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INFRARED LUMINESCENCE OF GeS: Nd LAYERED CRYSTALS

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Abstract. In presented work luminescence properties of GeS alloyed with Nd were studied for the first time. Investigation of photoluminescence and excitation spectra were carried out at room temperature. Our investigation show that intense luminescence peaks observed in the infrared region are due to the intracenter-luminescence lines of neodymium ions in wavelength ranges of 1100-1180,1250-1350 and 1400-1700 nm. These lines are due, to the $^4F_{s/2}$ - $^4I_{11/2}$, $^4F_{s/2}$ - $^4I_{13/2}$, $^4F_{s/2}$-$^4I_{15/2}$ transitions, respectively.

Keywords: *Photoluminescence, excitation, layered crystal, germanium sulfide, neodymium, ntracenter transitions.*

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1. Introduction

Semiconductor materials are materials that have applications in various fields. The study of their functional properties further expands the possibilities of application (Georgobiani *et al.*, 2010; Tagiev *et al*., 2012; Alekperov *et al.*, 2019, 2021; Madatov *et al.*, 2020; Asadullayeva *et.al*, 2021). Layered semiconductor crystals are considered promising materials for the next generation of technological devices due to their optoelectronic, photovoltaic, thermoelectric and other physical properties (Buscema *et al*., 2015; Furchi *et al.*, 2014; Xia *et al.*, 2014; Alakbarov *et al.*, 2021, Tagiyev *et al*). The GeS compound with an orthorhombic crystal structure is in the center of attention among the layered crystals due to its specific anisotropic properties (Lan *et al.*, 2015; Makinistian & Albanesi, 2006; Gomes & Carvalho, 2020). According to ref. (Lan *et al.*, 2015) GeS nanoribbon is a promising semiconductor nanomaterial for high-performance broadband visible light sensors. In the ab initio calculation of electronic structure using LDA and GGA with and without taking into account spin-orbit interaction in contrast to other previous experimental and theoretical works was observed several critical points in the valence and

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conduction bands, which compete in determining the gap (Makinistian & Albanesi, 2006). In the theoretical work (Gomes & Carvalho, 2020) discussed the appearance of spin-orbit splitting, piezoelectricity, and ferroelectricity as a result of the polar nature of monolayers.

Photoluminescence properties of $Ge_{1-x}S_x$ chalcogenide glass were studied in work (Seki *et al.*, 2003). It has been shown that luminescence occurs due to electron-hole recombination. The intensity of luminescence depends on the concentration of defects. In (Pan *et al.*, 2011) reports on the technology and optical properties of amorphous GeS_x (x = 2, 4, 6) thin films. The value of the band gap of the films was determined from the absorption and transmission spectra. Anisotropic optical properties of layered GeS were studied in (Tan *et al.*, 2017). In paper (Postorino *et al.*, 2020), the cathodoluminescence properties of the layered germanium sulfide crystal with a thin layer of boron nitride film were studied. An emission peak with an energy of 1.69 eV was observed in the visible region. It was shown that this maximum can be explained by the radiative recombination of the first free bright bound exciton associated with the mixing of direct transitions near the Γ point. In (Ulaganathan *et al.*, 2015), provided information on optoelectronic properties of a multilayer GeS nanosheet. It is showed that the wide spectral range and long-term stability properties of this material make it a highly qualified candidate for future optoelectronic applications. The results of first-principles calculations and photoluminescence properties are presented within the framework of the density functional theory of the electronic spectrum of GeS crystal. It has been shown that the intensity of luminescence observed at 695 nm increases sharply by introducing a Gd atom into the GeS crystal. This is due to the fact that the internal transition of the GeS crystal and the Gd atom falls on the same wavelength (Dashdemirov *et al.*, 2021).

From all the listed research works, obviously that despite the fact that there are a lot of studys (Seki *et al.*, 2003) in the literature devoted to the optical properties of a layered GeS crystal, almost luminescent studies is not yet reported for GeS:Nd. Taking into account that by doped neodymium atom in germanium sulfide it is possible to obtain optical amplification and lasing, conducting luminescent studies is of great interest and importance.

