INFLUENCE OF Nd IMPURITY ATOMS AND GAMMA IRRADIATION ON ROENTGENOGRAPHIC SPECTRUM OF GeS LAYERED SINGLE CRYSTAL

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The roentgenograms of layered single crystals GeS and $Ge_{0.995}Nd_{0.005}S$ before and after gamma irradiation are investigated. It is revealed that at identical conditions after gamma irradiation by dose 30 krad, the reflex intensity of GaS single crystal roentgenogram increases in 2,25 times and for $Ge_{0.995}Nd_{0.005}S$ single crystal this value achieves up to 35. It is supposed that neodymium atoms form the complex aggregates in compositions of which the oxygen atoms consist in. The crystal temperature increases under the influences of quantum small doses and complexes are destroyed. As a result, the oxygen atoms leave the crystal, neodymium crystals take the cation vacancies migrating in crystal and this leads to crystal structure ordering.

Keywords: rare-earth elements, self-compensation irradiation, annigilation, associate, complexing.
PACS:72.40.+W,76.30Kg,78.20,79.60.-i

INTRODUCTION

The germanium monosulfide belongs to $A^{IV}B^{VI}$ semiconductor class with conductivity of *p*-type and is characterized by orthorhombic crystal structure D_{2h}^{16} (structure type SnS, sp. gr. P_{cmn}). GeS also has the layered crystal structure where the atomic layers are connected by only Van der Waals forces [1]. In this connection, the uncompleted electron levels are absent on GeS single crystal surface and because of it the material surface is characterized by high chemical stability.

The heightened interest to GeS layered crystals is caused by the possibility of their application in electric memory devices [2] in the capacity of the mediums for hologram recording [3], the formation of sun cells and detectors of linear-polarized radiation [4] on their base. The scientists of North Carolina University USA create the unique device from GeS in the form of flower. Because of its small size and thin structure, it allows us to increase the capacity of lithium-ion batteries in many times. Such material is used in the capacity of the raw material at production of compact sun super-condensers [5]. The single crystal tapes grown up by the method of chemical precipitation from gas phase on GeS base are perspective nano-materials for the devices with high sensitivity of visible light [6, 7].

The traditional approach on the expansion of region of semiconductor material practical use is based on the use of doping processes by the impurities. Moreover, the task is the right choice of doping impurity. In contrast to other impurities, the rare-earth element (REE) impurities are characterized by low solubility limit of crystal lattice and chemical activity [8, 9]. In result of Coulomb and chemical interactions with main substance atoms REE form the complexes of different types. Many complexes forming as a result of such interactions, have the enough high stability and influence on semiconductor properties, being the effective scattering centers of ionizing radiations. The complex formation processes are obeyed by controlling interactions. The irradiation is the one of the controlling influence. Such opinion, which had been up to 80th of the former century that penetrating radiation causes only the radiation damages [10, 11] in semiconductor materials. The carried investigations establish that the radiation (in the dependence on semiconductor material) in definite doses can serve the effective technological method which allows us to obtain the high-quality semiconductor materials. The use of gamma irradiation is perspective in technological processes of semiconductor device preparation [12, 13]. The condition for structure ordering is formed at irradiation of semiconductor by gamma-quantums. The reliability of revealed effect is confirmed by X-ray and electron-microscopic investigations.

SAMPLES AND INVESTIGATION METHODS

The germanium with resistivity 50 Om·cm, sulfur by “B5” mark, neodymium “Нд-2” are used in the capacity of initial materials. The calculated stoichiometric weighted samples of these elements are put in quartz ampoules by length 10÷15 cm and inner diameter 1,0÷2,0 cm. The ampoule is evacuated up to pressure 10^{-3} mm of mercury and it is soldered. In order to avoid the explosion, the germanium is grinded in powder and substance quantity is limited by 10÷15 gr.

The synthesis process is carried out in two stages. Firstly, the ampoule in the furnace is heated with velocity 3÷5 degree/min up to 300 ºC and it is endured up to 10÷12 hours. Further, the temperature is increased with velocity 2÷3 degree/min up to total melting of germanium and ampoule is endured 18÷20 hours.

