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EFFECT OF Cu → Tm CATION-CATION SUBSTITUTIONS ON STRUCTURAL PROPERTIES OF Cu_2Se

Y.I. Aliyev[a,b]*, A.O. Dashdemirov[a], T.M. Ilyasli[c], S.R. Azimova[d], M.E. Aliyev[e], H.J. Huseynov[d]
[a]Azerbaijan State Pedagogical University, Baku, AZ-1000, Azerbaijan
[b]Western Caspian University, Baku, AZ-1001, Azerbaijan
[c]Baku State University, Baku, AZ-1148, Azerbaijan
[d]Institute of Physics, Ministry of Science and Education, Baku, AZ-1143, Azerbaijan
[e]Nakhchivan State University, Nakhchivan, AZ-7012, Azerbaijan
Corresponding Author e-mail: yusifafshar@gmail.com

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$Cu_{2-x}Tm_xSe$ (x = 0.1, 0.2, 0.3) system compounds were synthesized and their structural properties were studied. Research was carried out by X-ray diffraction method at room temperature. It was determined that the crystal structure of these compounds corresponds to rhombohedral symmetry with R-3m(166) space group. Lattice parameters and atomic coordinates were assigned for each compound. The difference between the crystallographic parameters of $Cu_{1.9}Tm_{0.1}Se$, $Cu_{1.7}Tm_{0.3}Se$ and $Cu_{1.5}Tm_{0.5}Se$ compounds was explained by the difference between the ionic radii of Cu and Tm atoms.

Keywords: *Cu_2Se; Rare-earth element; Chalcogenide; X-ray diffraction*
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1. INTRODUCTION

It is very important to study the structure and physical properties of functional materials. Because the results obtained in the course of these studies determine the possibilities of their application. Therefore, recently, extensive research has been conducted to obtain, process and study the properties of new functional materials [1-5]. It is known that the physical and chemical properties of materials can change under the influence of temperature, pressure and ionizing radiation. For this reason, materials that can maintain their functions in areas exposed to external influences are considered more interesting. The processes occurring under external influences are studied at the atomic level using modern research methods [6-10].

Copper-containing chalcogenide semiconductors are materials with interesting physicochemical properties. Therefore, the physical properties of these materials are widely studied. It was determined that interesting thermal, optical and electrical properties are observed in these compounds [11-15]. When adding rare earth elements to chalcogenide compounds, changes in optical properties are observed. Therefore, optically active systems have recently been obtained by introducing Eu, Nd, and Gd into chalcogenide matrices [16-20]. Making these substitutions in copper chalcogenides can lead to new optical materials. Cu – Se systems can serve as a basis for obtaining such materials.

During the analysis of the crystal structures of the compounds of the Cu-Se system, it was found that the factor that most affects the crystal structures of these compounds is valence variation. In these compounds, Se chalcogen atoms show stable valency. It was determined that depending on the valence and concentration of copper atoms in the compound, Cu_2Se [21-24], CuSe [25], $Cu_{1.78}Se$ [26], $Cu_{0.87}Se$ [27], Cu_3Se_2 [28], $CuSe_2$ [29], $Cu_{1.95}Se$ [30], $Cu_{1.77}Se$ [24], $Cu_{1.89}Se$ [24] and $Cu_{1.8}S$ [31] are available. Obtaining these compounds depends on the synthesis conditions, including the stoichiometric amount of Cu and Se elements during the synthesis process. As a result of the classification of Cu–Se system compounds, it was found that the Cu_2Se compound is the most studied among these compounds. As a result of the analysis of the X-ray diffraction patterns by the Rietveld method, it was found that single crystals of the Cu_2Se compound have a monoclinic syngonium crystal structure with space group C2/c (15) under normal conditions and at room temperature. The parameters of the elementary core are: a = 7.1379(4) Å, b = 12.3823(7) Å, c = 27.3904(9) Å, β = 94.308(5) ° and V = 2414.0(4)8 Å^3. Apparently, the crystal structure of the Cu_2Se compound does not have high symmetry. Therefore, each of the atoms that make up the crystal lattice stands in different crystallographic positions. Copper atoms occupy 12 and selenium atoms occupy 6 different positions [32]. The crystal structure of the Cu_2Se compound consists of the arrangement of $CuSe_4$ tetrahedra formed by selenium atoms along the $\vec{c}$ axis. Copper atoms are located in the centre of these tetrahedra. It is known that the physical properties of materials mainly depend on their crystal and electronic structures. The fact that these compounds have semiconducting properties mainly depends on the electronic configurations of the copper and selenium atoms included in their composition.

