OPTICAL ABSORPTION AND LUMINESCENCE IN InSe NANOPARTICLES OBTAINED BY LASER ABLATION

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InSe nanoparticles obtained by the interaction of laser radiation with the element In and a solution of SeO_2 were experimentally studied. A pulsed Nd:YAG laser with a wavelength of λ=1064 nm, with a duration of 10 ns and an energy of 135 mJ per pulse was used as a radiation source. In the colloidal solution, the formation of nanoparticles with a diameter of 7 to 30 nm was observed. With the help of diffraction analysis of X-rays, a scanning electron microscope, an atomic force microscope, and spectroscopy of the dispersed energy of X-rays, the internal structure and structure of X-rays were studied samples. It is shown that the observed features in the luminescence spectra of InSe nanoparticles are due to the collective interaction of excitons. At high levels of optical excitation, stimulated radiation was detected in InSe nanoparticles.

Keywords: InSe nanoparticles, laser ablation, absorption, stimulated radiation.
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1. INTRODUCTION

The production and study of nanostructures based on poorly studied and at the same time the most promising semiconductor compounds of indium selenide (InSe), due to its high nonlinear susceptibility, high electron mobility and direct optical bandgap, opens up great opportunities for their application in nonlinear optics, high-speed electronics, and solar cells [1-16]. One of the most common methods for producing semiconductor nanoparticles is pulsed laser ablation (SLA) of solid targets in a vacuum or in an ambient gas or liquid [17-20]. Laser ablation is a fairly simple, fast and direct way to synthesize nanoparticles. In this method, it does not require long times to carry out chemical reactions, as well as the high temperatures and pressures or multi-step processes characteristic of chemical synthesis. The IL method is applicable with an almost unlimited combination of target materials and liquids, which allows the synthesis of the LF shape, size, size distribution, composition and structure for each target material - depend on the parameters of the laser used for ablation (radiation wavelength, pulse duration and repetition rate, pulse energy) as well as on the surrounding conditions (vacuum, fixed gas pressure, or liquid). It should be noted that laser ablation, as a rule, uses semiconductor crystals grown by various methods (Bridgman, zone melting, Czochralski, etc.), which are by no means a simple technological task, high temperature (~1000 ^{0}C), uncontrolled impurities, defects, a large waste of time (sometimes several days), numerous technical equipment, etc.).

We propose a completely different method of synthesizing nanoparticles using the elements that make up the components of the initial substance in the appropriate solution. As our experimental studies have shown, the structural characteristics and optical properties of nanoparticles obtained by this method are significantly superior to those of nanoparticles obtained from bulk crystals. This work is devoted to the synthesis of nanoparticles InSe by laser ablation of In atoms with SeO_2 solution.

2. EXPERIMENT METHODOLOGY

InSe nanoparticles were synthesized by laser ablation of a solid target in a liquid medium. Extra pure In (99%) in SeO_2 solution were used as the initial raw material. The reaction was based on the following formula:

$$In + SeO_2 + H_2O = InSe + H_2O + O_2 \qquad (1)$$

A pulsed Nd:YAG laser with built-in 2nd and 3rd harmonic generators was used as a radiation source, designed to generate radiation with a wavelength of 1064, 532 and 335 nm. The duration of the laser pulse was 10 ns, the pulse repetition frequency was 10 Hz, and the maximum power was ~ 12 MW/cm^2. The intensity of the radiation was varied using calibrated neutral density light filters. The optical absorption and luminescence spectra of InSe nanoparticles were studied using an automatic monochromator M833 with double dispersion (spectral resolution ~0.024 nm at a wavelength of 600 nm), with computer control and a detector that registers radiation in the wavelength range of 350-2000 nm.

Laser radiation focused by a positive lens (*f=11* cm) was used to ablate InSe nanoparticles (Fig. 1, a). Laser ablation of the InSe crystal was carried out in a quartz cell containing pure In and 5 mL of SeO_2 solution without the addition of any surfactants. The ablation process was carried out by laser radiation with

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a wavelength of λ=1064 nm, with a pulse energy of 135 mJ for ~ 10 min.

