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Determination of nonlinear absorption in InSe nanoparticles synthesized by laser ablation in liquid

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Abstract

InSe nanoparticles obtained by laser ablation in liquid were experimentally studied. A pulsed Nd:YAG laser with a wavelength of λ=1064 nm, a duration of 10 ns and an energy of 135 mJ per pulse was used as a radiation source. Using X-ray diffraction analysis, the structure and size of the nanoparticles were determined, which turned out to be 10-45 nm. It was shown that the observed features in the absorption and luminescence spectra of InSe nanoparticles are due to interband transition and discrete energy levels located above the conduction band. Nonlinear optical phenomena caused by a change in the refractive index of the medium were detected in InSe nanoparticles.

Keywords: InSe nanoparticles, laser ablation, absorption, luminescence, optical nonlinearity.
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1. Introduction

The production and study of nanostructures based on poorly studied and at the same time promising semiconductor compounds of indium selenide (InSe), due to its nonlinear optical properties, high electron mobility and direct optical band gap, opens up wide possibilities for their application in high-speed electronics, solar cells

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and other areas of optoelectronics [1-3]. The ionic-covalent bond between atoms in the layers and the weak Van der Waals interaction between them cause strong anisotropy of their physical properties and are the main reason for observing a number of effects that are not characteristic of other anisotropic semiconductors. Ultrathin nanolayers of indium monoselenide have unique physical properties that qualitatively distinguish them from other two-dimensional crystals. In the obtained two-dimensional samples of indium monoselenide, the electron mobility is the highest (~9000 $cm^2/W \cdot sec$) [4]. This parameter is extremely important from the point of view of increasing the speed of devices that can be created on their basis. This paper considers the synthesis of InSe nanoparticles by laser ablation in liquid, conducting a structural analysis and studying their nonlinear optical properties.

1.1. Experimental methodology

Laser ablation was performed using undoped InSe single crystals grown by the Bridgman method. A pulsed Nd:YAG laser with built-in 2nd and 3rd harmonic generators designed to generate radiation with wavelengths of 1064, 532 and 335 nm was used as a radiation source. The laser pulse duration was 10 ns, the pulse repetition rate was 10 Hz, and the maximum power was ~ 12 MW/cm^2. The radiation intensity was varied using calibrated neutral light filters. The optical absorption and luminescence spectra of InSe nanoparticles were studied using an M833 automatic monochromator with double dispersion (spectral resolution ~ 0.024 nm at a wavelength of 600 nm), with computer control and a detector recording radiation in the wavelength range of 350-2000 nm. Luminescence kinetics was performed using a technique that allows recording single nanosecond pulses on the screen of a storage oscilloscope (Le Croy 9400). Laser radiation with a wavelength of 1064 nm, focused by a positive lens (f=11 cm), was used to ablate InSe crystals with a diameter of ~1.5 cm. The experiments were carried out in a quartz cuvette, in distilled water, without adding any surfactants (Fig. 1,a). The ablation process was carried out at normal pressure with a laser energy of 135 mJ in a pulse with a frequency of 10 Hz and an ablation time of 10 min.

It was found that the color of fresh colloidal InSe suspension depends on the laser flux density. For InSe nanoparticles synthesized at low laser flux density, the color was light orange, which changed to dark orange after increasing the laser flux density, while InSe crystals have a dark gray color.

To determine the nonlinear optical parameters of InSe nanoparticles, the Z-scan method introduced by Sheikh-Bahae [5] was applied. The Z-scan method is a simple and highly sensitive method for determining the nonlinear refractive index and nonlinear absorption coefficient.

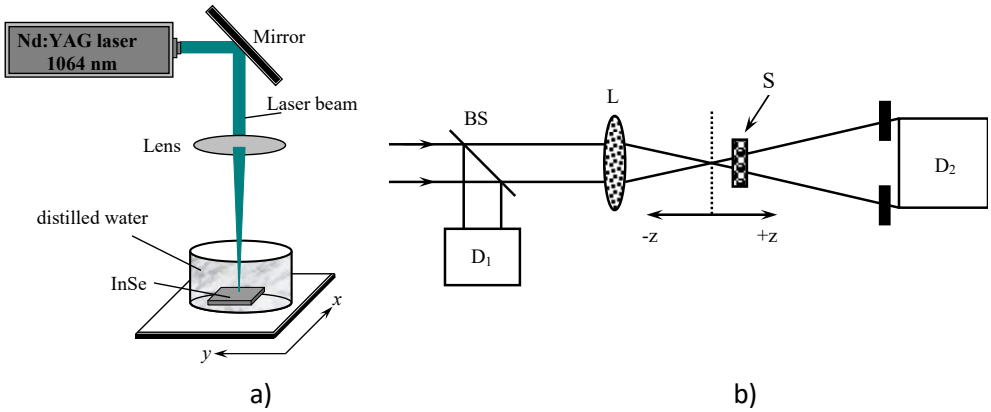

Fig. 1. *a* – Schematic diagram of the experimental setup for ablation of InSe nanoparticles, *b* – experimental scheme for the z-scan technique: BS – laser beam splitter; D1 – detector tracking fluctuations of laser radiation; L – focusing lens; S – sample; D2 – detector recording radiation passed through the sample.

