our case, the multiple scattering of radiation by nanoparticles and the nanoparticles' interaction with each other can be neglected. Let us introduce two coordinate systems with the same origin (Fig. 1).

One of the systems $\{\alpha_1, \alpha_2, \alpha_3\}$ corresponds to the coordinates coinciding with the principle axes of the particle polarization tensor with the unit vectors (n_1, n_2, n_3) . The other system is the Cartesian laboratory coordinate system $\{x, y, z\}$ with the unit vectors (n_x, n_y, n_z) . We suggest that the electromagnetic wave polarized along the z -axis $E = \{0, 0, E\}$ is incident on the composite. We chose the x -axis to be directed collinearly with a wave vector.

The optical transmittance of the HDN depends on the extinction coefficient, the path of the light beam in the material and the

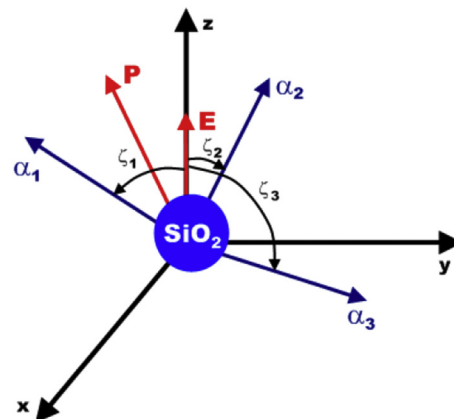


Fig. 1. The coordinate system used in the theoretical study.

optical reflectance from the HDN boundary. For normal incidence of the light beam onto the boundary of the planar nanocomposite layer arranged normally to the x-axis, the transmittance expression can be written as [20]

$$T(\omega, N) = \frac{(1 - R^2)^2 e^{\beta L}}{1 - R^2 e^{-2\beta L}} \quad (3)$$

Here, β is the extinction coefficient, R is the optical reflectance of the boundary (in experiments, R is much smaller than unity) and L is the interaction length of the light beam with the HDN.

In the case of a single scattering approximation, the extinction coefficient can be expressed in terms of the scattering $\sigma_s(\omega, a)$ and absorption $\sigma_a(\omega, a)$ cross-sections of the HDN unit volume as

$$\beta(\omega, a) = \sigma^a(\omega, a) + \sigma^s(\omega, a) + a^m(\omega) \quad (4)$$

where $\alpha_m(\omega)$ is the extinction coefficient of the matrix material and a is the characteristic nanoparticle dimension. For the above indicated orientation of the nanocomposite layer, the scattering and absorption cross-sections in the laboratory coordinate system can be expressed in terms of the polarizability component of the HDN unit volume $\chi_{zz}(\omega, a)$ by the relations [20,21]

$$\sigma^a(\omega, a) = \frac{4\pi\omega}{c} \text{Im}\chi_{zz}(\omega, a) \quad (5)$$

$$d\sigma^s(\omega, a) = \frac{\omega^4}{c^4} |\chi_{zz}(\omega, a)|^2 \sin^2\theta \, d\Omega$$

Here, θ is the angle of the vector directed along the scattering direction, and c is the speed of light in vacuum.

We introduce the effective polarizability tensor for a nanoparticle in the matrix $\alpha = \{\alpha_{ij}\}$ in such a way that the components of the nanoparticle electric dipole moment P induced by the external plane polarized monochromatic electromagnetic field E with frequency ω are determined directly in terms of the external field rather than the local field $P_i = \alpha_{ij}E_j$. In the coordinate system $\{\alpha_1, \alpha_2, \alpha_3\}$, the polarization vector of the nanoparticle is

$$P = \sum_j^3 a_{ij}(n_j E) n_j \quad (6)$$

If the vector E is directed along the z-axis, the z component of the polarization vector is

$$P_z = \sum_j^3 a_{ij} E (n_j n_z)^2 \sum_j^3 a_{ij} E \cos^2\theta_j \quad (7)$$

