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EFFECT OF THE GAMMA IRRADIATION ON THE STRUCTURE AND EXCITON PHOTOCONDUCTIVITY OF LAYERED GeS:Sm SINGLE CRYSTAL

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Abstract. The layered GeS:Sm single crsytal were grown by Bridgmen method and the structure and photoconductivity spectra have been investigated before and after low dose gamm irradiation (40 krad). It was determined that the lattice parameters did not change under the influence of low dose gamma irradiation, but eleminated defects of various natures. Exiton photoconductivity detected in the temperature range of 200-300 K increase in the photoconductivity spectra of layered GeS:Sm single crystal.

Keywords: *layered single crystal, crystal structure, gamma irradiation, exiton photoconductivity, rare-earth element, Frenkel defects.*

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1. Introduction

In the 1970s, holographic recordings on the surface of the GeS layered crystal, electric switches, solar cells based on the GeS layered crystal, and linearly polarized light detectorsincreased interest in the crystal (Wiley, 1979). Rapid development of material technology has led to the use of silicon as a basic element in semiconductor electronics, creating the conditions for large-scale production of high-purity silicon. Therefore, interest in alternative semiconductor compounds, including GeS crystals, has decreased.

Starting from 1990s, nanoelectronics began to develop rapidly as an independent science.The use of silicon alone was not sufficient to ensure the massive production of low dimensional, multifunctional devices. Among these materials, GeS layered single crystal was no exception as a promising material.The simple growth technology of layered single crystals (particularly, the sublimation method) and the acquisition of surfaces with a highpolishing degree have revived interest in this type of crystal.

Over the last decade, thedevelopment of nanostructures (Chun *et al.*, 2012) and high-frequency field-effect transistors (Ulaganathan *et al.*, 2016) based on GeS layered single crystal increase an interest to these types of semiconductors.

Different dopants, as well as rare-earth metals (REM) are used to expand application capabilities of crystals including layered semiconductor compounds. Recently, great achievements have been made in the direction of the synthesis of rare-earth doped nanomaterials with tunable morphology and luminescent-optical properties

Therefore, REM doped functional materials are intesively investigated by researchers (Chen *et al.,* 2014; You *et al.,* 2018; Bouzigues *et al.,* 2011; Huang *et al.,* 2019).

Space electronics is one of the rapidly growing areas of electronics. The development of radiation-resistant devices and electronic devices is one of the priorities of the world leading scientific centers and universities in the deeper study of both the Earth atmosphere and the lunar surface, and the transmission of information to Earth without distortion.In this sense, radiation, including gamma radiation, is widely used to test the resistance of semiconductor nanomaterials to cosmic radiation (Abbasova *et al.,* 2010). Until the 1980s, there was a misconception that small doses of radiation did not affect the physicochemical properties of substances, including semiconductor crystals, or that they had no theoretical or practical significance.Due to degradation,the system loses its properties under the influence of high doses of radiation (Smirnov, 1977).However, improvements in research methods, devices, and equipment have proved this to be wrong.

It was found that radiation at doses below 10^6 rad are effectively influence to structure, physical and chemical properties of many solids, including semiconductors and this phenomenon is called the “small dose” effect (Mak, 1989).The aim of the study is to investigate the effect of both theSm rare earth metal dopant and low-dose (30 krad) gamma radiation on the structure and exciton photoconductivity of the GeS layered single crystal.

2. Experiments

Germanium polycrystal with 50 Om·cm specific resitivity, “B-5” sulfur and “Sm-1” samarium were used to synthesis GeS:Sm polycrystal. Stoichiometric mixtures were weighed electronic scale, then filled into quartz ampoule with diameter 10-15 mm and 10^{-3} torr vaccum were obtained in the ampoule.