To determine the nonlinear optical parameters of InSe nanoparticles, the Z-scan method introduced by Sheikh-Bahae [5] was applied. The Z-scan method is a simple and highly sensitive method for determining the nonlinear refractive index and nonlinear absorption coefficient. This method is based on the dependence of the refractive index on the intensity and measuring the change in the refractive index depending on the intensity of the incident beam. The induced lens inside the sample has different focal lengths for each position of the sample, and the focal length depends on the intensity of the laser beam. Figure 1b shows a schematic setup for the Z-scan experiment. The excitation source was an Nd:YAG laser, which was focused on the sample using a lens with a focal length of 5 cm, the measured beam waist radius was 15.8 mm. The thickness of the quartz cell containing the sample was 1 mm.

2. Experimental results and their discussion

Figure 2 shows the XRD pattern of InSe nanoparticles from droplets of a colloidal solution dried on a glass substrate (a) and the XRD pattern of a crystal β-InSe. (b) The radiation sources used were CuK_{α}, λ=1,544178 A^0 SSFOM: F17-610.0.5.10.60. Comparison of diffraction patterns of nanoparticles and the original material β-InSe [9] showed that the nanoparticles we obtained have a hexagonal structure and the formation of oxides during ablation in water is not observed. Based on the X-ray diffraction patterns, the sizes of the obtained nanoparticles were calculated using the Debye-Scherrer formula [6]:

$$D = \frac{k\lambda}{\beta \cos\theta}, \quad (1)$$

where D is the size of the nanoparticles, k = 0.9 is the shape factor, β = 0,035 rad Full Width at Half Maximum (FWHM), λ – X-ray wavelength (λ=1,54 A^0), θ – Bragg angle (cosθ =0,727). As can be seen from Table 1, the sizes of InSe nanoparticles vary in the range of ~ (10-45) nm.

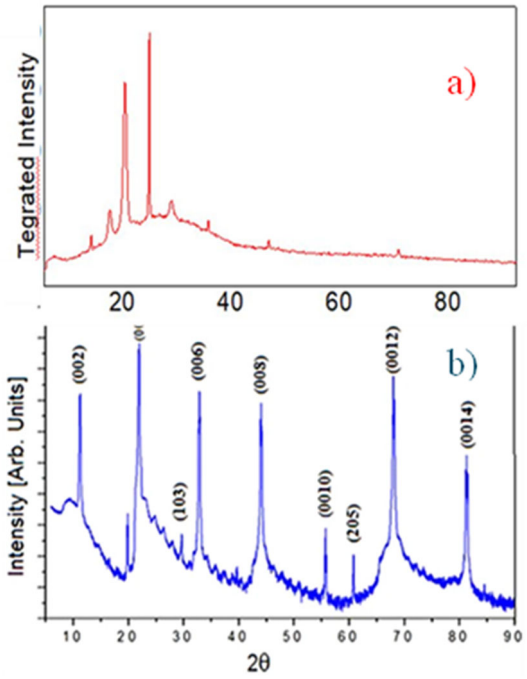

Fig. 2. XRD pattern of InSe nanoparticles (a) and XRD pattern of β-InSe crystal (b) [9].

Table 1. Position (2θ) and sizes of peaks of InSe nanoparticles.

2θ	**Crystallite size**
15.13(5)	13.29 nm
17.924(9)	11.94 nm
22.356(6)	43.62 nm
26.42(4)	10.93 nm
33.26(2)	45.6 nm
44.4(3)	52.739 nm
68.30(7)	45.589 nm

Figure 3 shows the transmission spectrum of InSe nanoparticles deposited on quartz glass substrates. As can be seen from the figure, the spectrum exhibits a broad absorption band in the spectral range of 500-1100 nm. The spectra of pure bulk crystals of these materials do not exhibit broad absorption bands; only a narrow band in the near IR range is observed.