Figure 1,b shows a photograph of an InSe colloidal solution obtained by laser ablation. As can be seen from the figure, the color of the colloidal solution is light orange, whereas the InSe crystals had a dark gray color.

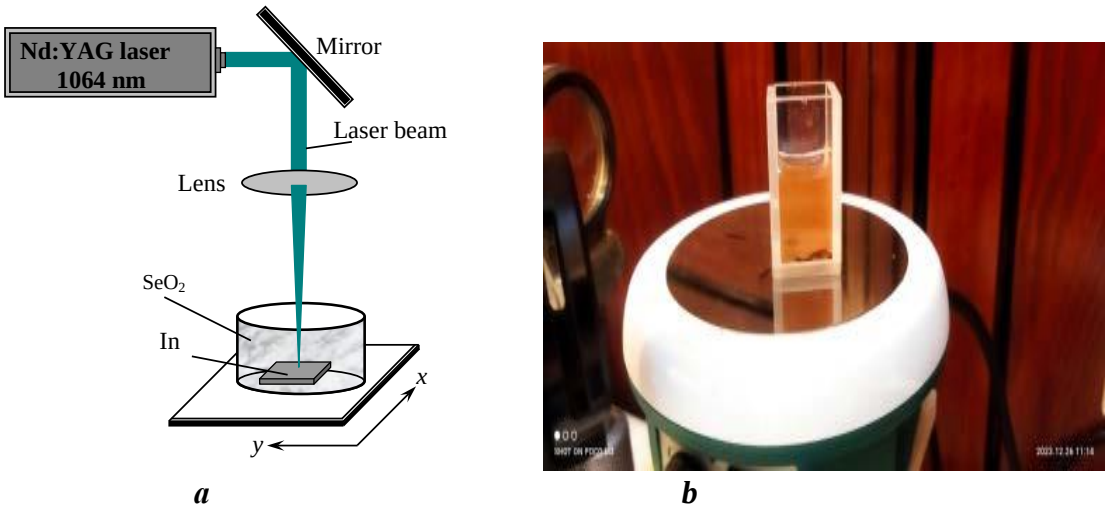


Fig.1. a- Diagram of the experimental facility for ablation of InSe nanoparticles, *b* - InSe colloidal solution obtained by laser ablation in a liquid medium.

3. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 2 shows a difractrogram (XRD) of InSe nanoparticles from colloidal solution droplets dried on a glass substrate. CuK_α, λ=1.544178 A^0 SSFOM: F17-610.0.5.10.60 were used as a radiation source. X-ray diffraction analysis revealed that InSe nanoparticles have a hexagonal structure.

The table shows the positions (2θ) of the diffractogram peaks of InSe nanoparticles. The identification of diffraction lines for InSe nanoparticles obtained by us and presented in [21] is in satisfactory agreement.

Based on radiographs, the Debye-Scherer formula [22] was used to calculate the size of the resulting nanoparticles:

$$D = \frac{k\lambda}{\beta \cos\theta} \qquad (2)$$

where *D* is the size of the nanoparticles, k = 0.9 is the shape factor, β = 0.035 A0 is the Full Width at Half Maximum (FWHM), λ is the X-ray wavelength (λ=1.54 A^0), *and* θ is the Bragg angle ($\cos\theta$ =0.727).

Estimates show that the size of InSe nanoparticles varies in the range of ~ (7 – 30) nm.