2. Materials and methods

2.1. Synthesis of GeS:Nd layered crystal

The synthesis of GeS was carried out with the aim of using it for growing single crystals by the Bridgman method. One of the simplest and most common methods for obtaining semiconductor compounds IV-VI is the method of fusing the initial components taken in stoichiometric ratios. By the same method, we synthesized GeS compounds doped with neodim rare earth elements. The starting materials were germanium (99.9%) and sulfud (99.9%). Neodima impurities were introduced into the batch before synthesis. All single crystals obtained by us were grown by the Bridgman method by slow cooling of an ingot at a constant temperature gradient. GeS: Nd^{+3} compounds were synthesized by direct fusion of elements in evacuated ones to 10^{-3} mm Hg. Art. pointed quartz ampoules 12–20 mm in diameter. Given the high vapor pressure of sulfur, a two-zone semi-horizontal furnace was used in the synthesis of the GeS compound. The ampoules were placed in the oven so that parts of it were outside the oven. The furnace temperature was raised to 400 ℃ (the melting point of germanium sulfide is 820 ℃) and maintained for 2 hours. Then the furnace temperature was raised to 1000 ºC under the condition of the ampoule vibration. When traces of sulfur disappeared in the cold part of the ampoule, it was completely pushed into the furnace and covered with asbestos. Kept at this temperature also for 2 hours, after which the oven temperature was lowered to 900 ºC, maintaining that for 2 hours, and then the oven was turned off.

2.2. Growing GeS:Nd layered crystal

The temperature difference in the furnace, between the upper and lower parts, is 213-173 ºC. After the ampoule is placed in the furnace, the furnace temperature rises above the melting point of the substance and at this temperature (~ 820 ºC) the ampoule is kept for 2-3 hours. Then the motor is turned off and the oven starts to move at a certain speed (1-5 mm/h), while the ampoule is rigidly fixed. Perfect single crystals were obtained at a furnace speed of 3 mm/h. An ingot is obtained single-crystal if a single nucleus spontaneously forms in the sharpened part of the ampoule. Sometimes several nuclei appear, but with their further growth, some of them gradually pinch out and one or more large single-crystal grains grow in the direction of the temperature gradient coinciding with the axis of the ampoule. As you move to the bottom of the oven, the temperature drops to room temperature. Due to this, there was a constant and slow transition of a substance from a molten to a solid state.

2.3. Photoluminescence properties

Photoluminescence (PL) and excitation (PLE) measurements were performed using PL/PLE/Raman spectrometer (Tokyo Instruments, Inc.) at room temperature. The emission of the samples was excited by different laser beams (532 nm, 642 nm and 785 nm). Photoluminescence from the sample was dispersed through a grating (100 $g \cdot mm^{-1}$) monochromator MS 3401 I (SOL Instruments, Inc) and detected by CCD multiplier DU 491A-1.7 (Tokyo Instruments, Inc.). PL spectra were plotted after correcting the spectral sensitivity of the detection system.

3. Results and discussion

3.1. Photoluminescence properties

In present work, photoluminescence and excitation properties of a GeS layered crystal alloyed doped with the Nd^{+3} ion was stydied for the first time. Fig. 1 shows the photoluminescence spectra of undoped (solide line) GeS and neodymium activated GeS layered crystals, recorded at 300 K.

Emission spectra of undoped GeS layered crystals cover the wavelength range of 1200-1400 nm, with peaks at 1220 and 1300 nm. Luminescence spectra GeS:Nd^{+3} recorded upon excitation by different laser sources with λ_{exc} = 532 (1), 642 (2) and 785 (3) nm. How we can see from comparison of photoluminescence spectra in dependence of the excitation wavelength GeS:Nd^{+3} crystal possess nonequivalent luminescence centers, which are characterized by somewhat different intensities.

The lowest intensity photoluminescence was observed with a 532*nm* laser, and the strongest with a 785 nm laser. The intense luminescence peaks observed in the infrared region are due to the intracenter-luminescence lines of neodymium ions in wavelength ranges of 1100-1180,1250-1350 and 1400-1700 nm. These lines are due, to the $^4F_{s/2}$ - $^4I_{11/2}$, $^4F_{s/2}$ - $^4I_{13/2}$, $^4F_{s/2}$-$^4 I_{15/2}$ transitions, respectively (Sviridov *et al.*, 1976).

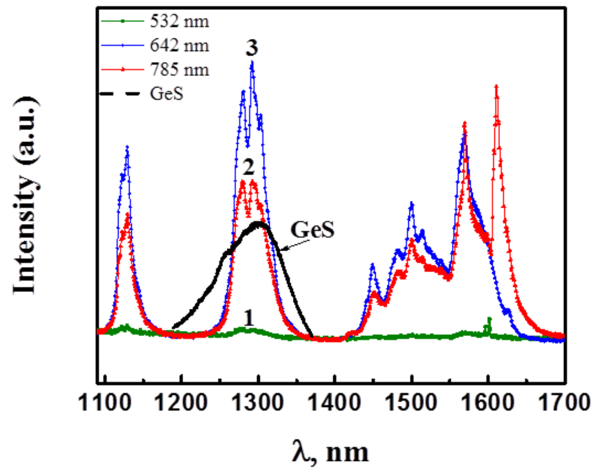

Fig. 1. PL spectra of pure GeS (solid line) and GeS:Nd at room temperature.
(1-532 nm, 2-642 nm, 3-785 nm laser)

It has been observed that the peak of the pure GeS crystal at 1300 nm and the $^4F_{3/2}$--$^4I_{13/2}$ intraatomic transition of the Nd-doped GeS crystal fall at the same wavelength. In the spectrum of the GeS Nd crystal, the peak of the pure crystal becomes completely invisible. This is related to the transfer of the energy of the absorbed photon in the pure crystal. This important fact make this compound practically useful in optoelectronics (Asadullayeva & Eyyubov, 2019; Asadullayeva *et al.*, 2021).

