

OBTAINED AND STUDIED STRUCTURAL ASPECTS OF THE $\text{Ge}_{0.9}\text{Er}_{0.1}\text{S}$ COMPOUND WITH $\text{Ge} \rightarrow \text{Er}$ SUBSTITUTIONS

R.Z. Ibaeva^{a*}, G.B. Ibragimov^a, A.S. Alekperov^{b,c},  R.E. Huseynov^a

^aInstitute of Physics, Ministry of Science and Education Republic of Azerbaijan, Baku, AZ-1143, Azerbaijan

^bAzerbaijan State Pedagogical University, Baku, AZ-1000, Azerbaijan

^cBaku Engineering University, Khirdalan, AZ-0101, Azerbaijan

*Corresponding Author e-mail: raidabayeva1@gmail.com

Received July 30, 2024; revised October 3, 2024; accepted October 11, 2024

In this work, $\text{Ge}_{0.9}\text{Er}_{0.1}\text{S}$ was synthesised by partially replacing Ge atoms with Er atoms. The crystal structure of the resulting compound was studied by X-ray diffraction. The research found that Er atoms can completely replace Ge atoms in the crystal structure. Therefore, the compound can crystallize into one phase. It was established that the structure of this compound corresponds to orthorhombic symmetry and space group Pnma. The crystallographic parameters of the $\text{Ge}_{0.9}\text{Er}_{0.1}\text{S}$ compound were determined by analyzing the X-ray diffraction spectrum using the Rietveld method. Based on the obtained structure on different atomic planes, an explanation of the crystal structure of the $\text{Ge}_{0.9}\text{Er}_{0.1}\text{S}$ semiconductor is given. It is established that one of the main elements in the formation of the crystal structure are the ionic radii of the elements Ge, Er and S.

Keywords: $\text{Ge}_{0.9}\text{Er}_{0.1}\text{S}$; Crystal structure; X-ray diffraction; Lattice parameters

PACS: 61.05.cp; 61.82.Fk

1. INTRODUCTION

Materials with semiconductor properties are materials with wide application potential in modern electronics and spintronics. Recently, theoretical and experimental research has been carried out in the direction of studying the optical, magnetic, thermal and electrical properties of functional materials [1-5]. It is known that the physical properties of semiconductors depend on their electronic and crystal structure. Therefore, the structural properties of these materials are studied using modern research methods. One such material is GeS crystal. This crystal is a crystal with a layered structure. X-ray diffraction studies showed that the crystal structure of this compound corresponds to orthorhombic symmetry. In this compound, interesting optical properties are observed in compounds obtained by partial replacement of germanium atoms with rare earth elements. Therefore, $\text{Ge}_{1-x}\text{Ln}_x\text{S}$ crystals have been synthesized for a long time and various optical properties have been studied.

The photoconductivity of GeS and $\text{Ge}_{1-x}\text{Nd}_x\text{S}$ compounds ($x = 0.005$ and 0.01) was studied at low temperatures ($T = 80\text{-}300$ K). An analysis of the obtained spectra revealed that significant changes in photoconductivity are observed when Ge atoms are partially replaced by Nd atoms. Elementary excitation of the exciton type was observed in $\text{Ge}_{1-x}\text{Nd}_x\text{S}$ compounds in the temperature range $200\text{ K} < T < 350\text{ K}$ [6]. When Ge atoms were replaced by rare earth elements, optically active processes were also observed in the $\text{Ge}_{1-x}\text{Sm}_x\text{S}$ and $\text{Ge}_{1-x}\text{Gd}_x\text{S}$ compounds [7,8]. Previous studies have established that substitution with rare earth elements causes significant changes in the optical properties of semiconductors. But in many cases, rare earth elements cannot replace cations in a crystal. In this case, the crystal structure of the material is complex. Thus, a two-phase, three-phase system is formed [9]. With a complex crystal structure, it is difficult to study the structural aspects of the physical properties of substances. In the course of structural studies of $\text{Ge}_{1-x}\text{Ln}_x\text{S}$ crystals, it was established that Ln atoms can completely replace Ge atoms. Therefore, it is possible to study these systems. Data obtained from studying such systems can be used as a model when studying compounds with similar physical properties and structures.