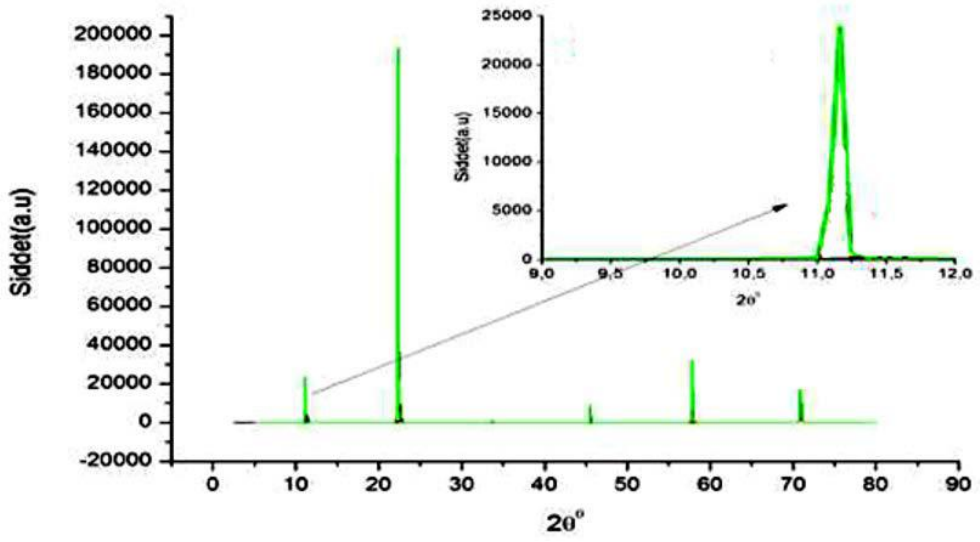


Fig.2. Difractrogram (XRD) of InSe nanoparticles.

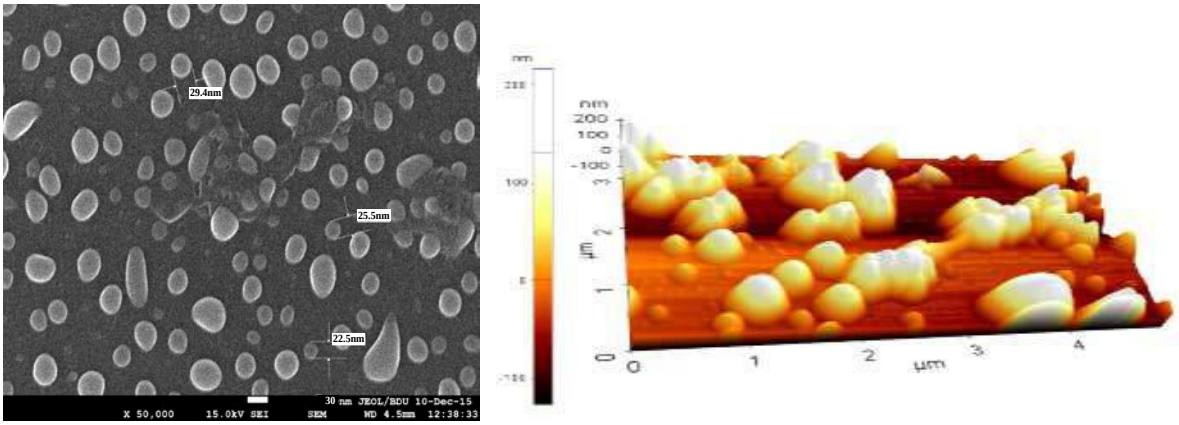
Table.

Positions (2 θ) of the diffractogram peaks of InSe *nanoparticles*.

2-Theta	d(A)	BG	Height	I%	Area	I%	FWHM	XS(A)
11.060	7.9935	43	6844	18.1	59049	10.7	0.147	744
16.603	5.3349	32	71	0.2	1652	0.3	0.396	210
22.259	3.9904	67	37912	100.0	554108	100.0	0.248	356
28.473	3.1322	33	48	0.1	934	0.2	0.331	260
33.658	2.6606	23	807	2.1	6937	1.3	0.146	779
39.503	2. 2794	14	49	0.1	759	0.1	0.263	346
45.420	1.9952	27	5540	14.6	56795	10.2	0.174	603
57.721	1.5958	84	19737	52.1	174802	31.5	0.151	806
58.617	1.5736	35	103	0.3	1569	0.3	0.259	381
70.817	1.3294	76	15633	41.2	142057	25.6	0.154	828
71.801	1.3136	46	69	0.2	1232	0.2	0.304	342

Figure 3 shows SEM (*a*) and AFM (*b*) images of InSe nanoparticles on a glass substrate. SEM images show that the resulting substances consist of spherical nanocrystals with ~ (7–30) nm sizes, which are assembled in a polydisperse form. Homogenous particle distribution is not observed in the AFM image.

