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# Absorption and luminescence spectra of nanoheterostructures InSe/GaSe

Vaqif M. Salmanov*[1], Ali G. Guseinov[1], Gusein B. Ibragimov[2],
Rovshan M. Mamedov[1], Fidan Sh. Akhmedova[1], Valida I. Hajiyeva[3]

[1]Baku State University, AZ1148 Baku, Azerbaijan,
[2]Institute of Physics of the Ministry of Science and Education, AZ1143 Baku, Azerbaijan
[3]Nakhchivan State University, AZ1148 Nakhchivan, Azerbaijan

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## Abstract

The transmission and luminescence spectra of InSe and GaSe nanoparticles and an InSe/GaSe nanoheterostructure synthesized by laser ablation in liquid were experimentally studied. It was shown that the growth of a wide-bandgap GaSe nanoparticle on a narrow-bandgap InSe nanoparticle results in the formation of a hybrid core/shell nanoheterostructure. An energy diagram of the InSe/GaSe nanoheterostructure is presented.

**Keywords**: InSe/GaSe nanoheterostructures, laser ablation, transmission and luminescence spectra.
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## 1. Introduction

The current stage of development of solid-state physics is characterized by the fact that the main objects of research are increasingly not massive semiconductor crystals, but thin films, multilayer thin-film structures, conducting threads and crystallites. Semiconductor nanoparticles are of increasing interest from the point of view of both fundamental research and practical application as materials for light-emitting diodes, transistors and solar cells. The unique functional properties of semiconductor nanoparticles are due to the effect of size quantization, which mani-

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**Corresponding author* – Tel.: (+994) 50 346 78 69
*e-mail*: vagif_salmanov@yahoo.com; ORCID ID: 0009-0009-9974-0618

fests itself depending on the physical properties of the nanoparticles, on their geometric dimensions. Along with varying the size, one of the key parameters allowing modification of the band structure is the shape of the semiconductor nanoparticle. In addition, the creation of nanoscale semiconductor heterostructures allows direct control of the spatial distribution of charge carriers [1]. Nanostructured materials are obtained by various methods: gas-dynamic, chemical, plasma, beam [2-9]. One of the most promising methods for synthesizing semiconductor nanoparticles is pulsed laser ablation in liquids [10-12]. Laser ablation of nanoparticles in liquids has attracted considerable interest due to its simplicity, the lack of need for surfactants, and good control over the size and shape of the synthesized nanoparticles. With this method, the characteristics of the synthesized nanoparticles can be influenced by many parameters, such as laser energy density, laser wavelength, pulse duration, and the type of colloidal solution.

Layered semiconductors play an important role in nanotechnology due to their unique properties and potential applications in various fields, including electronics, optoelectronics, and sensors. Layered semiconductors are materials consisting of thin layers of atoms bound together by weak van der Waals forces. These materials exhibit unique properties and are characterized by high two-dimensionality, which allows them to exhibit unique properties distinct from bulk semiconductors. Previously, we synthesized nanoparticles of layered indium selenide (InSe) and gallium selenide (GaSe) semiconductors using laser ablation of a solid target in liquid [13, 14].

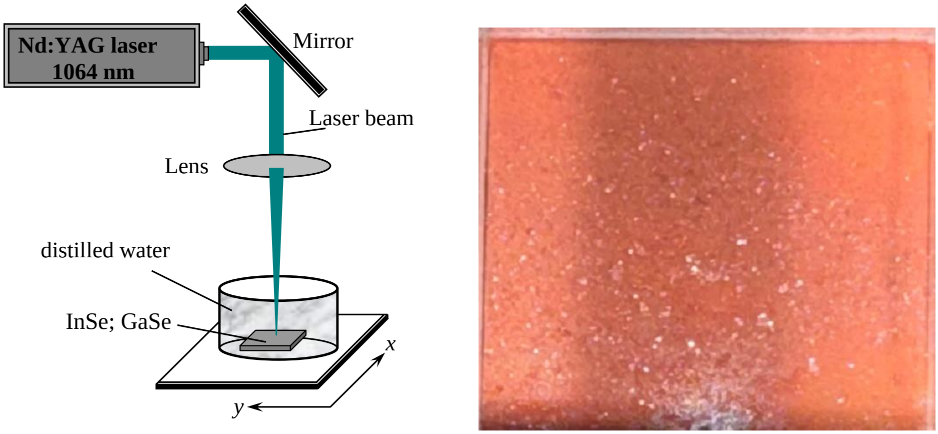
Using X-ray diffraction analysis, scanning electron microscopy, atomic force microscopy, and X-ray energy dispersive spectroscopy, we studied the internal structure and structure of the resulting nanoparticles. It was shown that InSe and GaSe nanoparticles retain the crystalline structure of the original material and have sizes of (2–20) nm. The absorption and luminescence spectra of InSe and GaSe nanoparticles under the influence of laser radiation were experimentally studied. The band gap width of InSe and GaSe nanoparticles, calculated using the formula [15]:

$$E_{nano} = E_g + \frac{2\pi\hbar^2}{2m_{eff}d^2},$$

where $m_{eff}$ is the effective mass, $E_g$ is the band gap for the bulk sample, and d is the nanoparticle size, were found to be $E_g = 2.15$ eV and $E_g = 2.64$ eV, respectively. These values are (0.6-0.9) eV larger than the band gap of the aforementioned InSe and GaSe crystals [16, 17]. This paper presents the experimental results of obtaining InSe/GaSe nanoheterostructures by laser ablation in a liquid medium and studying their optical and luminescent properties.