It is known that changes in interatomic distances occur due to differences in ionic radii during cation-cation substitutions. These changes can affect the crystal structure. As the concentration increases during the substitutions, changes in the crystal structure also increase. Therefore, the structure of new materials obtained by cation-cation and anion-anion substitution requires careful study. Although the structure of many compounds included in the GeS and $\text{Ge}_{1-x}\text{Ln}_x\text{S}$ system has been studied, the structure of compounds obtained by replacing Ge atoms with Er atoms has not been sufficiently studied. It is known that Er atoms have a smaller ionic radius compared to the elements Nd, Sm and Gd [10]. Consequently, in compounds included in the $\text{Ge}_{1-x}\text{Er}_x\text{S}$ system, a crystal structure with higher symmetry is possible. In this work, the compound $\text{Ge}_{0.9}\text{Er}_{0.1}\text{S}$ was synthesized and its crystal structure was studied by X-ray diffraction. Crystallographic parameters: space group, syngony, lattice parameters, atomic coordinates, interatomic distances and angles between bonds were determined by analyzing the spectrum obtained at room temperature.

2. EXPERIMENTAL PART

2.1. Synthesis of samples.

The process of synthesis of the $\text{Ge}_{0.9}\text{Er}_{0.1}\text{S}$ compound was carried out according to standard methods under vacuum conditions at high temperatures according to the synthesis of the chalcogenide semiconductor GeS. The synthesis used germanium with a resistivity of $\rho = 50 \text{ Ohm}\cdot\text{cm}$. The stoichiometric amounts of each of the elements Ge, S and Er were calculated, weighed on a high-precision electronic balance, taken in appropriate quantities and mixed. The resulting mixture was placed in a vacuum (10^{-3} mm Hg) in a quartz tube with a length of $l = 15 \text{ cm}$ and a diameter of $d = 2 \text{ cm}$. To prevent the explosion of the ampoule, the germanium element was ground into powder and $m = 10 \text{ g}$ was taken. Once the material is ready, the synthesis process begins. This process was carried out in two stages. In the first stage, the ampoule was placed in an oven and heated to a temperature $T = 300 \text{ }^\circ\text{C}$ at a rate of $5^\circ\text{C}/\text{min}$. The synthesis was carried out at this temperature for 12 hours. Then the temperature was increased to the melting temperature of germanium ($T = 930 \text{ }^\circ\text{C}$) at a rate of $3 \text{ }^\circ\text{C}/\text{min}$. The synthesis was carried out at this temperature for 12 hours. The temperature of the upper part of the furnace is 50°C higher than the melting point of germanium, and the temperature of the lower part is lowered by 50°C . Then the ampoule was lowered from above at a speed of $3 \text{ mm}/\text{h}$. Upon completion of this process, a $\text{Ge}_{0.9}\text{Er}_{0.1}\text{S}$ single crystal with geometric dimensions of $10 \times 8 \times 6 \text{ mm}^3$ was obtained. Because this compound has a layered crystal structure, it can be easily separated in parallel planes. Therefore, samples for research were prepared by grinding them into small particles.

2.2. Structural analysis

The crystal structure of the $\text{Ge}_{0.9}\text{Er}_{0.1}\text{S}$ compound was studied by X-ray diffraction. This method allows one to determine phase analysis, crystal structure, and structural phase transitions in chalcogenide semiconductors with fairly high accuracy [11,12]. The samples were first ground in a mortar and then analyzed on a $\text{CuK}\alpha$ 40 kV, 40 mA, $\lambda = 1.5406 \text{ \AA}$ X-ray diffractometer (D8 Advance, Bruker, Germany). The studies were carried out at room temperature and under normal conditions. The resulting spectra were analyzed by the Rietveld method in the Mag2Pol program.

3. RESULTS AND DISCUSSIONS

The crystal structure of the $\text{Ge}_{0.9}\text{Er}_{0.1}\text{S}$ compound was studied by X-ray diffraction in the diffraction angle range $5^\circ \leq 2\theta \leq 50^\circ$. The spectrum obtained at room temperature and under normal conditions is shown in Figure 1.