Analysis of the structure of InSe nanoparticles by X-ray dispersion energy spectroscopy (EDAX) shows that the ratio of indium to selenium is In: Se = 1:1, showing that the composition of the substance is in a stoichiometric ratio (Fig. 4).



a b

Fig.3. SEM (***a***) and AFM (***b***) images of InSe nanoparticles on glass Underlay.

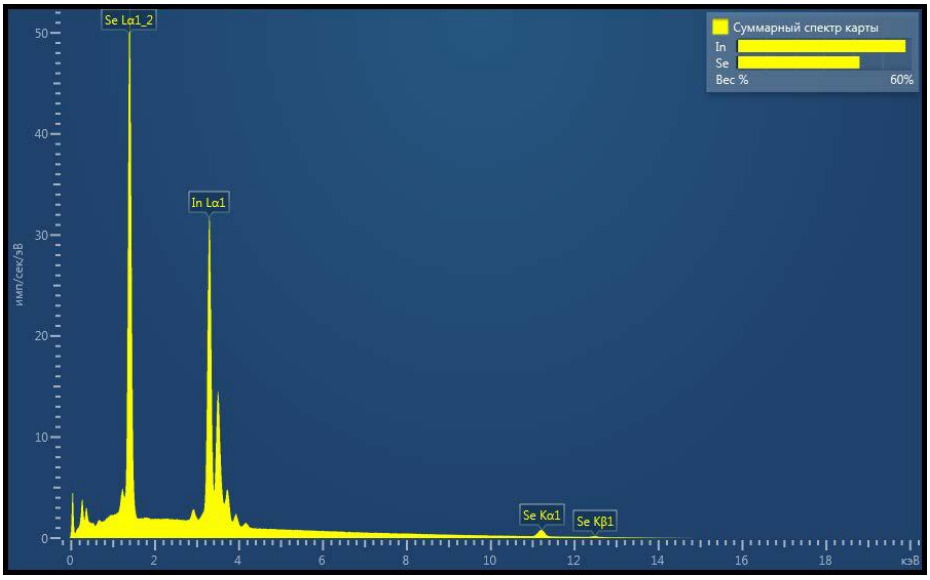


Fig.4. EDAX images of InSe nanoparticles.

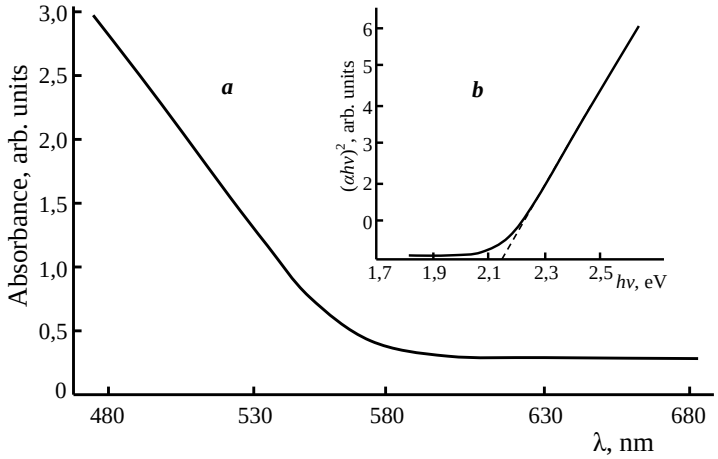


Fig.5. Absorption spectrum (*a*) and dependence $\alpha^2 \sim f(h\nu)$ (*b) of* InSe nanoparticles.