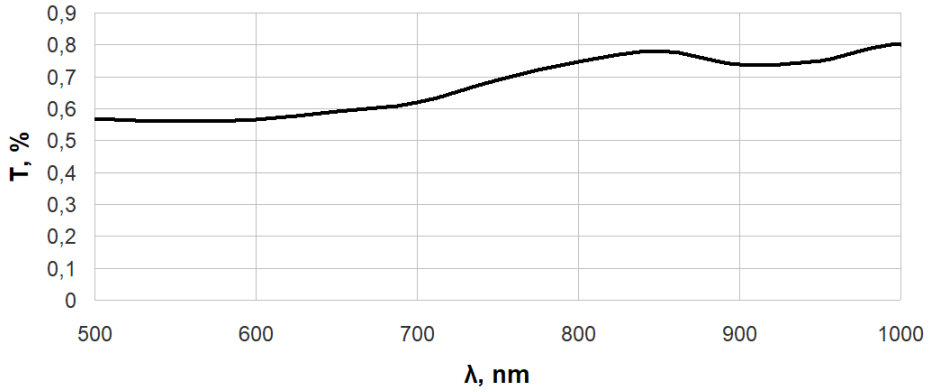

Fig. 3. Transmission spectrum of InSe nanoparticles deposited on quartz glass substrates.

The absorption curve of InSe nanoparticles is shown in Figure 4,a. From the dependence $\alpha^2 \sim f(h\nu)$**,** the width of the forbidden zone of the studied samples was determined, which turned out to be equal to E_g=2.15 eV (Fig. 4,b). This value is 0.9 eV greater than the width of the forbidden zone of the bulk material (E_g=1.25 eV).

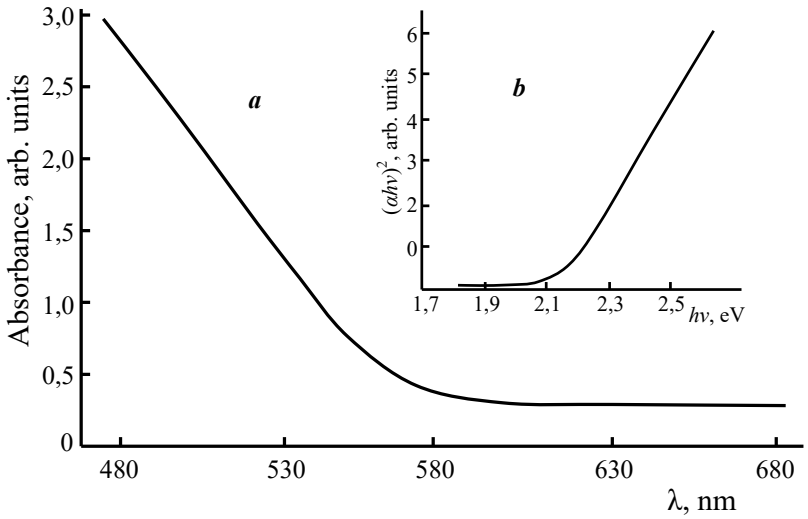

Fig. 4. Absorption spectrum (a) and dependence $\alpha^2 \sim f(h\nu)$ (b) of InSe nanoparticles.

Luminescence spectra of InSe nanoparticles excited by the second harmonic of a Nd:YAG laser ($\hbar\omega = 2{,}34eV$), are shown in Figure 5. As can be seen from the figure, the spectrum contains two emission lines, with maxima $\lambda_1 = 555\,nm$ and $\lambda_2 = 576\,nm$. The dependences of the luminescence intensity (for both lines) on the pump power change according to the law $I_{lum.} \sim I_{las.}^{1.5}$.