The synthesis was carried out in two stages: In first stage, the ampoule wea heated up to 300°C with 3-5 deg/min rate and kept at this temperature for 10-12 hours. In the second stage, the temperature of the furnace increased to 1000°C with 2-3 deg/min rate and kept this temperature for 18-20 hours, and then the furnace was cooled together with sample. Structural parameters of the synthesized GeS:Sm polycrystal were investigated at D8 ADVANCE x-ray diffractometer. Measurement was carried out with CuK_{α} anticatod (λ=1.5418 Å) at the condition of 10-100° range and 0.01° steps (Madatov *et al.,* 2015).

As a result of investigations, it was determined that two method are are more suitable for growing a single crystal of germanium monosulfide: Bridgman and sublimations methods.

Although the sublimation method is short-time (20-24 hours) and allows the production of larger (12x15 mm^2), high-quality layered crystals, the Bricman method was used due to problems with the transfer of heavy Sm atoms.

The photoconductivity measurements of GeS:S layered single crystal was performed optical device assembled on the basis of MDR-2 monochromator. Photocurrent generated in the crystal was amplified by an E6-13 teraohmmeter and recorded by an H-307/2 self-recording device. Nitrogen cryostat was used for temperature measurements in the range of 80-350 K to measure photoconductivity spectra of the sample. The temperature of the sample was controlled using platinum sensor.

Gamma irradiation of the sample was performed at room temperature at РХУНД-20000 device using Co^{60} source. The radiation flux was $1.4 \cdot 10^{11}$ quantum/sec·cm^2, the energy of gamma quantums was 1.25 MeV, radiation dose was $D_\gamma = 90$krad (Alekperov, 2015).

3. Results and discussion

It is known that GeS singe crystal is photosensitive, direct band-gap semiconductor material in the visible and infrared reagion of the spectrum. Recently, a supercapacitor based on the GeS nanostructure has once again confirmed its research potential (Chun *et al.*, 2012). Moreover, rare earth elements have the property of creating beam recombination centers in different semiconductor matrices (Dieke *et al.*, 1968).

It is clear that REE atoms can affect the photoelectric and optical properties of germanium monosulfide. For this purpose, both the structure of the Sm doped GeS:Sm layered single crystal and the photoconductivity (PC) spectrum over a wide temperature range (80−350K) were studied.

X-ray diffraction analysis showed that Sm atoms do not affect the space symmetry of the GeS crystal (Pcmn−2hD16), but the lattice parameters slightly changed. As for the PC spectrum, in contrast to the GeS single crystal, additional maxima are recorded in the region of impurity conductivity (E = 1.3 eV) in the temperature range of $200\text{K} \le T \le 300\text{K}$ (Fig. 1*a*).

Since the 1980s, the small-dose effect has been used to influence the physical and chemical properties of both metals and semiconductors, expanding their practical application (Mak, 1989). For this purpose, x-ray diffraction analysis of both GeS and GeS:Sm layered mono-crystals, as well as PC spectra were studied before and after low-dose (30 krad) gamma irradiation. As can be seen from Fig 1b, the maximum at the region of impurity conductivity loses in the PC spectrum of the GeS: Sm layered single crystal after gamma radiation.