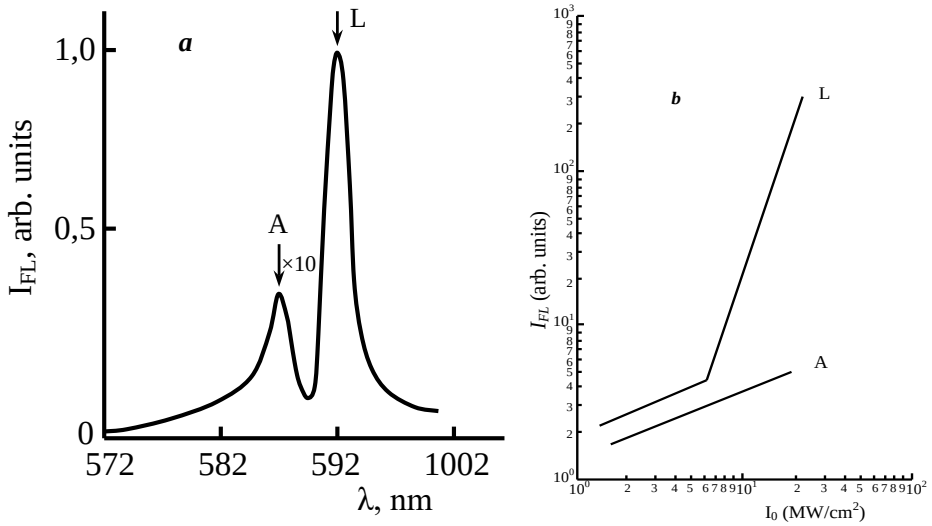


Fig.6. a- Luminescence spectra of InSe nanoparticles excited by the second harmonic of the Nd:YAG laser ($\hbar\omega = 2{,}34$ eV), b- Dependence of the luminescence intensity of the A-line and L-line on the power of laser radiation.

The absorption curve of InSe nanoparticles is shown in Figure 5, a. From the dependence $\alpha^2 \sim f(h\nu)$, the bandgap of the studied samples was determined, which turned out to be equal to Eg=2.15 eV (Fig. 5, b). This value is 0.9 eV greater than the bandgap of the bulk material (E_g=1.25 eV) [23].

The luminescence spectra of InSe nanoparticles excited by the second harmonic of the Nd: YAG laser ($\hbar\omega = 2{,}34$ eV) are shown in Figure 6, a. As can be seen from the figure, two emission lines are observed in the spectrum, with maxima of 587 nm (line A) and 592 nm (line L). As the intensity of excitation increases, the L line becomes dominant in the emission spectrum. With a pumping power of 10 MW/cm^2, the intensity of the L line is 2 orders of magnitude higher than the intensity of the A-line. It should be noted that depending on the intensity of the excitation, the position of the L-line changes, and its shift towards long waves is observed. With a laser power of ~ 8 MW/cm^2, the displacement of the L-line is ~15 MeV.

Figure 6,b shows the luminescence intensity of the A-line and L-line as a function of the laser radiation power. As can be seen from the figure, the intensity of the A-line is linearly dependent on the power of the laser, whereas for the L-line, the linear relationship observed at low excitation levels is replaced by a quadratic one at high excitation levels. In our opinion, such a super linear dependence indicates the observation of the phenomenon of stimulated emission in InSe nanoparticles.

Comparison of the luminescence spectrum of nanoparticles with the absorption spectrum of InSe suggests that the A-line observed in the luminescence spectrum is due to the annihilation of free excitons. This is evidenced by its stability, narrow width (~10 A^0) and the location of this line in the long-wavelength region of the spectrum from the edge of the

fundamental absorption band by an amount equal to the binding energy of the excitons in InSe (E=20 MeV).