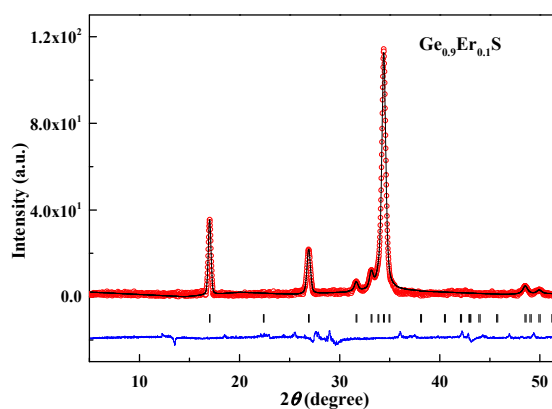


Figure 1. X-ray structural spectrum of the compound $\text{Ge}_{0.9}\text{Er}_{0.1}\text{S}$.

Shown are the experimentally obtained spectrum points (red dots), the curve calculated in the Mag2Pol program (black line), atomic planes corresponding to the Miller indices (vertical lines), and the difference between theory and experiment (blue line). As can be seen from the spectrum, three main diffraction maxima are observed in the resulting spectrum over a wide range. These maxima correspond to the diffraction angles $2\theta = 17^\circ$, 27° and 34° . During the analysis in the Mag2Pol program, it was found that this spectrum corresponds to orthorhombic symmetry with the space group Pnma , and the central diffraction maxima correspond to $(2\ 0\ 0)$, $(2\ 0\ 1)$ and $(4\ 0\ 0)$. aircraft. During the calculation, it was determined that the lattice parameters of the $\text{Ge}_{0.9}\text{Er}_{0.1}\text{S}$ crystal are: $a = 4.318(3) \text{ \AA}$, $b = 3.649(6) \text{ \AA}$, $c = 10.491(2) \text{ \AA}$ and $V = 165.43 \text{ \AA}^3$ ($R_p = 6.23$, $R_{wp} = 5.02$ and $\chi^2 = 1.32\%$). The $\text{Ge}_{0.9}\text{Er}_{0.1}\text{S}$ compound was synthesized in a single-phase case. This is because Er atoms can completely replace Ge atoms in the crystal structure. It is known that Ge atoms when forming the GeS compound are in a divalent state and form covalent bonds with divalent S atoms. Lanthanides form compounds in both divalent and trivalent states. When Er atoms replace Ge atoms, they become divalent. Another reason why Er atoms can replace Ge atoms in a crystal structure is that the difference in the ionic radii of these atoms is small. Thus, in the divalent case, the ionic radius of germanium atoms is $R_{\text{Ge}^{2+}} = 0.72 \text{ \AA}$, the ionic radius of erbium atoms is $R_{\text{Er}^{2+}} = 1.09 \text{ \AA}$, and the difference between them is $\Delta R_{\text{Er-Ge}} = 0.37 \text{ \AA}$ [10]. As you can see, this value is not so large compared to interatomic distances. Therefore, replacements were possible. Obtaining a single-phase system by substitution is very important for explaining the structural features of the physicochemical processes occurring in these compositions.

To obtain more accurate information about the crystal structure, it is important to determine the coordinates of the atoms. The coordinates of Ge, Er and S atoms were determined by analyzing the X-ray diffraction spectrum of the $\text{Ge}_{0.9}\text{Er}_{0.1}\text{S}$ compound (Fig. 1) using the Rietveld method. It has been established that Ge and Er atoms upon substitution are located in the same crystallographic position. The coordinates of their atoms correspond to: $x/a = 0.622$, $y/b = 0.25$, $z/c = 0.372$, and the coordinates of the S atoms: $x/a = 0.848$, $y/b = 0.25$, $z/c = 0.501$.