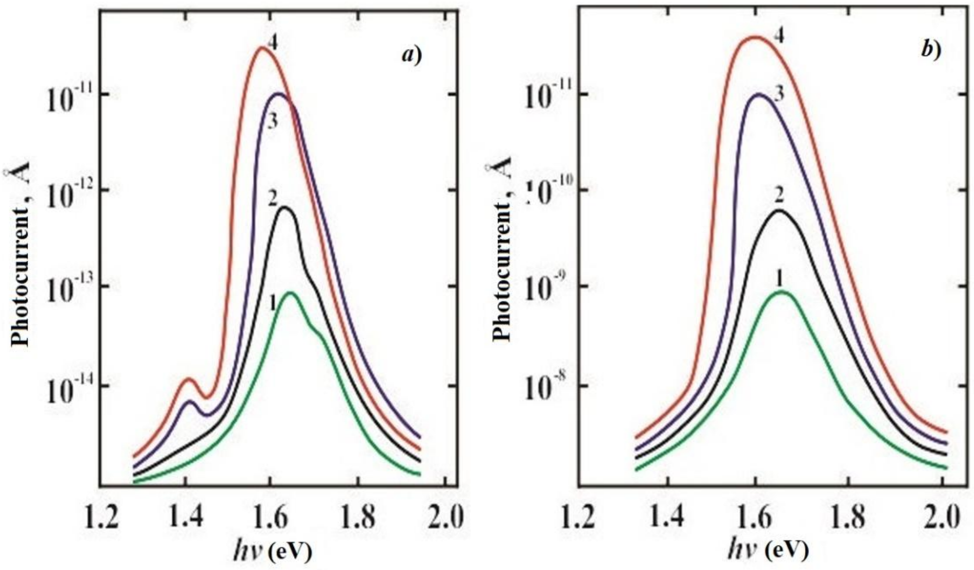

Fig 1. Photoconduvtivity spectra of GeS:Sm layered single crystal
a) Before irradiation, *b*) After 30 krad irradiation

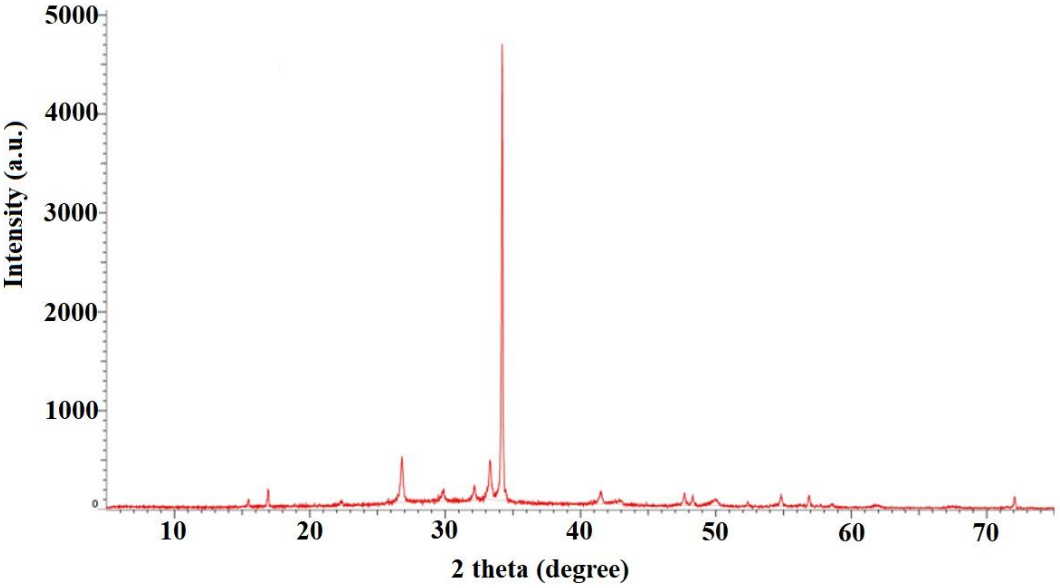

Fig. 2*a*. X-ray diffarction spectra of GeS crystal (before irradiation)