Here, θ_j is the angle between vector E and the α_j -axis; this angle specifies the nanoparticle orientation in the external electromagnetic field in the laboratory coordinate system. Because the nanoparticles are randomly oriented, we assume that the polarizability tensor of the medium $\chi = \{\chi_{ij}\}$ is diagonal and the polarization vector of the HDN unit volume in the laboratory coordinate system is $P_z = \chi_{zz}E$. Comparing this expression with Eq. (7), we obtain

$$\chi_{zz} = N(a_0 + \Delta a_1 Q_1 + \Delta a_2 Q_2) \quad (8)$$

where

$$a_0 = \frac{a_{11} + a_{22} + a_{33}}{3} \quad (9)$$

$$\Delta a_1 = a_{11} - a_{33}$$

$$\Delta a_2 = a_{22} - a_{33}$$

The values averaged over all possible orientations

$$Q_1 = \left\langle \cos^2\theta_1 - \frac{1}{3} \right\rangle \quad (10)$$

$$Q_2 = \left\langle \cos^2\theta_2 - \frac{1}{3} \right\rangle$$

are the orientation order parameters of the nanoparticles ensemble in the external field. The angle distribution function of nanoparticles and the order parameters Q_1 and Q_2 depend on the laser radiation intensity and, via the components α_{ij} , on the radiation frequency. The quantities Q_1 and Q_2 as functions of the intensity exhibit saturation at $I > I_p$, irrespective of the matrix material.

The low-threshold, nonlinear, optical response occurs if the transmittance spectrum of the nanoparticles' array exhibits a lack of broad absorption bands in the bulk sample spectrum [7–9,24]. The polarizability tensor components α_{ij} of the nanoparticle reach their maxima corresponding to the dipole transitions of the charge carriers from the state $\langle n|$ to the state $|g\rangle$ within this frequency region. In addition, the diagonal tensor components in the coordinate system of the principal axes within this frequency region can be expressed as [22]

$$\alpha_{ij}(\omega) = \sum_{n,g} \frac{|\langle n|e r_j|g\rangle|^2}{(\omega - \omega_{ng} + i\Gamma_{ng})} \Delta\rho_{ng} \quad (11)$$

The summation is performed over all allowed optical transitions of charge carriers of the nanoparticles with the frequency transition ω_{ng} from the states $\langle n|$ to the states $|g\rangle$, being the component of the electric dipole moment of the transition $p_{ng}^j = \langle n|e r_j|g\rangle$ and the transitions width Γ_{ng} . We can write the expression for only one nonzero polarizability tensor component in the laboratory coordinate system related to the individual nanoparticle using expressions (8) and (11) and introducing the definition $\Delta\omega_{ng} = \omega - \omega_{ng}$:

$$\chi(\omega, Q_1, Q_2) = N \sum_{n,g} \left[\frac{A_{ng} \Delta\omega_{ng}}{(\Delta\omega_{ng}^2 + \Gamma_{ng}^2)} - i \frac{A_{ng} \Gamma_{ng}}{(\Delta\omega_{ng}^2 + \Gamma_{ng}^2)} \right] \Delta\rho_{ng} \quad (12)$$

The next definition is included in expression (12)

$$A_{ng}(Q_1, Q_2) = \frac{1}{3} |\rho_{ng}|^2 + Q_1 (|\rho_1^{ng}|^2 - |\rho_2^{ng}|^2) + Q_2 (|\rho_3^{ng}|^2 - |\rho_2^{ng}|^2) \quad (13)$$

The quantity A_{ng} is proportional to the squared magnitude of the dipole moment of the transitions from state $\langle n|$ to the state $|g\rangle$ provided certain optical radiation intensities, frequencies and specified parameters of the nanocomposite matrix. The population difference induced by radiation between the states $\langle n|$ and $|g\rangle$ is a function of the incident radiation intensity. Using a two-level system approximation [22], this difference is

$$\Delta\rho_{ng}(I) = \left(1 - \frac{\frac{I}{I_s}}{\Delta\omega_{ng}^2 + \Gamma_{ng}^2 \left(1 + \frac{I}{I_s} \right)} \Gamma_{ng}^2 \right) \Delta\rho_{ng}^0 \quad (14)$$

where $\Delta\rho_{ng}^0$ is the thermal-equilibrium difference and I_s is the intensity of saturation, when the $\Delta\rho/2$ carriers are in the upper energy level. Separating the real and imaginary parts of the polarizability tensor component (12) and taking into account expression (14), we introduce the definitions

$$P = \int \sin^2\theta d\Omega$$

$$B_{ng}(\omega, I) = \frac{I/I_s}{\Delta\omega_{ng}^2 + I_{ng}^2 \left(1 + \frac{I}{I_s}\right)} I_{ng}^2 \quad (15)$$