3.2. Excitation properties

The main absorption bands at 895, 908 , 915, 935 and 950 nm were observed in the excitation spectrum obtained by monitoring the 1100-1300 nm fluorescence region at room temperature of Nd^{3+} and are shown in Fig. 2. It is evident that the absorption bands in the infrared contribute most of the usable energy to the fluorescence output.

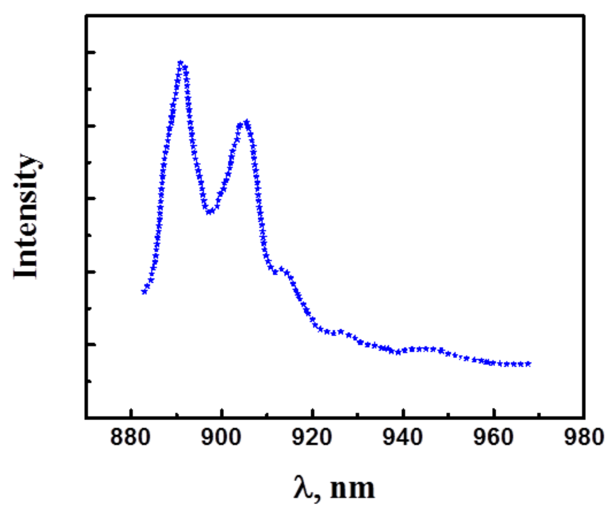

Fig. 2. Excitation spectrum of GeS: Nd at room temperature

The spectrum exhibits characteristic excitation bands determined by the f-f transitions in the Nd^{+3} ion. Two intense peaks are observed at 895 nm (11173.18 cm^{-1}) and 908 nm (11013.22 cm^{-1}) at the PLE spectra, which correspond to transitions from the lower Stark sublevel of the $^4I_{9/2}$ state to two sublevels of the $^4F_{3/2}$ state ($^4F_{s/2}$ splitting of 159 cm^{-1}) (Sviridov *et al.*, 1976).

As we already know, using excitation spectrum of luminescence it is possible to determine the positions of energy levels. Luminescence peaks, transitions and positions of the energy levels of the Stark component by the multiplet are given in Table 1.

Table 1. Position of luminescence bands in the spectrum GeS: Nd

Length waves, nm	Length waves, sm^{-1}	Transition	position of multiplet levels. sm^{-1}
1120	8928	$^4F_{3/2}$--$^4I_{11/2}$	2245
1128	8865	$^4F_{3/2}$--$^4I_{11/2}$	2308
1278	7824	$^4F_{3/2}$--$^4I_{13/2}$	3349
1295	7722	$^4F_{3/2}$--$^4I_{13/2}$	3451
1301	7686	$^4F_{3/2}$--$^4I_{13/2}$	3487
1448	6906	$^4F_{3/2}$--$^4I_{13/2}$	4267
1500	6631	$^4F_{3/2}$--$^4I_{15/2}$	4542
1513	6609	$^4F_{3/2}$--$^4I_{15/2}$	4564
1541	6489	$^4F_{3/2}$--$^4I_{15/2}$	4684
1568	6377	$^4F_{3/2}$--$^4I_{15/2}$	4796
1591	6285	$^4F_{3/2}$--$^4I_{15/2}$	4888
1609	6238	$^4F_{3/2}$--$^4I_{15/2}$	4935
1625	6153	$^4F_{3/2}$--$^4I_{15/2}$	5020
1778	5624	$^4F_{3/2}$--$^4I_{15/2}$	5549

4. Conclusions

The excitation and luminescence properties of Nd 3^+ germanium sulfide crystal have been studied experimentally. Our research has shown that neodymium ions can be successfully doped into germanium sulfide, and due to its intracenter transitions luminescence spectrum has very intensive maxima. On the other hand, the optical transitions of undoped GeS in wavelength (1300 nm) overlapping with the radiation lines of Nd^{+3} atom at the same energy. In this case, absorbed photon energy in the wide region of GeS compound is transform to the Nd^{+3} ions transition $^4F_{3/2}$--$^4I_{13/2}$. This result suggests that it will be possible to obtain fiber-optic amplification and lasing by doped neodymium atom in germanium sulfide.

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