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Article



Israil Musa Oglu Mammadov

Azerbaijan Pedagogical State University
PhD of physical sciences, Baku Azerbaijan
israil.memmedov.66@bk.ru

Rasim Kochari Oglu Huseinov

Ganja State University
Phd of physical sciences, associate professor

Rizvan Muhammed Ali Oglu Imanov

Ganja State University
Phd of physical sciences, associate professor

Vusala Sirac Kizi Zarbalieva

Azerbaijan State Agrarian University
Senior Lecturer Ganja .Azerbaijan

Leyla Elman Kizi Usubova

Azerbaijan State Agrarian University
Assistant, Ganja Azerbaijan

PREPARATION AND PHOTO LUMINESCENT PROPERTIES OF LAYERED GES SINGLE CRYSTALS

Abstract: One of the most interesting phenomena that has provided a lot of information about defects in single crystals is photoluminescence (PL). This paper presents data on edge and near-infrared (IR) luminescence of layered GeS single crystals. In the layered high-resistivity semiconductor compound GeS, local centers have been studied using both photoelectric and optical methods. Comprehensive studies of photoelectric and optical properties indicate that the recombination scheme of GeS is quite complex and contains a number of local levels.

Key words: photoluminescence, luminescence, PL spectra, single crystals, rare earth elements, semiconductor compounds.

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Introduction

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Semiconductor compounds of the AIVBVI type are considered promising materials for use in various fields of electronics, such as thermionic elements, solar cells, memory elements and others, or have already found their application. The fundamental

characteristics of these compounds, such as a narrow band gap, high dielectric constant, relatively high radiation resistance, high carrier mobility, and the predominance of ionic bonding, increase the possibility of their use. To study the energy spectrum of the bottom of the conduction band and the top of the valence band, the dispersion law, and the mechanism of charge carrier scattering in

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semiconductor compounds and their hard alloys, doping with donor and acceptor impurities is widely used. By doping, filling electron or hole states, one can change the location of the Fermi level, and this significantly simplifies the calculation of band parameters.

From this point of view, doping the AIVBVI type GeS binary compound with rare earth elements or obtaining solid solutions of low concentrations and a comprehensive study of their physical properties is of interest. The resulting substances containing rare earth elements (REE) are widely used in the manufacture of energy converters and photoresistors that are resistant to radiation, pressure and humidity. The resulting materials with the participation of rare earth elements, in which the 4f-5d-6s transition occurs, due to the ease of complete filling of the 4f level of the electronic structure, and the appearance of variable valence due to the movement of electrons at the 4f level in atoms, are interesting objects of research. From this point of view, melts and compounds based on the participation of rare earth elements make it possible to obtain new promising materials with the required physical properties, which is important for their research. Alloys of the GeS and Ge_{0.995}Nd_{0.005}S system were synthesized from the starting elements in quartz ampoules evacuated to 0.1333 Pa. The synthesis was carried out in two stages: initially, ampoules with the substance were heated at a rate of 4-5 degrees/min. to the melting point of selenium and kept at this temperature for 3-4 hours, after which the temperature

was raised to 950-1000°C, depending on the composition, and kept for 8-9 hours. When synthesizing ternary alloys of the Ge_{0.995}Nd_{0.005}S system, elements of special purity were used as starting components.

The synthesized samples for complex physicochemical analysis and electrophysical studies were annealed for 100-140 hours. Homogenizing annealing of the resulting single-phase samples was carried out in an environment of spectrally pure argon at 800 K. After annealing, samples with dimensions of 2 x 4 x 18 mm were cut from the crystal ingots in an electric spark installation. The interaction in the Ge_{0.995}Nd_{0.005}S system was studied using differential thermal analysis (DTA), X-ray diffraction (XRD), microstructural analysis (MSA), as well as microhardness measurements and density determination. XRF was carried out on a model D-2 PHSER X-ray device using CuK α radiation and a Ni filter.