## 2. Experimental technique

InSe and GaSe crystals were grown using the Bridgman method. Because these crystals have a layered structure, it was possible to obtain very thin single-crystal plates by mechanically cleaving them from thick samples. This immediately produced mirror-like optical surfaces with thicknesses of ~ (20-50) microns. 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 ablation process was performed with an Nd:YAG laser with a wavelength of $\lambda$ = 1064 nm, a duration of 10 ns, a pulse energy of 135 mJ, and a repetition rate of 10 Hz for ~10 min., in a quartz cuvette with distilled water (Fig. 1, a). The optical transmission and luminescence spectra of InSe and GaSe nanoparticles and the InSe/GaSe nanostructure were studied using an M833 automatic double-dispersion monochromator (spectral resolution ~0.024 nm at 600 nm) with computer control and a detector recording radiation in the wavelength range of 250–2000 nm.



a) b)

**Fig. 1.** *a*-Scheme of the experimental setup for ablation of InSe, GaSe nanoparticles and InSe/GaSe nanostructure in a liquid medium, *b*- Colloidal solution of InSe/GaSe nanostructure synthesized by laser ablation in a liquid medium.

## 3. Experimental results and their discussion

To form the InSe/GaSe nanostructure, InSe nanoparticles were first synthesized, followed by GaSe nanoparticles synthesized in a colloidal InSe solution under vigorous magnetic stirring. Figure 1b shows an image of the colloidal InSe/GaSe nanostructure solution dried on a glass substrate.

The transmission spectrum of the colloidal InSe/GaSe nanostructure solution dried on a glass substrate is shown in Figure 2. The transmission spectra of InSe and GaSe nanoparticles are also shown for comparison. As can be seen from the figure, the transmission spectrum of InSe nanoparticles is located in the long-wavelength region of the spectrum, with an absorption band edge at a wavelength of λ = 576 nm (curve 1). The absorption band edge of GaSe nanoparticles is located in the shorter-wavelength region of the spectrum at λ = 470 nm (curve 2). In contrast to the transmission spectra of InSe and GaSe nanoparticles, the transmission spectrum of the InSe/GaSe nanostructure covers a wider range in the interval from 400 nm to 650 nm (curve 3).

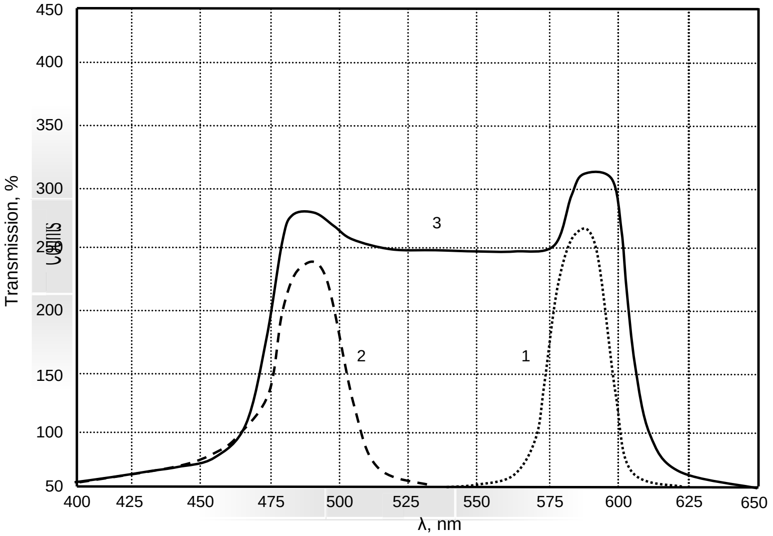


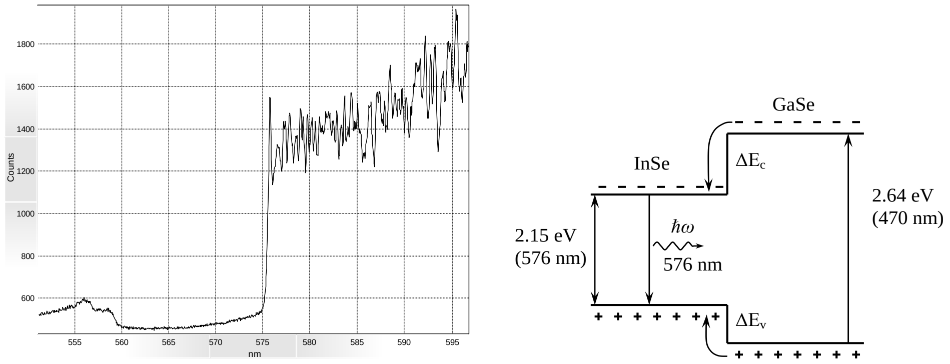
**Fig. 2.** Transmission spectra of InSe nanoparticles (curve 1), GaSe (curve 2) and InSe/GaSe nanostructure (curve 3).