Of greatest interest is the nature of the L-band on which stimulated emission occurs. In our opinion, this band is associated with the exciton-exciton interaction that occurs in semiconductors at high levels of optical excitation [23-25]. Indeed, when InSe nanoparticles are excited by laser radiation, electrons and holes bind into excitons. Subsequently, with an increase in the intensity of excitation, the density of excitons increases, and when it reaches a certain critical value, there is an interaction between excitons, which leads to the decay of excitons and the formation of free electron-hole pairs. This phase transition is called the Mott test for excitons. Knowing the effective masses of electrons and holes (m_e=0.12m_0, m_h = 0.6 m_0), as well as the Bohr exciton radius $a_{ex.}$ =37 A^0 for InSe, it is possible to determine the concentration of excitons (n_{Mott}) at which the interaction of excitons occurs:

$$n_{Momm} = \frac{\pi}{3}\left(\frac{1{,}46}{4a_{экс.}}\frac{m_0}{m_e+m_h}\right)^3 \qquad (3)$$

The critical concentration of excitons for InSe, calculated by the formula (3), turned out to be equal to n_{Mott} ~2.5×1016 cm^{-3}. The estimates show that the density of nonequilibrium carriers created by a laser with an intensity of I_0=1.5x10^{25} photon/cm2·and a duration Δt=3×10^{-9} s is:

$$\Delta n = \alpha I0\Delta t = 4.5\times10^{19}\ cm^{-3} \qquad (4)$$

where $\alpha \approx 10^3$ cm^{-3} is the absorption coefficient at the edge of self-absorption.

As can be seen from the comparison of formulas (3) and (4), the obtained values of the concentration of nonequilibrium carriers exceed the exciton density required for the Mott transition.

The exciton-exciton interaction can be described by the following formula [26]:

$$h\nu = E_g - 2E_b - E_k E_{k'} - \frac{\hbar k^2}{2\mu} = E_g - 2E_{св} - \Delta E \qquad (5)$$

where E_g is the bandgap, $\mu = \left(\frac{1}{m_e}+\frac{1}{m_h}\right)^{-1}$ is the effective mass of the electron-hole pairs, $\frac{\hbar^2k^2}{2M}$ is the total kinetic energy of the electron-hole pairs, $M = m_e + m_h$ and E is the binding energy of the exciton, $\hbar k_e$*нач.* (*кон.*) is the moment of the electron before (after) the collision, $E_{kk'}$ and is the kinetic energy of the excitons before the collision. The formula determines:

$$\Delta E = \frac{1}{\mu}\frac{h^2}{8}\left(\frac{3}{8\pi}\right)^{2/3}\left(\frac{N}{V}\right)^{2/3} \qquad (6)$$

where N/V is the rate of generation of free media per unit volume. Experiments show that the dependence Δ E of on the intensity of excitation is $\Delta E' \sim I_0^{1/3}$.

Estimates according to formula (6) show that with a value of me=0.12m0, m_h = 0.6m_0 and A laser of ≈ 10 MW/cm^2, ΔE is equal to ~15 MeV, which is comparable to the experimentally found values for ΔE.

Based on the above, it can be argued that the L line, which dominates in the luminescence spectrum of InSe nanoparticles, is due to the exciton-exciton interaction.

4. CONCLUSION

InSe nanoparticles with sizes of 7 – 30 nm were synthesized by laser ablation of In atoms with a liquid solution of SeO_2. The bandgap of the InSe nanoparticle, calculated from the dependence, $\alpha^2 \sim f(h\nu)$ turned out to be equal to E_g=2.15 eV. In the luminescence spectra of InSe nanoparticles excited by the second harmonic of the Nd:YAG laser ($\hbar\omega = 2{,}34$eV), along with the emission of free excitons (λ=587 nm), long-wave radiation with a maximum of λ=592 nm associated with the interaction of excitons is also observed. The intensity of long-wave radiation by two orders of magnitude exceeds the intensity of free exciton radiation. The superliner dependence in the luminescence spectra indicates the presence of stimulated emission in InSe nanoparticles.

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