we obtain the integrated scattering and absorption cross-sections of the united volume of the HDN in a single scattering approximation:

$$\sigma_a(\omega, a, I) = \frac{4\pi\omega N}{c} \sum_{ng} \frac{A_{ng} \Gamma_{ng} \Delta\rho_{ng}^0}{\Delta\omega_{ng}^2 + I_{ng}^2} (1 - B_{ng}) \quad (16)$$

$$\sigma_s(\omega, a, I) = \frac{P\omega^4 N^2}{c} \sum_{ng} \left\{ A_{ng} A_{kl} \frac{(\Delta\omega_{ng} \Delta\omega_{kl} + \Gamma_{ng} \Gamma_{kl}) \Delta\rho_{ng}^0 \Delta\rho_{kl}^0}{(\Delta\omega_{ng}^2 + I_{ng}^2)(\Delta\omega_{kl}^2 + I_{kl}^2)} (1 - B_{ng}) \right. \\ \left. \times (1 - B_{kl}) \right\} \quad (17)$$

The dependence of the cross-sections on the nanoparticle dimensions can be found by the function of the relation between A_{ng} and the nanoparticle dimension. Given $\alpha < \alpha c$, the dipole moment of the nanoparticle is proportional to its dimensions. Therefore, as follows from expression (13), we can separate the dependence of A_{ng} on the nanoparticle dimensions as $A_{ng} = S_{ng}(I)a^2$. Here, $S_{ng}(I)$ is a function of the radiation intensity and depends on the nanoparticle shape.

Let us estimate the ratio between the scattering and absorption cross-sections. We assume that transitions occur from only one level $\langle n \rangle$, and the width of the excited level Γ_g has a low dependence on g . Taking into account that the frequencies ω and ω_g are of the same order of magnitude, the thermal equilibrium difference between the states is close to unity, and following the expressions (16) and (17), we obtain

$$\frac{\sigma_s(\omega, a)}{\sigma_a(\omega, a)} \approx \frac{NP\omega^3 a^2}{4\pi c^3 I} \sum_{ng} \{S_{ng}(I)(1 - B_{ng}(I))\} \quad (18)$$

The quantity of σ_s/σ_a does not exceed N^*10^{-9} in any intensity region provided the nanoparticle dimensions $\alpha = (10; 100)$ nm in the frequency range $(10^{13}; 10^{16})$ Hz and $\Gamma = 10^9$ Hz. Given $N^*10^{-9} < 1$, the scattering cross-section can be omitted from the expression for the extinction coefficient.

We can define $S_{ng}(I) = c_{ng}I$ and follow expression (16) within the radiation intensities region $I/I_s \ll 1$ to obtain the following

$$\sigma_a(\omega, a, I) \approx \frac{4\pi\omega N}{c} a^2 I \sum_{ng} c_{ng} \frac{\Gamma_{ng}}{(\Delta\omega_{ng}^2 + I_{ng}^2)^2} \Delta\rho_{ng}^0 \quad (19)$$

The absorption cross-section reaches a maximum at some intensity $I = I_p$ under increasing radiation intensity, which follows from equation (16). This cross-section corresponds to the complete

nanoparticle's orientation along the electric vector of the optical field and to the maximum value of $A_{ng}(I)$. This effect is responsible for a sharp enhancement of radiation absorption by the HDN unit volume. A further intensity increase yields a noticeable increase of $B_{ng}(\omega, I)$ and a decrease of the absorption cross-section at a constant value of $A_{ng}(I)$. Given $I \gg I_s$, the value of $B_{ng}(\omega, I)$ is approximately equal to unity, resulting in an increase of the HDN transmittance. In this case, the absorption cross-section can be written as

$$\sigma_a(\omega, a, I) \approx \frac{4\pi\omega N}{c} a^2 \sum_{ng} S_{ng} \frac{I_s}{I_{ng}} \Delta\rho_{ng}^0 \quad (20)$$

i.e., the result is inversely proportional to the radiation intensity.