Different crystal structures can be obtained depending on the stoichiometric amount of metal and chalcogen elements included in Cu–Se compounds and synthesis conditions. The most widely studied of these compounds is the Cu_2Se compound. Because in this structure, copper atoms are in a monovalent state. Therefore, this system becomes more stable. Although many physical properties of the Cu_2Se compound have been studied, structural changes occurring during

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Cu → Tm cation-cation substitutions have not been studied. In this study, compounds $Cu_{1.9}Tm_{0.1}Se$, $Cu_{1.8}Tm_{0.2}Se$ and $Cu_{1.7}Tm_{0.3}Se$ were synthesized and their structural properties were studied.

2. EXPERIMENTS

The research objects $Cu_{2-x}Tm_xSe$ ($x = 0.1, 0.2, 0.3$) were synthesized in high-temperature stoves under high vacuum conditions by the standard method available for synthesizing chalcogenide semiconductors. Stoichiometric amounts of Cu, Tm and Se were taken according to the compounds. First, the furnace temperature was raised to $T = 400$ K. After keeping it at that temperature for $t = 4\text{-}5$ hours, it raised to $T = 1400$ K. Next keeping it at the specified temperature for $t = 4\text{-}5$ hours, the oven was cooled at a rate of 60 degrees/hour. Then the mixture is heated to the boiling point for about $t = 750$ hours at $T = 450$ K for homogenization of the mixture and further studies were carried out.

XRD (X-ray diffraction) is one of the modern methods for studying the crystal structure of solids. The crystal structure of the $Cu_{1.9}Tm_{0.1}Se$, $Cu_{1.8}Tm_{0.2}Se$ və $Cu_{1.7}Tm_{0.3}Se$ compounds at room temperature was studied by X-ray diffraction. For structural studies, we used a D8 Advance diffractometer (Bruker, Germany) with Cu$K\alpha$ radiation, parameters: $\lambda = 1.5406$ Å, 40 kV, 40 mA. The experimental X-ray diffraction spectrum was analyzed by the Rietveld method in the Fullprof program.

3. RESULTS AND DISCUSSIONS

In order to study the crystal structures of $Cu_{2-x}Tm_xSe$ ($x = 0.1, 0.2, 0.3$) compounds, crystal studies were carried out. The X-ray diffraction spectrum obtained for the $Cu_{1.9}Tm_{0.1}Se$ compound is given in Figure 1.

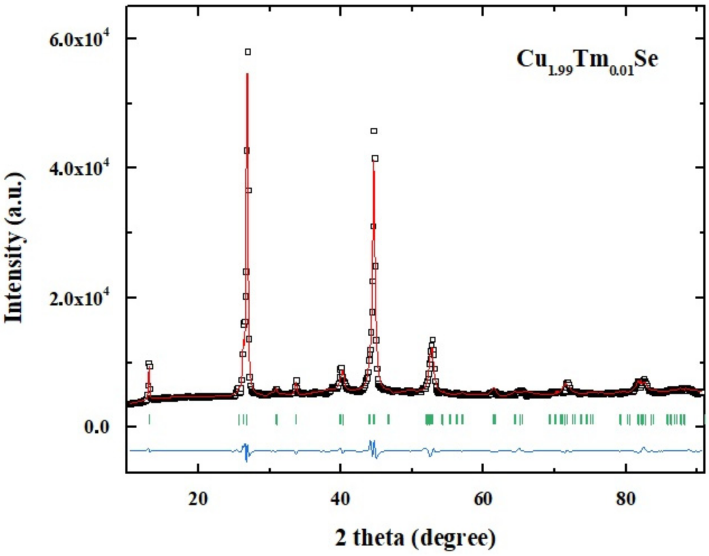

Figure 1. X-ray diffraction spectrum of compound $Cu_{1.9}Tm_{0.1}Se$.

It was determined from the analysis of the spectrum that the crystal structure of the $Cu_{1.9}Tm_{0.1}Se$ compound corresponds to the rhombohedral symmetry R-3m (166) space group structure. The values of the lattice parameters are set to: $a = b = 4.06405(4)$ Å, $c = 20.32801(7)$ Å, $V = 290.78(5)$ Å^3. The coordinates of copper and selenium atoms standing in different positions were also determined. The obtained values are given in Table 1.

Table 1. Atomic coordinates in the elementary lattice of compound $Cu_{1.9}Tm_{0.1}Se$.