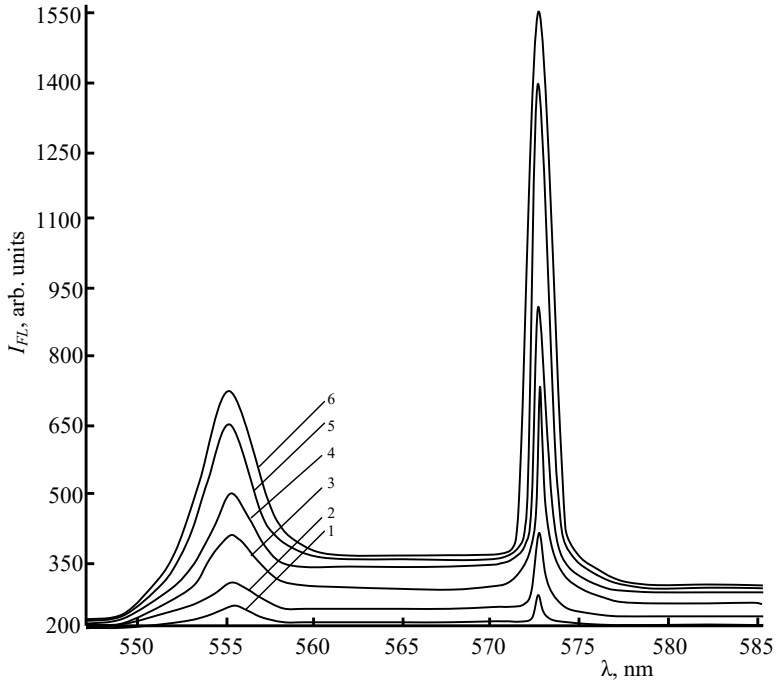

Fig. 5. Luminescence spectra of InSe nanoparticles at different pump powers excited by the second harmonic of an Nd:YAG laser ($\hbar\omega = 2{,}34\ eV$), I_{pump}, MW/cm^2: 1 – 0.5; 2 – 1.3; 3 – 2.1; 4 – 3; 5 – 6; 6 – 10.

Comparison of the luminescence spectra with the absorption spectrum of InSe nanoparticles suggests that the emission line with a maximum $\lambda_2 = 576\,nm$ is due to the band-to-band transition. As for the short-wave emission line with a maximum $\lambda_1 = 555\,nm$, in our opinion, this line is associated with the appearance of discrete energy levels located above the conduction band. It is known that in nanostructures, a change in the energy spectrum of electrons and holes occurs. A decrease in dimensionality leads to quantization of the corresponding component of the momentum and the energy proper [7].

Figure 6 shows the experimental dependences of the transmitted radiation energy density (E_{trans}) on the incident radiation energy density (E_{in}) at the radiation wavelength λ_1=576 nm (curve 1) and λ_2=555 nm (curve 2) for InSe nanoparticles.

In this experiment, the above-mentioned Nd:YAG laser of the LQ529*LP603 brand was used, which, along with three harmonics, allows obtaining radiation with a tunable wavelength in the range from 400 to 700 nm at the output of the laser system.

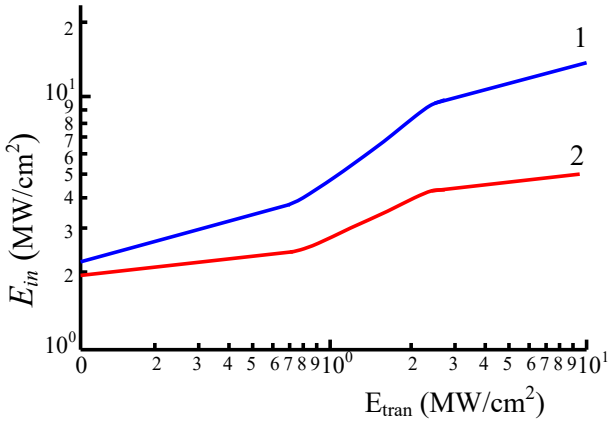

Fig. 6. Dependence of the energy density passed through the sample on the energy density of the incident radiation. λ_1=576 nm (curve 1) and λ_2=555 nm (curve 2)

It is evident from the figure that at low radiation intensity, the transmission of the samples is linear. However, starting from a certain threshold energy density (~8 W/cm^2.) optical nonlinearity appears, which manifests itself in the limitation of radiation. With a further increase in the energy of the incident radiation, the dependence $E_{trans}.(E_{pad})$ again becomes linear. The region of nonlinearity is strongly expressed for $\lambda_1 = 576\ nm$. For $\lambda_1 = 555\ nm$ at the deviation of E_{trans} (E_{pad}) from the linear dependence is small. It is known that nanometer-sized semiconductor particles exhibit enhanced nonlinear optical properties due to their large nonlinear optical response caused by the quantum-dimensional effect. To determine the effect of the refractive index on their nonlinear optical properties, experiments were conducted using the Z-scan method. The open aperture Z-scan technique was used to measure the dependence of the total transmitted intensity (sample transmission) as a function of the sample position (Fig. 7,a). As can be seen from the figure, this dependence is symmetrical relative to the focus of the lens (Z=0 mm), where the minimum transmission is observed. T_v is the transmittance of the sample at low intensity of incident radiation (in the absence of nonlinear effects), T_P is the transmittance of the sample at high intensity of incident radiation.