The $\text{Ge}_{0.9}\text{Er}_{0.1}\text{S}$ compound has a very simple crystal structure. So, since the Ge(Er) and S atoms have the same concentration, then the number of their atoms in the elementary lattice is the same. To visualize the crystal structure, the crystal structure of the $\text{Ge}_{0.9}\text{Er}_{0.1}\text{S}$ compound was determined on the $\vec{a}\vec{b}$, $\vec{a}\vec{c}$ and $\vec{b}\vec{c}$ planes in the Diamond 3.2 program. The resulting structure at different levels is presented in Figure 2 and the $\vec{b}\vec{c}$ plane, as can be seen from the given structure, there are 4 germanium (erbium) atoms and 4 sulfur atoms in the elementary lattice, therefore $Z = 4$. The elementary lattice consists of two different layers. If the bonds were located inside the layer and formed a high symmetry parallel to the \vec{a} , \vec{b} and \vec{c} axes, then an elementary lattice with cubic systems would be obtained. However, as can be seen, the $\text{Ge}_{0.9}\text{Er}_{0.1}\text{S}$ compound crystallizes in orthorhombic systems with slightly lower symmetry. This structural effect can also be observed in the angle values of the interconnects. Thus, the Ge-S-Ge bond takes on 4 different values depending on its distance in the elementary lattice: 132° , 90° , 56° , 37° . It is known that the ideal crystal structure with high symmetry for binary b-compounds is the NaCl model. If the $\text{Ge}_{0.9}\text{Er}_{0.1}\text{S}$ compound crystallized according to this model, then the intervalence angles would be 90° and 45° . The difference in contact angle values is explained by the difference in the symmetry of the crystal structure.

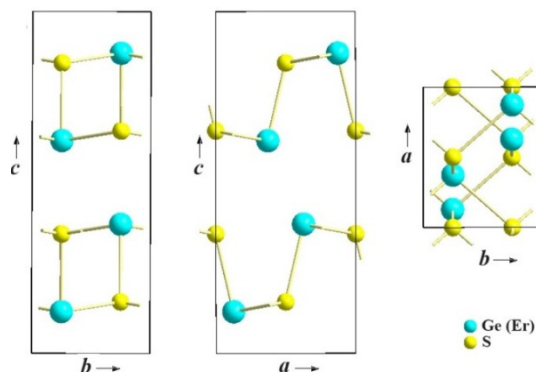


Figure 2. Crystal structure of the $\text{Ge}_{0.9}\text{Er}_{0.1}\text{S}$ compound along the $\vec{a}\vec{b}$, $\vec{a}\vec{c}$ and $\vec{b}\vec{c}$ planes

A layered crystal structure is also observed in interatomic distances. Thus, it was determined that the distance between the Ge(Er) and S atoms inside the layer is $l_{\text{Ge(Er)-S}} = 2.44 \text{ \AA}$, and the interatomic distances between the layers are $l_{\text{Ge(Er)-S}} = 3.27 \text{ \AA}$. Thus, the layered $\text{Ge}_{0.9}\text{Er}_{0.1}\text{S}$ crystal is located parallel to the planes and has a shape that can be easily separated from each other mechanically.

Many interesting physical properties are observed in semiconductor compounds with a layered crystal structure. Thus, during some physical processes, the interlayer distances and other crystallographic parameters change. During these changes, not only the mechanical properties change but also the physical properties of the material as a whole. During the structural studies of the TlGaSe_2 crystal at high pressures, it was found that the structural phase transition occurs at a pressure of $P = 0.5 \text{ GPa}$. However, during the analysis, it was found that the symmetry of the crystal was monoclinic $C2/c$ both before and after the phase transition [13]. It was determined that the main reason for the phase transition is a sharp decrease in the value of the distance between the layers under the action of pressure. As you can see, the distance between the layers also plays an important role in layered semiconductors. Therefore, it is important to understand the structural elements when studying these crystals. For this reason, the results obtained in the study of the crystal structure of the $\text{Ge}_{0.9}\text{Er}_{0.1}\text{S}$ semiconductor are very important. These results are very important both from the point of view of studying the structure of the crystal and from the point of view of explaining the structural aspects of its physical properties. Thanks to the simple crystal structure, it is possible to explain the physicochemical processes occurring in the $\text{Ge}_{0.9}\text{Er}_{0.1}\text{S}$ compound.