Bridgman method is applied for growing of GeS and $Ge_{0.995}Nd_{0.005}S$ single crystals. The temperature of top part of furnace is 50ºC on higher and bottom of furnace is on 50ºC less than melting point of the

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corresponding substance. The ampoule lowering speed in furnace is 2÷3 mm/h that is the condition for formation of single crystals. The single crystals grow up in the form of plane-parallel plates by $10x8x0,1mm^3$ dimension and needles. The layered single crystals obtained from big ingots are easily delaminated directly before measurements along plane perpendicular to *c* axis. They are not endured by the further mechanical and thermal treatment because of well mirror surface. The crystal melting point is obtained by differentially-thermal analysis in installation "Perkin-Elmer". The crystal structure and phase composition of materials are investigated by the method of roentgen beam diffraction with use of D8 ADVANCE diffractometer on CuK_{α} (λ=1,5418Å) radiation [14, 15]. The data of X -ray investigations confirm the appliance of obtained crystals to orthorhombic syngony with parameters given in table 1.

Table 1

Parameters of alloy crystal lattice

Single crystals	*a*, Å	*b*, Å	*c*, Å
GeS	4.297	3.641	10.471
$Ge_{0.995}Nd_{0.005}S$	4.319	3.651	10.492
$Ge_{0.995}Nd_{0.005}S$ (after irradiation)	4.332	3.645	10.485

The morphology of single crystals is investigated by screening method of electron microscopy on electron microscopy by SIGMA VP VAT mark. The sample irradiation by gamma quantums is carried out at room temperature on installation РХУНД-20000 from source ^{60}Co with phase power in irradiation zone ~1,37 R/sec.

THE INVESTIGATION RESULTS AND THEIR DISCUSSION.

The series of additional effects connected with defect formation because of the composition inclination from stoichiometric one appears at doping of GeS compounds by Nd atoms. The introduction in compound the substitutional impurity in essential quantities in Ge element sublattice leads to additional change of main component concentration in the crystal. At essential difference of introduced impurity atom dimensions (r_{Nd}=0,96Å) and replaced atom (r_{Ge}=0,72Å) the doping process can be accompanied by the generation of additional eigen point defects and change of their disposition form in the crystal. The big quantity of cation vacancies (10^{17}÷$10^{18}cm^{-3}$) essentially influence on introduction character of impurities in Ge lattice. In small concentration region Nd atoms directly dissolve in vacancies, the solubility in vacancies depends on vacancy concentration in initial material. The impurity solubility in vacancies is limited and it is always less than vacancy concentration. At the existence of free vacancies, it is possible the solubility of Nd impurity in essential quantities by the way of germanium exchange in lattice nods. Taking under consideration these data one can suppose that the main mechanism of small concentration solubility of Nd impurity in germanium mono-sulphide leads to "recovering" of cation vacancies.

The one significant property-ability to make material "purification" at definite conditions is emphasized in semiconductors with investigation of electron structure of REE atoms. Moreover, one can decrease the background impurities in A^4B^6 compounds on 2÷3 order and essentially increase the electron mobility. The main difficulty with REE work is in their special chemical activity. REE are covered by the film of corresponding oxide the elimination of which is practically impossible.

It is obvious, that the real picture of defect formation in GeS at inclination from stoichiometry and doping has the complex character and consist in the complex formation of eigen point defects, impurity atoms, oxygen atoms. It is possible that because of Coulomb and chemical interactions, the formation of electro-neutral complexes Nd_2O_3 in interstitial space of germanium mono-sulphide matrix which "pure" the crystals from impurities and eigen defects. As a result, the intensity of roentgen reflexes in $Ge_{0.995}Nd_{0.005}S$ single crystal exceeds in ~2,5 times the corresponding reflexes of GeS single crystals before irradiation (fig. 1a and fig. 2a). The similar method is the one from technological methods for the obtaining of perfect crystals [16].

There are two opinions at explanation of crystal "purification": 1 is that REE chemical reactions with background impurity take place in liquid phase, the forming compounds stay in slag and aren't introduced in solid phase; the second one is that REE complexes with non-metal impurities introduce in growing crystal but they are electrically neutral one. Comparing the mobility of electrons in the crystals the authors [17] lead to conclusion on formation of REE micro-inclusions with non-metal impurities.