The PL spectra excited by laser radiation ($\lambda=6328\text{\AA}$, maximum intensity $L=1020\text{ kV}/(\text{[cm]}^2 \text{ s})$) were measured in the temperature range $T=77-300\text{ K}$ using an MDR-2 and DFS-13 monochromator. Registration was carried out according to a standard scheme using synchronous detection. FEU-62 and photoresistor PvS served as radiation detectors. A preamplifier assembled on the basis of a low-noise microcircuit was included as a matching element between the receiver and the U2-8 amplifier.

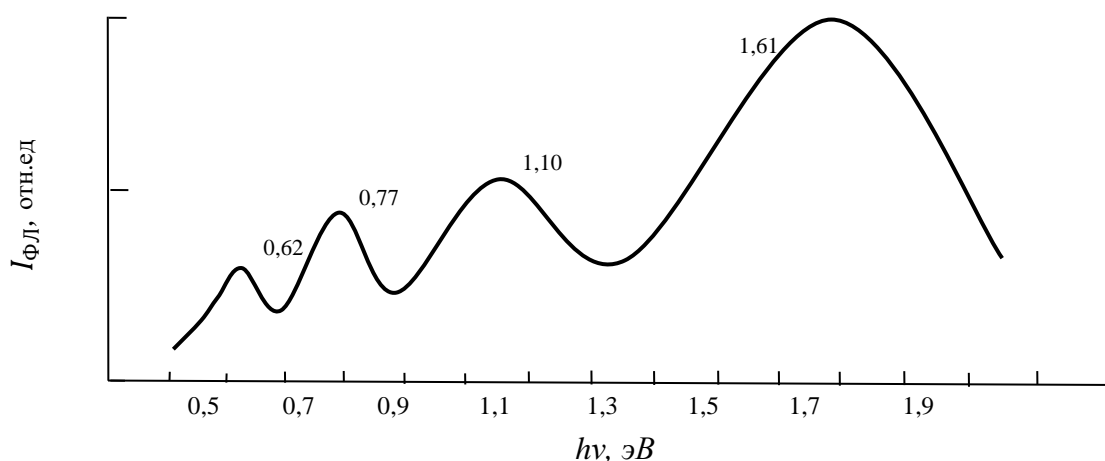


Fig.1. PL spectrum of a GeS single crystal at 77K.

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microcircuit was included as a matching element between the receiver and the U2-8 amplifier.

In the PL spectra at temperatures $77\text{K} \leq T \leq 300\text{K}$ three bands with maxima of 0.62, 0.77 and 1.1 eV are observed (Fig. 1). The ratio between the intensities of the bands varies from sample to sample, however, in the same sample, the intensity of these bands remains practically unchanged when the temperature changes from nitrogen to room temperature.

REE atoms (in the particular case Nd atoms), introduced as impurities into GeS, form energy levels inside the band gap. Luminescence of rare earth elements is intracenter. The radiation from these centers is a set of characteristic lines. REEs have an incomplete 4f electron shell, which is shielded by

more outer shells. Each rare earth element has its own characteristic spectrum, which depends on the degree of filling of this shell. Under the influence of an external field, splitting of energy levels appears. Optical, including luminescent spectra of rare earth elements are determined by transitions of f-electrons, which are well screened by 5d electrons. The position and number of excited states depend on the number of electrons in the 4d shells.