Atom	*x*	*y*	*z*
Cu1	0.666(7)	0.333(3)	0.614(3)
Cu2	0.301(7)	0.488(4)	0.694(6)
Se1	0.666(7)	0.333(3)	0.157(5)
Se2	0.666(7)	0.333(3)	0.650(3)

Analyzing the data obtained on the crystal structure of the $Cu_{1.9}Tm_{0.1}Se$ compound, it was determined that the crystal structure of this compound has a higher symmetry compared to the Cu_2Se compound. This is due to the fact that when there are Tm elements inside the crystal, more arrangement occurs. Therefore, the symmetry of the crystal structure increases. In order to clarify the effect obtained in the crystal structure of $Cu_{1.9}Tm_{0.1}Se$ compound and the influence of Cu→Tm substitutions, the crystal structure of $Cu_{1.8}Tm_{0.2}Se$ compound obtained with higher concentrations of Tm atoms was studied. The X-ray diffraction spectrum taken at room temperature is shown in Figure 2.

From the analysis of the spectrum given in Figure 2, it was determined that the crystal structure of the $Cu_{1.8}Tm_{0.2}Se$ compound corresponds to the R-3m (166) space group structure with rhombohedral symmetry, as well as the crystal structure of the $Cu_{1.9}Tm_{0.1}Se$ compound. The values of the lattice parameters are set to: $a = b = 4.04116(4)$ Å, $c = 20.31306(2)$ Å, $V = 287.28(1)$ Å^3. The coordinates of Cu and Se atoms are given in Table 2.

Table 2. Atomic coordinates in the elementary lattice of compound $Cu_{1.8}Tm_{0.2}Se$.

Atom	***x***	***y***	***z***
Cu1	0.666(7)	0.333(3)	0.530(7)
Cu2	0.421(7)	0.585(5)	0.654(3)
Se1	0.666(7)	0.333(3)	0.160(2)
Se2	0.666(7)	0.333(3)	0.629(6)

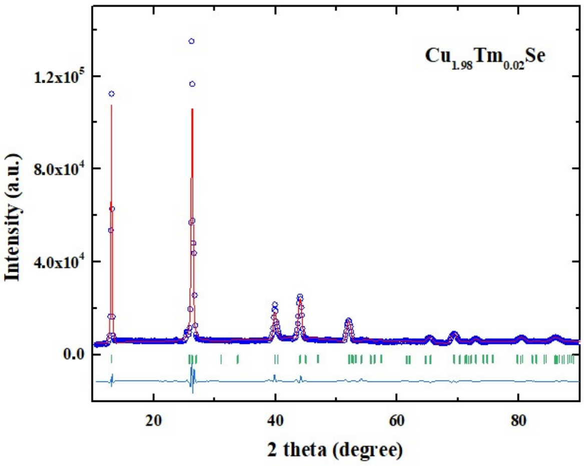

Figure 2. X-ray diffraction spectrum of compound $Cu_{1.8}Tm_{0.2}Se$

The analysis of the information obtained about the crystal structure of the $Cu_{1.8}Tm_{0.2}Se$ compound has shown that compared to the $Cu_{1.9}Tm_{0.1}Se$ compound, the volume of the elementary cell of this compound is smaller. It is known that the ion radius of Cu atoms is R_{Cu} = 0.96 Å, and the ion radius of Tm atoms is R_{Tm} = 1.36 Å [33]. Therefore, an increase in the concentration of Tm elements should have led to an increase in the volume of the elementary cell. However, a decrease has been observed instead. This is related to the fact that as the concentration of Tm elements inside the crystal increases, it seems as if the vacancies inside the crystal are filled and a more compact arrangement occurs. In order to clarify this effect, the crystal structure of the $Cu_{1.7}Tm_{0.3}Se$ compound with higher concentrations of Tm atoms has also been investigated. The X-ray diffraction spectrum obtained at room temperature is shown in Figure 3.

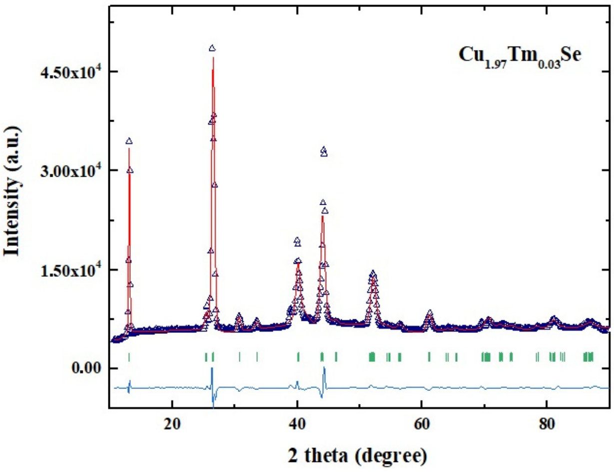

Figure 3. X-ray diffraction spectrum of the compound $Cu_{1.7}Tm_{0.3}Se$.