The main deceleration mechanisms are the elastic collisions with nuclei and inelastic collisions with electrons at transmission of high energy particles through crystals [18]. At enough high value of incident particle the target atom shift from angular position takes place that leads to appearance of interstitial atom and vacancy (Frenkel pairs).

In the beginning of 80^{th} of former century it had been known that irradiation of crystals, metals and alloys by charged particles and gamma-quantums lead to destroy of their structure [19, 20]. It is the general accepted point of view according to which the there are no changes take place at radiation by particle fluxes which are less on several orders of charge carrier concentration value in semiconductor crystals [21, 22]. However, as a result of experimental investigations it is established that [23] the interaction process of ionizing radiation with crystals don't correspond to general accepted conceptions in the case when absorbed dose is ~10^5 gr. The radiation of gamma-quantums by shown absorbed dose of ionizing radiation of semiconductor crystals leads not to defect accumulation and vice versa, to their elimination and ordering of material structure [24].

The crystal structure reconstruction at irradiation by small doses of gamma quantums takes place because of disposal of accumulated energy in the crystal. The decrease of defect quantity in the crystal in irradiation process is accompanied by heat release caused by annihilation and defect reconstruction [25, 26].

In GeS crystal the dislocation loops which are formed at join of small associations of point defects under influence of gamma quantums, the defect concentration and micro-stresses decrease. The structure ordering under influence of gamma quantums takes place very weak and reflex intensity increases only in 2,25 times (fig. 1a, 1b).

The structure ordering effect in more bright form is revealed in GeS crystal by Nd doped atoms after irradiation by gamma quantums and intensity of super-structure maximum increases after irradiation by small dose 30 (krad) of $Ge_{0.995}Nd_{0.005}S$ single crystal increases (~35 times) (fig. 2a, 2b).