As can be seen from Fig. 2, the spectrum of a layered GeS single crystal activated by Nd³⁺ atoms consists of separate groups of lines. Analysis of the luminescence spectrum allows one to obtain information about the structure of the optical rare-earth center, in particular, to determine its symmetry

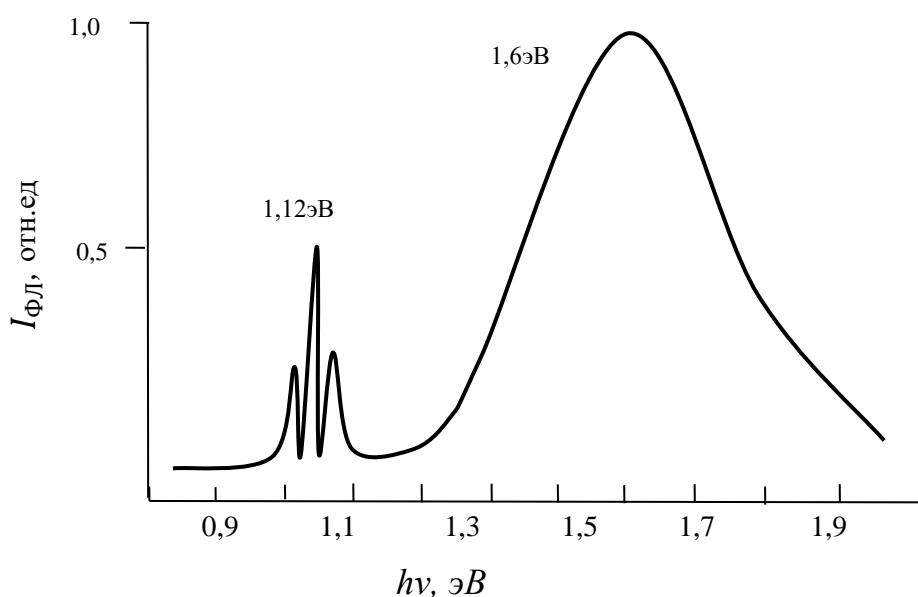


Fig. 2. The FL spectrum of a Ge_{0.995}Nd_{0.005}S single crystal at 77K.

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In contrast to ordered systems, in disordered systems, including “soft” crystals, instead of a group of narrow lines, a blurred band with more or less pronounced maxima is observed. They look as if the lines of the crystal spectrum have increased in width, remaining in the same place, partially superimposed on each other.

The tendency of rare earth elements to oxidize promotes glass formation during cooling of a Ge_{1-x}Nd_xS single crystal ($x=0.005$). The most common glass former is SiO₂, from which quartz ampoules are made, where single crystals are grown.

Thus, in the “soft” GeS matrix, the optical centers - Nd³⁺ impurity atoms are in their own specific field, and this position manifests itself in the form of elimination of spectral lines. Unlike other rare earth elements, it is possible to obtain high radiation powers on neodymium ions due to a four-level scheme; in rare earth elements, in addition to 4f → 4f transitions, allowed electric dipole transitions 5d → 4f are observed [4]. Due to the fact that these transitions are resolvable, the intensity of the corresponding bands in comparison with the 4f → 4f lines will be high, and the emission time will be short. But since the crystal field has a greater influence on the 5d shell

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(than on the 4f shell), the bands will be wide, and their position will depend on the matrix.

As can be seen from Fig. 2, at a low concentration ($x=0.005$) of Nd³⁺, REE can be considered as an independent set of emitting centers. Obviously, in this case, the luminescence intensity will be linearly related to the REE concentration. When a certain concentration of rare earth elements increases, the interaction of ions and resonant energy transfer between Nd³⁺ ions begins. During resonant transmission, the probability of non-radiative energy loss increases. Therefore, the intensity of REE luminescence decreases with increasing concentration. At low concentrations of Nd³⁺, we can assume that spontaneous radiative transitions

determine the dynamics of luminescence decay. At high Nd³⁺ concentrations, non-radiative transitions make an additional contribution to the luminescence decay.

Thus, a study of the PL spectrum of single crystals shows that

1. The recombination scheme of a GeS single crystal is quite complex and contains local levels.

2. The luminescence of rare earth elements is intracenter and the emission of these centers is a set of characteristic lines.

3. With increasing REE concentration, the probability of non-radiative energy loss increases and the intensity of luminescence associated with REE decreases.

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