The broad optical absorption bands are manifested in the electronic structure of the dielectric nanoparticles and are absent in the corresponding bulk sample. In addition, the allowed electron energy sub-band (e.g., excitons, impurities) with the width $\Delta\omega_1$ lying in the band gap and adjoining the conduction band bottom, as well as the size-quantization levels (mini-bands) with width $\Delta\omega_2$ in the conduction band, are typical for the electronic structure of HDN electrons. Taking into account the electronic structure of the nanoparticle, we substitute the summation over $|g\rangle$ states with integration from $(\omega_n - \Delta\omega_1)$ to $(\omega_n + \Delta\omega_2)$ with state densities of exciton g_1 and quantum-size g_2 levels, respectively. Let us choose one of the absorption bands as an example. Changing the summation to integration over the frequency in Eq. (16) and introducing the definitions

$$\Delta\omega_n = \omega - \omega_n$$

$$F(I) = \sqrt{\frac{I_s}{I + I_s}} \quad (21)$$

we obtain the expression for the absorption cross-section of light within the absorption band:

$$\sigma_a = \frac{4\pi\omega N a^2}{c} F(I) \left[g_1 S_1 \tan^{-1} \left(\frac{\Delta\omega_1 \Gamma_n F(I)}{\Gamma_n^2 + F^2(I) \Delta\omega_n (\Delta\omega_n - \Delta\omega_1)} \right) \right. \\ \left. + g_2 S_2 \tan^{-1} \left(\frac{\Delta\omega_2 \Gamma_n F(I)}{\Gamma_n^2 + F^2(I) \Delta\omega_n (\Delta\omega_n - \Delta\omega_2)} \right) \right] \quad (22)$$

The quantities S_1 and S_2 are defined as the average form factors of nanoparticles $S_{ng}(I)$ for transitions to the upper and lower energy bands, respectively.

We obtain the expression for the HDN optical transmittance in the absorption band with the central frequency ω_n from expressions (3) and (22):

$$T(\omega, N, I) \approx e^{-L \frac{4\pi\omega N}{c} D F(I)} \quad (23)$$

where

$$D = a^2 g_1 S_1 \tan^{-1} \left(\frac{\Delta\omega_1 \Gamma_n F(I)}{\Gamma_n^2 + F^2(I) \Delta\omega_n (\Delta\omega_n - \Delta\omega_1)} \right) \\ + a^2 g_2 S_2 \tan^{-1} \left(\frac{\Delta\omega_2 \Gamma_n F(I)}{\Gamma_n^2 + F^2(I) \Delta\omega_n (\Delta\omega_n - \Delta\omega_2)} \right) \quad (24)$$

4. Theoretical outputs and discussion

It follows from expression (23) that the optical transmittance of the HDN depends on the laser radiation intensity I (Fig. 2). This dependence exhibits a minimum I_p corresponding to the lowest light transmittance of the HDN. As the intensity is changed near I_p , we can see the effect of the limitation of low-intensity radiation. The insert in Fig. 2 is the experimental result obtained from Ref. [2]. Because $I_{out} = I_{in} e^{-\alpha L}$ and $T = I_{out}/I_{in}$ provided low reflection and absorption, we suppose $T = e^{-\alpha L}$ and use the data of α from Ref. [2]. The theoretical and experimental results are in good agreement.

The curves from Fig. 3 show the basic features of the dependences of the HDN transmittance on the radiation wavelength. In the general case, the transmittance spectrum is asymmetric because there is a difference between $\Delta\omega_1$ and $\Delta\omega_2$. The insert in this figure is the experimental spectrum of the HDN based on SiO₂ nanoparticles [2]. The behaviour of the experimental curve reflects the features of the theoretical curve.

The largest dipole moment is induced at the central frequency ω_n in the absorption band. The expression for D at the central frequency of the absorption band ($\omega = \omega_n, \Delta\omega_n = 0$) is given by

$$D = a^2 gS \left\{ \tan^{-1} \left(\frac{\Delta\omega_1 F(I)}{\Gamma_n} \right) + \tan^{-1} \left(\frac{\Delta\omega_2 F(I)}{\Gamma_n} \right) \right\} \quad (25)$$

Therefore, the HDN transmittance near the central frequency can be written as

$$T(I) = e^{-L \frac{4\pi\omega_n N}{c} a^2 gS \left\{ \tan^{-1} \left(\frac{\Delta\omega_1 F(I)}{\Gamma_n} \right) + \tan^{-1} \left(\frac{\Delta\omega_2 F(I)}{\Gamma_n} \right) \right\}} F(I) \quad (26)$$