The closed aperture Z-scan technique was used to determine the nonlinear refractive index. Since the spot size in the detector plane changes due to the self-focusing effect, placing a finite aperture diaphragm in front of the detector ensures that the nonlinear refractive index is measured. The characteristic shape of the

transmission function is shown in Figure 8. When a sample with a positive nonlinear refractive index Δn is far from the focus of the lens, the intensity of the radiation passing through the sample is low and, since the sample is not thick, the transmission changes little as it moves. As soon as the sample is closer to the focus, the intensity in the beam becomes sufficient for self-focusing to occur in the sample.

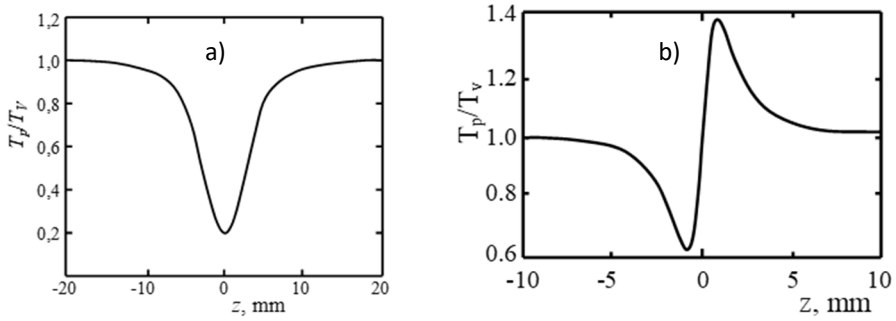

Fig. 7. a – Transmission as a function of the sample position relative to the focus of the lens with an open aperture, b – Transmission as a function of the sample position with a closed aperture, $\Delta n(\omega) > 0$.

The value of $\Delta n(\omega)$ can be determined by analyzing the transmittance as a function of the position of the sample relative to the focus of the lens. A change in the refractive index results in a change in phase $\Delta\Phi_0 = (2\pi/\lambda)\Delta n(\omega)L_{eff}$, where L_{eff}=$(1 - exp(-\alpha l)/\alpha$ – is the effective length of the sample and λ is the laser wavelength. The change in phase, and hence the change in refractive index, can be determined from the measured value of ΔT_{PV}, which is the difference between the peak and valley transmittances, $\Delta T_{PV} = T_P - T_V$, where $T_P(T_V)$ is the peak (valley) transmittance. It has been shown that $\Delta T_{PV} = 0.45(\Delta\Phi)$. The nonlinear refractive index $\Delta n(\omega)$ is given by the following equation:

$$\Delta n(\omega) = \frac{\Delta T_{PV} \cdot \lambda \cdot \alpha}{0.405 \cdot 2\pi(1 - exp(-\alpha l)}, \quad (2)$$

where λ is the laser wavelength (λ = 532 nm), $\alpha \approx 10^3\ cm^{-1}$ is the optical absorption coefficient, l = 20 nm is the thickness of the sample under study. Estimates show that in the case of excitation of InSe nanoparticles by laser radiation with a power of $W \sim 10\ MW/cm^2$, the change in the nonlinear refractive index is $\Delta n(\omega) \approx 0.24$.

3. Conclusion

InSe nanoparticles with sizes of 10 – 45 nm were synthesized in liquid by laser ablation. The band gap of InSe nanoparticles calculated from the dependence was found to be E_g=2.15 eV. In the luminescence spectra of InSe nanoparticles excited

by the second harmonic of a Nd:YAG laser ($\hbar\omega = 2{,}34\ eV$), two emission lines with maxima and are observed. Comparison of the luminescence spectrum with the absorption spectrum suggests that the emission line with the maximum is due to the optical transition between the valence and conduction bands. The short-wave emission line with the maximum is associated with the appearance of discrete energy levels in nanoparticles located above the conduction band. A nonlinear optical effect was detected in InSe nanoparticles. The change in the refractive index of InSe nanoparticles was experimentally studied using the Z-scan method and found to be $\Delta n(\omega) \approx 0.24$ at a laser radiation power of $W \sim 10\ MW/cm^2$. So, as it can be seen from the table 3, the temperatures we determined by the Z-scan method it differs little from the temperatures determined by other authors before us by this method. The reason of why the values in the last column are relatively more different is probably because the spectra taken in earlier years were obtained with a lower resolution. $F(4686)/F_\lambda$ ratio as a function of effective temperature has given in [2].

So, our results according to the HaII that mentioned in the literature, does not coincide with the curve showing the radiation of an absolute black body, including the curve constructed according to the Hammer-Mikhalas model. These deviations are likely due to the central star radiating as an absolute blackbody due to HaII and is due to the fact that assumptions such as the absorption of all ionizing quanta in the nebula are incorrect.

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