4. CONCLUSIONS

The compound $\text{Ge}_{0.9}\text{Er}_{0.1}\text{S}$ with a layered crystal structure was synthesized and its crystal structure was studied by X-ray diffraction. In the course of studies carried out by the Rietveld method, it was found that Er atoms can completely replace Ge atoms in the crystal structure. The X-ray diffraction spectrum obtained at room temperature was analyzed in the Mag2Pol program and the crystallographic parameters were determined. The structural features of the $\text{Ge}_{0.9}\text{Er}_{0.1}\text{S}$ compound are shown based on the values of interatomic distances and intervalence angles, and the crystal symmetry and layered structure are explained. The role of the values of ionic radii and valence of the atoms included in the composition in the formation of bonds is shown. It is known that oxidation is constantly occurring on the surface of materials. This process is observed even in some oxide materials of complex composition [14]. It is observed more in non-oxide materials. There are a number of methods to prevent this process and minimize oxidation. The main method is to ensure the saturation of all bonds in the synthesized sample. In this case, metal atoms cannot form bonds with oxygen atoms. In this

regard, the $\text{Ge}_{0.9}\text{Er}_{0.1}\text{S}$ compound can be considered stable. Therefore, elements made from this combination can work stably for a long time.

© R.E. Huseynov, <https://orcid.org/0000-0003-0636-3948>

REFERENCES

- [1] G.B. Ibragimov, and R.Z. Ibaeva, "Light absorption by free charge carriers with scattering mechanisms in a semiconductor superlattice," *Journal of Surface Investigation: X-ray, Synchrotron and Neutron Techniques*, **18**, 116-120 (2024). <https://doi.org/10.1134/S1027451024010099>
- [2] G.B. Ibragimov, and R.Z. Ibaeva, "Theory of intraband absorption of electromagnetic radiation in cylindrical quantum wires," *Journal of Non-Oxide Glasses*, **12**, 31-34 (2020). https://chalcogen.ro/31_IbragimovGB.pdf
- [3] T.K. Nurubeyli, "The effect of plasma density on the degree of suppression of analyte signals in ICP-MS," *Technical Physics*, **65**, 1963-1968 (2020). <https://doi.org/10.1134/S1063784220120166>
- [4] G.B. Ibragimov, R.Z. Ibaeva, A.S. Alekperov, and B.G. Ibragimov, "Light absorption by free charge carriers in the presence of phonons in an anisotropic quantum wire," *Advanced Physical Research*, **6**, 56-62 (2024). <https://doi.org/10.62476/apr61.62>
- [5] T.K. Nurubeyli, "Coefficient of relative sensitivity in mass spectrometers with inductively coupled plasma," *Inorganic Materials: Applied Research*, **11**, 552-557 (2020). <https://doi.org/10.1134/S2075113320030351>
- [6] A.S. Alekperov, A.O. Dashdemirov, A.E. Shumskaya, and S.H. Jabarov, "High-temperature exciton photoconductivity of $\text{Ge}_{1-x}\text{Nd}_x\text{S}$ crystals," *Crystallography Reports*, **66**, 1322-1327 (2021). <https://doi.org/10.1134/S1063774521070026>
- [7] A.O. Dashdemirov, S.G. Asadullayeva, A.S. Alekperov, N.A. Ismayilova, and S.H. Jabarov, "Electronic and optical properties of GeS and GeS:Gd ," *International Journal of Modern Physics B*, **35**, 2150305 (2021). <https://doi.org/10.1142/S0217979221503057>
- [8] A.S. Alakbarov, A.O. Dashdemirov, R.B. Bayramli, and K.S. Imanova, "Effect of the gamma irradiation on the structure and exciton photoconductivity of layered GeS:Sm single crystal," *Advanced Physical Research*, **3**, 39-45 (2021). <http://jomardpublishing.com/UploadFiles/Files/journals/APR/V3N1/5Alakbarov.pdf>
- [9] B.G. Tagiyev, O.B. Tagiyev, A.I. Mammadov, V.X. Quang, T.G. Naghiyev, S.H. Jabarov, M.S. Leonenya, *et al.*, "Structural and luminescence properties of $\text{Ca}_x\text{Ba}_{1-x}\text{Ga}_2\text{S}_4: \text{Eu}^{2+}$ chalcogenide semiconductor solid solutions," *Physica B: Condensed Matter*, **478**, 58-62 (2015). <https://doi.org/10.1016/j.physb.2015.08.061>
- [10] L.T. Bugaenko, S.M. Ryabykh, and A.L. Bugaenko, "A nearly complete system of average crystallographic ionic radii and its use for determining ionization potentials," *Moscow University Chemistry Bulletin*, **63**, 303-317 (2008). <https://doi.org/10.3103/S0027131408060011>
- [11] M.N. Mirzayev, S.H. Jabarov, E.B. Asgerov, R.N. Mehdiyeva, T.T. Thabethe, S. Biira, and N.V. Tjep, "X-ray diffraction and thermodynamics kinetics of SiB_6 under gamma irradiation dose," *Silicon*, **11**, 2499-2504 (2019). <https://doi.org/10.1007/s12633-018-0039-2>
- [12] Y.I. Aliyev, Y.G. Asadov, A.O. Dashdemirov, R.D. Aliyeva, T.G. Naghiyev, and S.H. Jabarov, "Polymorphic transformations and thermal expansion of some modifications in $\text{Ag}_{1.5}\text{Cu}_{0.5}\text{Se}$ and $\text{Ag}_{0.4}\text{Cu}_{1.6}\text{Se}$," *International Journal of Modern Physics B*, **33**, 1950271 (2019). <https://doi.org/10.1142/S0217979219502710>
- [13] S.H. Jabarov, T.G. Mammadov, A.I. Mammadov, S.E. Kichanov, V.B. Aliyeva, and E.V. Lukin, "Structural phase transition in TlGaSe_2 under high pressure," *Journal of Surface Investigation. X-ray, Synchrotron and Neutron Techniques*, **9**, 35-40 (2015). <https://doi.org/10.1134/S102745101501005X>
- [14] F.G. Agayev, S.H. Jabarov, G.Sh. Ayyubova, M.N. Mirzayev, S.V. Trukhanov, E.L. Trukhanova, M.A. Darwish, *et al.*, "Structure and thermal properties of $\text{BaFe}_{11.1}\text{In}_{0.9}\text{O}_{19}$ hexaferrite," *Physica B: Condensed Matter*, **580**, 411772 (2020). <https://doi.org/10.1016/j.physb.2019.411772>