Figure 3a shows the photoluminescence spectrum of an InSe/GaSe nanostructure excited by the third harmonic (ħω=3.51 eV) of a Nd:YAG laser. As can be seen from the figure, the emission maximum corresponds to a wavelength of 576 nm, and the line half-width is very narrow, amounting to ~5 Å.

In our opinion, hybrid core/shell nanoheterostructures are formed in a colloidal solution of InSe/GaSe nanoparticles obtained by laser ablation [18, 19]. When a shell of the wider-bandgap GaSe semiconductor is grown on the narrow-bandgap InSe semiconductor, the crystal lattice of the GaSe nanoparticles transforms into the lattice of InSe nanoparticles without disrupting the periodicity.

The main evidence for the formation of a core-shell nanoheterostructure is the presence of a wide range of the InSe/GaSe transmission spectrum (400-650 nm), encompassing the transmission spectra of InSe and GaSe, and an increase in luminescence intensity at a wavelength of λ = 576 nm, coinciding with the emission of

InSe nanoparticles, as well as the absence of emission in the region of GaSe nanoparticles (λ = 470 nm). This is also evidenced by the image of a nanoheterostructure consisting of various InSe and GaSe nanostructures with different band gaps (see Fig. 1b). As can be seen from the figure, the InSe nanostructures (dark band) are enveloped by a GaSe nanostructure (light red band).



a) b)

**Fig. 3.** *a*-Photoluminescence spectrum of InSe/GaSe nanoparticles, *b*-Energy diagram of nanoparticles.

In our opinion, the absence of luminescence in the InSe/GaSe nanoheterostructure over a wide range of the transmission spectrum can be explained as follows. Luminescence is known to be the inverse of absorption. An electron occupying a state with an energy higher than that under equilibrium conditions undergoes a transition to an unoccupied low-energy state; in this case, all or most of the energy difference between these states can be emitted as electromagnetic radiation. Therefore, most optical transitions (band-to-band, excitons, impurity transitions, and others) can also proceed in the opposite direction, producing characteristic radiation. However, there is an important difference between the information that can be obtained by studying transmission (absorption) and that which can be obtained by studying emission in a semiconductor. Absorption processes can involve all states in the semiconductor on both sides of the Fermi level, resulting in a broad spectrum, while radiative transitions occur between a narrow band of states containing thermalized electrons and a narrow band of empty states containing thermalized holes, and hence create a narrow spectrum [20].

Figure 3b shows the core/shell energy diagram of an InSe/GaSe nanoheterostructure, where a narrow-bandgap InSe nanoparticle serves as the core and a wide-bandgap GaSe nanoparticle serves as the shell. Electron-hole pairs in GaSe, photogenerated under laser radiation ($\hbar\omega$=3.51 eV), undergo partial separation of charge carriers into electrons and holes. Electrons initially located in the conduction band of GaSe upon relaxation migrate to the conduction band of InSe, while holes located in the valence band of GaSe migrate to the valence band of InSe. As a result of radiative recombination of electron-hole pairs, photoluminescence with a maximum at λ=576 nm is observed in the region of the InSe nanoparticles. A heterojunction formed by wide-bandgap and narrow-bandgap semiconductors, in which the conduction and valence band offsets have opposite signs, is energetically favorable for the electron and hole to localize in one part of the heterostructure—the narrow-bandgap semiconductor. In a colloidal InSe/GaSe solution, where the core is a narrow-bandgap InSe nanoparticle and the shell is a wide-bandgap GaSe nanoparticle, a type I oscillator junction is formed [10].

## 4. Conclusion

InSe and GaSe nanoparticles and InSe/GaSe nanoheterostructures were synthesized using liquid laser ablation. The ablation process was performed using a Nd:YAG laser with a wavelength of λ = 1064 nm, a pulse duration of 10 ns, a pulse energy of 135 mJ, and a repetition rate of 10 Hz for approximately 10 min in a quartz cuvette containing distilled water. Hybrid core/shell nanoheterostructures were shown to form in a colloidal solution of InSe/GaSe nanoparticles obtained by laser ablation. The transmission spectrum of the InSe/GaSe nanostructure extends from the edge of the fundamental absorption band of the InSe nanoparticle to the edge of the fundamental absorption band of the GaSe nanoparticles and covers a range of 400-650 nm. A core/shell energy diagram of an InSe/GaSe nanoheterostructure has been constructed, using a narrow-bandgap InSe nanoparticle as the core and a wide-bandgap GaSe nanoparticle as the shell. The luminescence of the InSe/GaSe nanoheterostructure, peaking at 576 nm, is due to the localization of electron-hole pairs generated by laser radiation in the narrow-bandgap region of the heterojunction, specifically in the region of the InSe nanoparticles.

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