As shown by expression (26), the depth of the absorption band in the transmittance spectrum depends on the radiation intensity and the nanoparticle dimensions. The orientation of nanoparticles along the vector E requires high radiation intensities, provided a solid HDN. In the case of a liquid matrix, this situation corresponds to the range of intensities $I > I_p$. Here, we assume that all particles are oriented along the direction of the vector E of the external optical field, so the order parameters are constant and S_n are independent of the intensity. This case indicates that the behaviour of the transmittance of solid and liquid matrices is similar. Therefore, the transmittance at the central frequency is

$$T(I) = e^{-L \frac{4\pi\omega_n N}{c} n^2 (gS_n)_{g=n} (\Delta\omega_1 + \Delta\omega_2) F^2(I)} \quad (27)$$

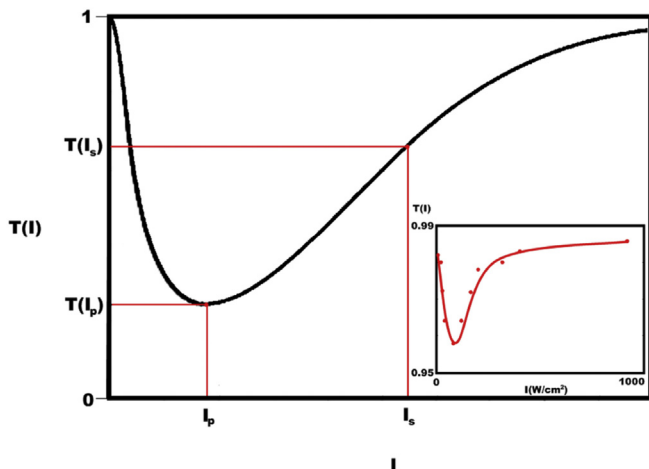


Fig. 2. The theoretical dependence of the HDN transmittance on the intensity of the input radiation. The insert is the experimental dependence of the HDN transmittance.

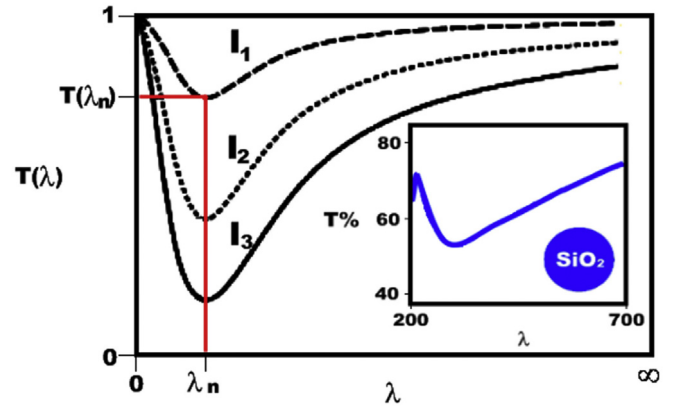


Fig. 3. The theoretical dependence of the HDN transmittance on the wavelength of the input radiation ($I_1 > I_2 > I_3$). The insert is the experimental spectrum of the HDN based on SiO₂ nanoparticles.

Expression (27) exponentially approaches unity when the radiation intensity is increased and the nanoparticle dimensions, the summation ($\Delta\omega_1 + \Delta\omega_2$) and multiplication of gS become larger.

In addition to the transmittance, scattering and spectral properties of the HDN, the theory can describe the behaviour of light refraction in the HDN (Figs. 4 and 5). Using expressions (11) and (14), we can obtain the theoretical dependence of the refractive index on the intensity. Because the value of $\Delta n(I)$ is negligible, the medium refractive index can be written as follows:

$$n(I, \lambda) \approx n_0 + \frac{2\pi\chi_{zz}(I, \lambda)}{n_0} \quad (28)$$

where n_0 is the HDN refractive index in the absence of radiation and χ_{zz} is defined by expression (8).