ОТРИМАНО ТА ДОСЛІДЖЕНО СТРУКТУРНІ АСПЕКТИ СПОЛУКИ $\text{Ge}_{0.9}\text{Er}_{0.1}\text{S}$ ІЗ ЗАМІНОЮ $\text{Ge} \rightarrow \text{Er}$

Р.З. Ібасва^а, Г.Б. Ібрагімов^а, А.С. Алекперов^{б,с}, Р.Е. Гусейнов^а

^аІнститут фізики Міністерства науки і освіти Азербайджанської Республіки, Баку, AZ-1143, Азербайджан

^бАзербайджанський державний педагогічний університет, Баку, AZ-1000, Азербайджан

^сБакинський інженерний університет, Хурдалан, AZ-0101, Азербайджан

У цій роботі шляхом часткової заміни атомів Ge на атоми Er було синтезовано сполуку $\text{Ge}_{0.9}\text{Er}_{0.1}\text{S}$. Кристалічна структура отриманої сполуки досліджена методом рентгенівської дифракції. Дослідження показало, що атоми Er можуть повністю замінити атоми Ge в кристалічній структурі. Тому сполука може кристалізуватися в одну фазу. Встановлено, що структура цієї сполуки відповідає орторомбічній симетрії та просторовій групі $R\bar{3}m$. Кристалографічні параметри сполуки $\text{Ge}_{0.9}\text{Er}_{0.1}\text{S}$ визначали шляхом аналізу рентгенівського спектру за методом Рітвельда. На основі отриманої структури на різних атомних площинах дано пояснення кристалічної структури напівпровідника $\text{Ge}_{0.9}\text{Er}_{0.1}\text{S}$. Встановлено, що одними з основних елементів у формуванні кристалічної структури є іонні радіуси елементів Ge, Er і S.

Ключові слова: $\text{Ge}_{0.9}\text{Er}_{0.1}\text{S}$; кристалічна структура; рентгенівська дифракція; параметри ґратки