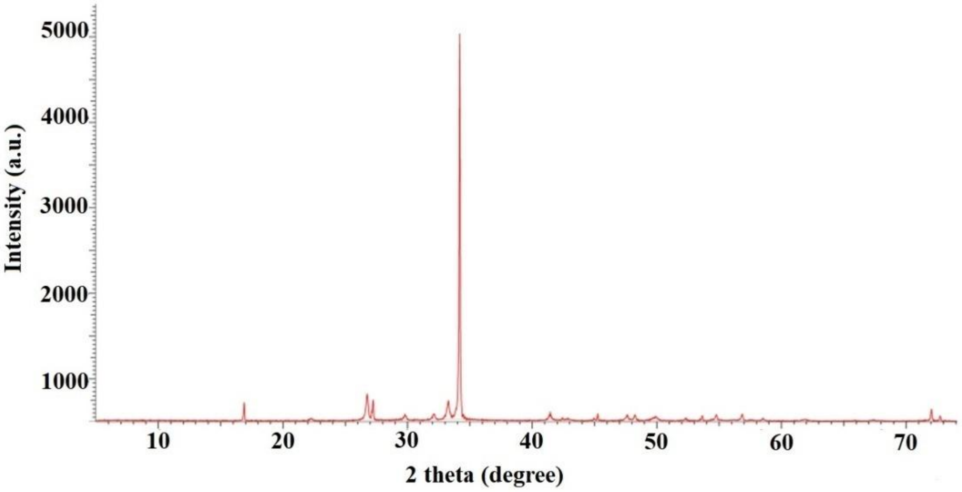

Fig. 2*b*. X-ray diffarction spectra of GeS crystal (after irradiation)

It was found that after gamma radiation, the intensity of reflections in the diffractograms of the GeS crystal increased by ~2 times (Fig. 2.*a*, *b*), while in the GeS:Sm crystal this index is ~10 times (Fig. 3.*a*, *b*).

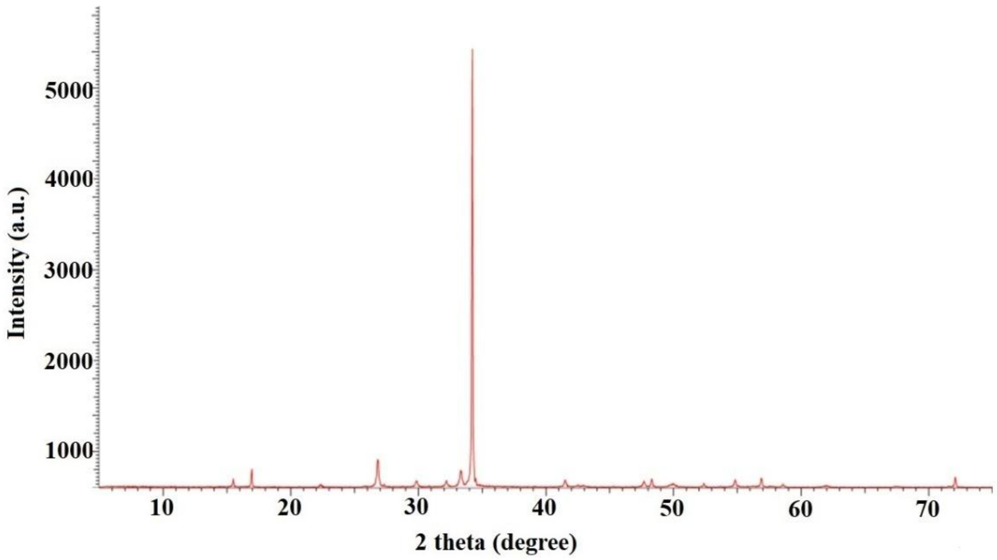

Fig. 3*a*. X-ray diffarction spectra of GeS:Sm crystal (before irradiation)