Because χ_{zz} is determined by α_{jj} , we can simplify equation (11) to perform the integration over the frequency; we assume $\Gamma_{ng} = \Gamma_n$ and the state density g_1 (g_2) and the values of Q_1 (Q_2) are independent of the frequency ω . Selecting the refraction real part

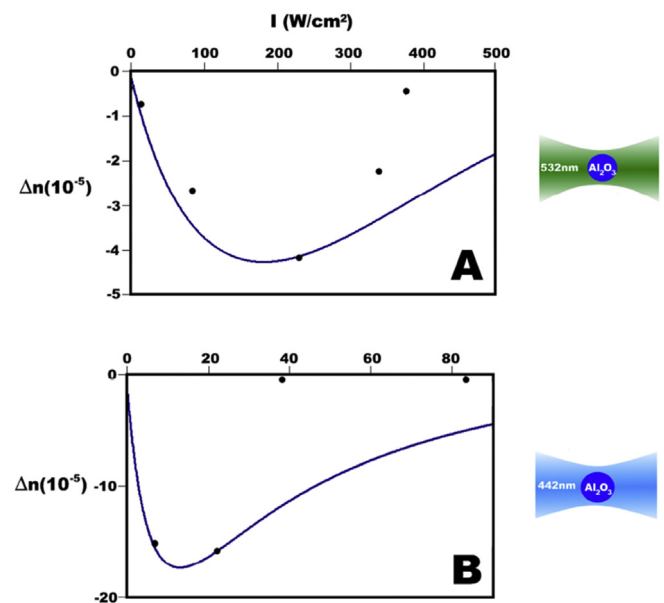


Fig. 4. Theoretical curves of the dependence of the refractive index of green (A) and violet (B) radiation on the intensity in the HDN based on Al₂O₃ nanoparticles (dotted curves are the experimental results).

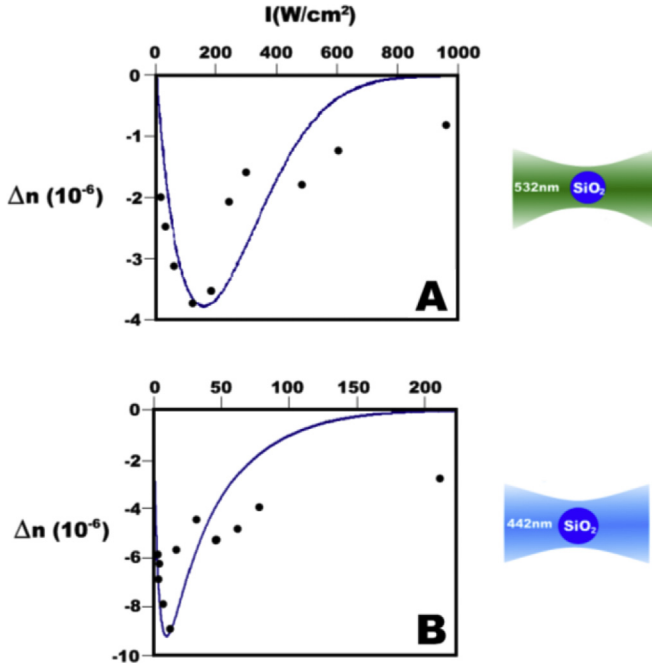


Fig. 5. Theoretical curves of the dependence of the refractive index of green (A) and violet (B) radiation on the intensity in the HDN based on SiO₂ nanoparticles (dotted curves are the experimental results).

from the resulting expression, we obtain [9] where $A_{ng}(Q_1, Q_2)$ is determined by expression (13).

$$n(I, \omega) = n_0 + \frac{1}{2} \sum_n \left\{ A_{ng}(Q_1, Q_2) \Delta \rho^0 \left(g_1 \ln \frac{(\omega - (\omega_n - \Delta \omega_1))^2 + I_n^2(1 + I/I_s)}{(\omega - \omega_n)^2 + I_n^2(1 + I/I_s)} + g_2 \ln \frac{(\omega - \omega_n)^2 + I_n^2(1 + I/I_s)}{(\omega - (\omega_n - \Delta \omega_1))^2 + I_n^2(1 + I/I_s)} \right) \right\} \quad (29)$$

Equation (29) indicates that the term A_{ng} does not vanish in the case of the propagation of unpolarized light through the medium ($Q = 0$), and the nonlinear response of the dielectric nanocomposite is not equal to zero, even in the case of a solid matrix.