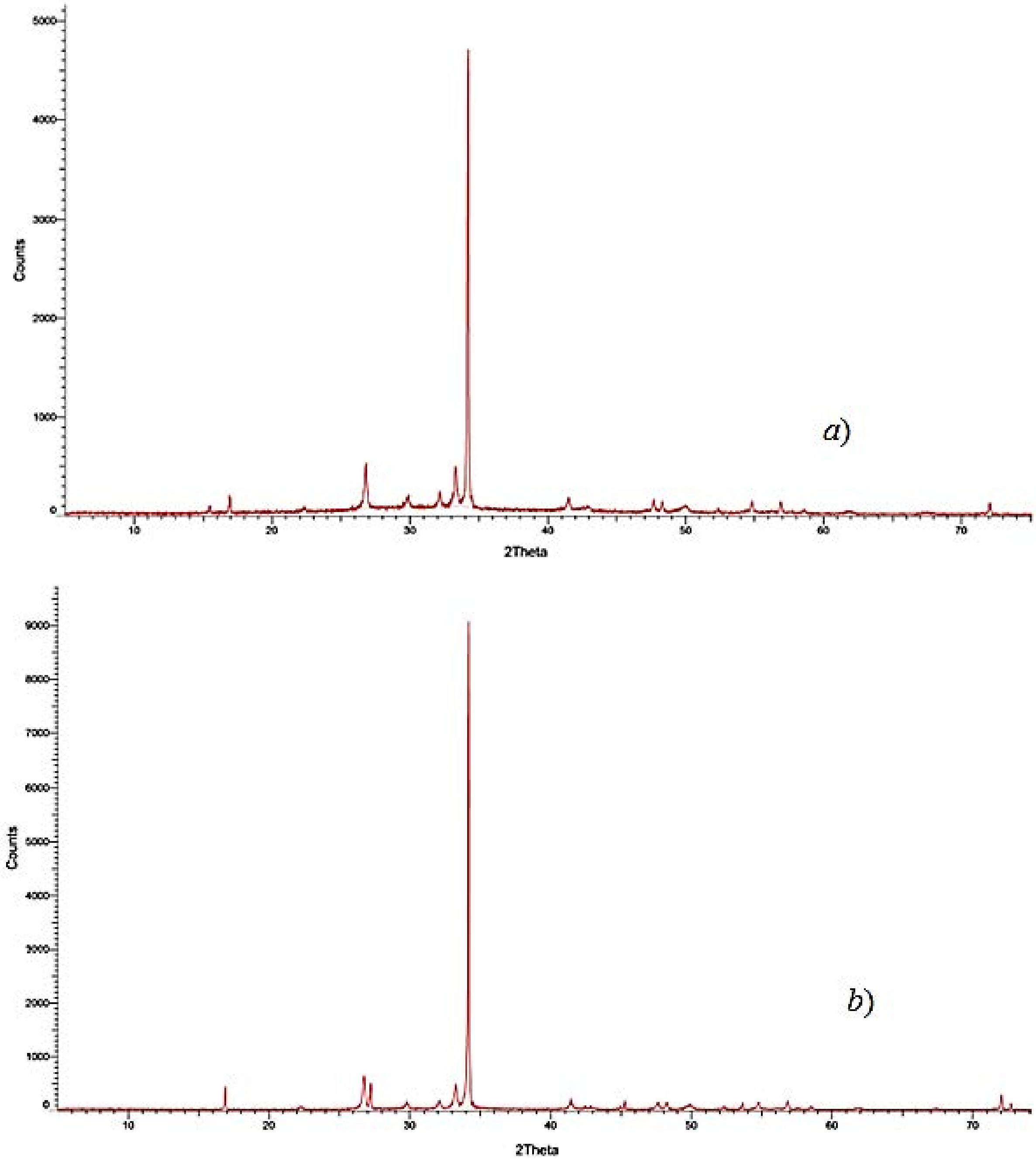

Fig. 1. Roentgenographic diffractograms of single crystals
a) GeS before irradiation; *b*) GeS after irradiation by dose 30 krad.