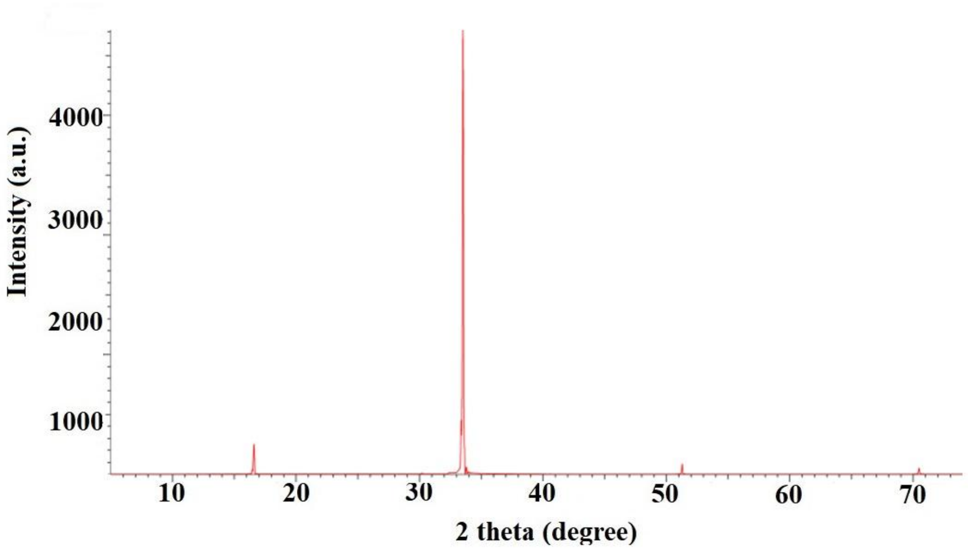

Fig. 3*b*. X-ray diffarction spectra of GeS:Sm crystal (after irradiation)

The rapid development of quantum electronics was ensured in the 60s of the last century with the invention of masers and lasers. The use of Nd atoms as active emission centers in solid-state lasers has strongly increased interest in rare earth elements. Over the next decade, the development of materials technology led to the massive production of REE with a high degree of purity. Extensive research of these metals, which were previously considered similar and sometimes identical in terms of physical and chemical properties, showed that REE has a strong effect on the mechanical, structural, electrophysical, photoelectric, optical, chemical properties of both metals and semiconductor matrices.

REE doped AIIBVI, AIIIBV, as well as AIVBVI, both during the synthesis of semiconductor compounds and during the growing of monocrystals, chalcogens in the substance, primarily by combining with oxygen atoms to form complex in the crystals and acts “cleaning effect” in the structure. Some of the atoms occupy the cation vacancies characteristic of these crystals. For example, Sm dopants (~ 1%) increase the specific resistivity of the p-GeS matrix by ~$10^2 - 10^3$ times.

Another important feature of REE elements is their ability to form exciton-impurity complexes (EIC) in crystals with a high degree of purity. These factors are typical for layered GeS crystals. Thus, REE atoms with an ionicradii ~1.5 times larger than Ge atoms are located in the interlayer space or in the elementary lattice, or compensate for cation vacancies. For this reason, the Sm atoms in the GeS matrix form SmO and SmS complexes with both oxygen and sulfur atoms. As the resulting complexes purify the crystalline slag and compensate for the cation vacancies, the specific resistance of the crystal increases sharply, and insignificant changes in the lattice parameters are recorded.

As for the maximum in the PC spectrum, the atomic complexes that annihilate cation vacancies create favorable conditions for the formation of excitons, as they "clean" the "foreign" atoms that penetrate the substance during crystal synthesis, primarily oxygen atoms. The excitons split into electron-hole pairs to form additional conductivity in the crystal at temperatures ≥200K.

Low doses (30 krad) of gamma rays break down the atomic complexes formed during synthesis in the crystal. While the decomposed oxygen atoms leave the crystal, the Sm atoms compensate for other cation vacancies by migrating in the crystal. The intensity of reflections in x-ray diffractions increases by ~10 times compared to the GeS crystal due to the high stability provided in the crystal are freed from existing atomic complexes.

In a crystal freed from complex atomic complexes, the excitons generated at $T \geq 200$K do not move freely in the crystal and collide, so the electron-hole pair is not generated and the exciton photoconductivity is not recorded.

4. Conclusion

As a result of the investigations, it was determined that like other REEs, Sm impurity atoms reduce the concentration of defects in the GeS matrix by partially compensating for the cation vacancies of complex atomic complexes. Exciton photoconductivity is recorded at temperature $T \geq 200$K. Low doses (30 krad) of gamma rays create high order in the crystal by destroying complex atomic complexes. Since the excitons migrating in the crystal do not collide, exciton photoconductivity is not recorded after gamma radiation.

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