The important conclusion from equations (13) and (29) is that the modulus of photo-induced electric dipole moments $|p_{ng}|$ defines the magnitude of the nonlinear optical response under continuous low-intensity radiation. In general, the orientation parameters and dipole moment modulus reach their maxima with an increase of the input power; however, this increase diminishes the population difference. Therefore, the change of Δn tends to zero. It is these two competing processes that define the nonlinear features of the HDN refractive index.

The numerical simulation of the change in the HDN refractive index was conducted using equation (29). Because the photon energy is less than the nanoparticle band gap, the dipole transition of electrons to the exciton state is most probable ($g_2 = 0$). In the case of low-intensity, continuous radiation and a low concentration of nanoparticles, equation (29) can be re-written as follows [9]:

$$\Delta n(I, \omega) \approx A(I) \ln \frac{(\omega - (\omega_n - \Delta \omega_1))^2 + I_n^2(1 + I/I_s)}{(\omega - \omega_n)^2 + I_n^2(1 + I/I_s)} \quad (30)$$

where the factor $A(I)$ defines the dependence of A_{ng} on the radiation intensity, as follows:

$$A(I) = A_0 \Delta \rho^0 (1 - e^{-aI}) \quad (31)$$

This dependence takes into account the magnitude of A_{ng} , which varies from zero to its maximum value with the increase of the external radiation intensity. The theoretical curves (Figs. 4 and 5, solid lines) of the dependence of Δn on the radiation intensity are constructed using equation (30) for the HDN based on Al₂O₃ and SiO₂ nanoparticles and irradiation with green and violet radiation. The parameters for good approximation were calculated according to the following considerations: Γ was taken from the T spectrum (Fig. 4); I_s , α and $A_0 \Delta \rho_0$ were calculated using the three-equation system (30) with known parameters I and Δn [2].

The lack of nonlinear refraction and the absorption of low-intensity continuous visible laser radiation in the HDN based on the nanoparticles of narrow-band dielectrics are caused by the absence of an absorption band in the frequency range (200; 700) nm. In order for the nonlinear optical properties of such an HDN to be observable, we must use high-energy pulsed radiation or change the input radiation frequency. If we use the pulsed radiation, we can obtain the typical nonlinearity of the nanocomposites caused by the nonlinear behaviour of excitons near the edge of fundamental absorption. High energy is required because there is a small dipole moment of the electron transition to the exciton states. On the other hand, if we change the input radiation frequency, it is possible to determine the defect energy levels in the HDN infrared spectrum. Therefore, non-typical nonlinearity can occur under low-intensity infrared radiation.

5. Conclusions

The ability to observe this nonlinearity is directly connected to the peculiarities of the energy spectrum of nanoparticle charge carriers. Because of the wide band gap of the bulk dielectric material, it is not possible to excite electron transitions to the conduction band using visible light. The energy spectrum of nanoparticle electrons is of a different structure: the band gap has defect levels containing many electrons due to the high density of crystal defects on the nanoparticle's surface; the small size and shape of nanoparticles lead to strong broadening of the band of the high-density exciton states from the bottom of the conduction band to the defect levels. The existence of an absorption band in the visible light spectrum is observed only for nanoparticles with broad-band dielectrics (Al₂O₃, SiO₂). Comparing the experimental and theoretical results, we conclude that the low-threshold nonlinearity of the HDN optical parameters (Δn , $\Delta \alpha$ and the scattering cross-section) is caused by the transitions of electrons from the defect levels to the exciton states and, photo excitation of electric dipole moments. However, experiments have shown that the nonlinear behaviour of the HDN optical parameters occurs when the matrix permittivity ϵ_{stat} is less than that of the nanoparticles (e.g., oil permittivity). Otherwise, the positive polarization

charges, concentrated along the nanoparticle's inner surface, destroy the defect states. This explains the absence of nonlinear optical properties in the HDN based on water and alcohol matrices. In view of the effect of the giant oscillator strength, the magnitude of the photo excited dipole moment is enormous. The large value of the oscillator's strength for electron transition to the exciton states is responsible for the low-threshold of the nonlinearity. As follows from the theory, the dipole moment orientation along the external E field makes a minor contribution to the nonlinearity; therefore, this response can also be observed under pulsed and unpolarized laser radiation in solid matrices. In addition, a qualitative agreement between the experimental and theoretical results was obtained, and the proposed theory model of optical nonlinearity can be applied to explain a number of phenomena in the physics of nanoscale dielectrics, e.g., proteins and blood bodies [23].

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