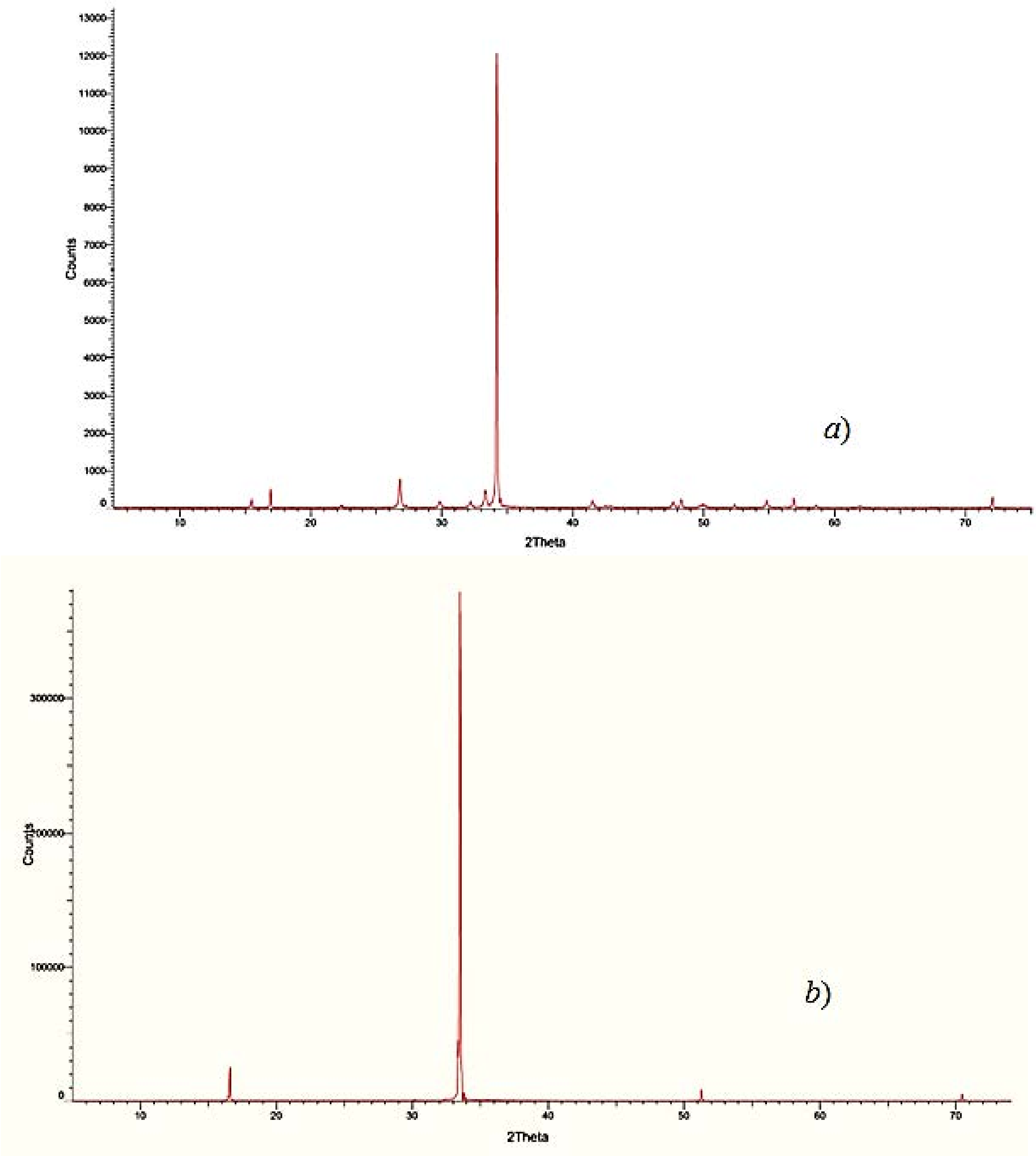

Fig. 2. Roentgenographic diffractograms of single crystals
a) $Ge_{0.995}Nd_{0.005}S$ before irradiation; *b*) $Ge_{0.995}Nd_{0.005}S$ after irradiation by dose 30 krad.

At the same time, as a result of joining of small associations of point defects the crystal blocks appear in crystal in the form of bright spots (fig. 3,a,b). The sizes of crystal blocks increase under the influence of gamma quantums (fig. 3c, d).

The picture of processes taking place in $Ge_{0.995}Nd_{0.005}S$ single crystal at influence of gamma radiation of small doses (30 krad) one can explain by the following way. The gamma quantums create the electron-hole pairs in the crystal. These pairs in the semiconductor crystals exist the enough long time. Migrating along the crystal, they are captured by defects forming the charged interstitial atoms and vacancies or their accumulations. The charged defects intensively interact between each other. The like defects join and form the bigger complexes of interstitial atoms and vacancies. In the case of unlike defect meeting the annigilation takes place and photon is formed at annigilation of electron and hole. Photon can interact with complexes and destroy them (in the composition of which REE and oxygen consist in). The released oxygen leaves the crystal and appeared free interstitial atoms annihilate with vacancies. At annihilation of Frenkel pairs the energy releases and the new electron-hole pairs appears because of this energy [27].

The described process changes the crystal state and leads to the crystal structure ordering. As it is seen from the table 1, the Nd impurity atoms and gamma irradiation of small dose insinglificantly influence on elementary cell parameters and phase transformation isn't revealed. Thus, $Ge_{0.995}Nd_{0.005}S$ crystal ordering state where Nd atoms are in crystal lattice nods, is formed under influence of gamma radiation of small dose. Note that that investigated effect is also observed in the example of single crystals $Ge_{0.995}Sm_{0.005}S$ and $Ge_{0.995}Gd_{0.005}S$.

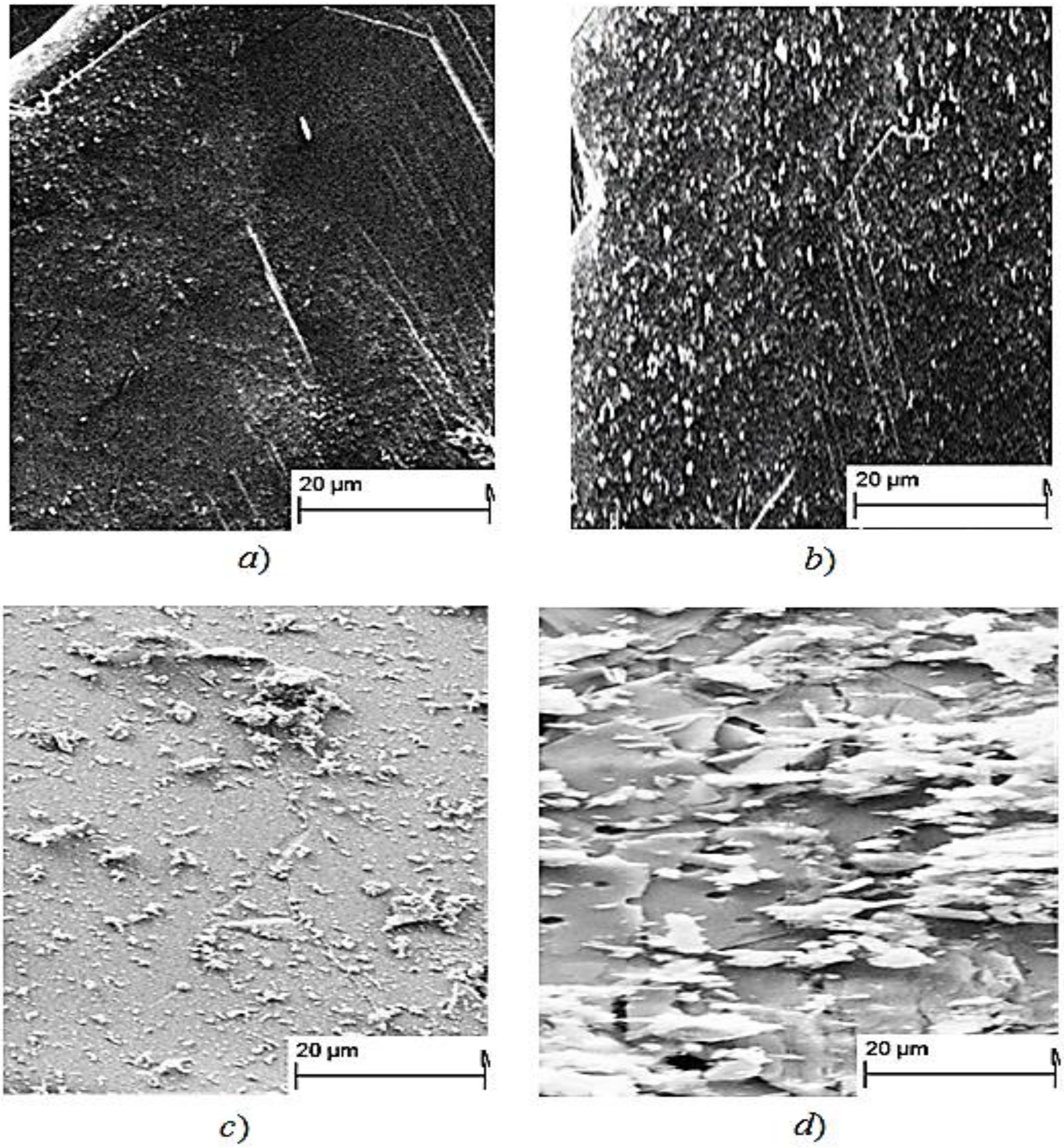

Fig. 3. Micro-photos of single crystal surfaces
a) GeS before irradiation; *b*) GeS after irradiation by dose 30 krad;
c) $Ge_{0.995}Nd_{0.005}S$ before irradiation; *d*) $Ge_{0.995}Nd_{0.005}S$ after irradiation by dose 30 krad.

CONCLUSION

Thus, summarizing the results of complex physical-chemical analysis one can conclude that the complex aggregates in the composition of which neodimium and oxygen atoms are included, form in $Ge_{0.995}Nd_{0.005}S$ single crystals during crystal synthesis.

The crystal temperature increases and the destroy of these complexes takes place under the influence of gamma irradiation of small doses (30 krad). The oxygen atoms leave the crystal migrating along the substance, Nd atoms are captured by cation vacancies as a result of which $Ge_{0.995}Nd_{0.005}S$ crystal structure ordering takes place.

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Received: 16.03.2020