The analysis of the spectrum given in Figure 3 shows that the crystal structure of the $Cu_{1.7}Tm_{0.3}Se$ compound corresponds to the crystal structure of $Cu_{1.9}Tm_{0.1}Se$ and $Cu_{1.8}Tm_{0.2}Se$ compounds, which is in accordance with the rhombohedral symmetry R-3m (166) phase group. The lattice parameters are determined as: $a = b = 4.01955(2)$ Å, $c = 20.26288(1)$ Å, $V = 283.51(3)$ Å^3. The coordinates of Cu and Se atoms are given in Table 3.

Table 3. Atomic coordinates in the elementary lattice of compound $Cu_{1.7}Tm_{0.3}Se$.

Atom	***x***	***y***	***z***
Cu1	0.666(7)	0.333(3)	0.459(9)
Cu2	0.452(2)	0.639(9)	0.622(9)
Se1	0.666(7)	0.333(3)	0.167(8)
Se2	0.666(7)	0.333(3)	0.611(7)

The analysis of the crystal structure of the $Cu_{1.7}Tm_{0.3}Se$ alloy has revealed that compared to the $Cu_{1.9}Tm_{0.1}Se$ and $Cu_{1.8}Tm_{0.2}Se$ alloys, this alloy has a smaller volume of the elementary cell. This effect can be explained by the rearrangement of atoms inside the crystal as the concentration of Tm elements increases. Similar phenomena have been observed in other structures affected by rare earth elements in previous studies [33]. Figure 4 shows the dependence of the cell parameters and the volume of the elementary cell on the concentration of Tm atoms.

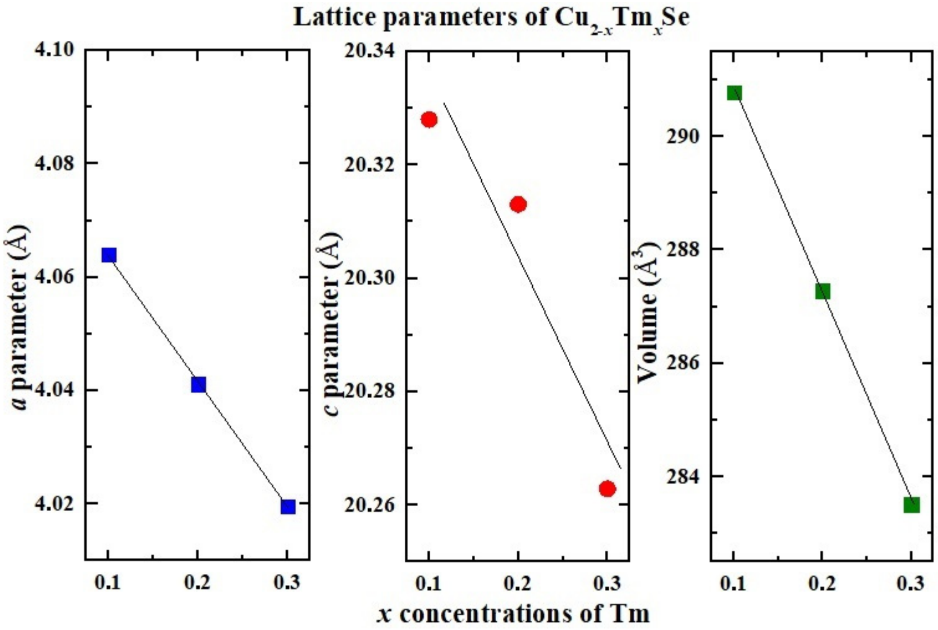

Figure 4. Dependence of lattice parameters of $Cu_{2-x}Tm_xSe$ compounds on the concentration of Tm atoms.

As can be seen from the dependencies shown in Figure 4, as the concentration of Tm atoms increases, both the values of lattice parameters and the volume of the elementary cell have decreased. The change in parameters has affected the c parameter the most. The mechanism of the change in the volume of $Cu_{2-x}Tm_xSe$ compounds depending on the concentration has occurred according to the law $\alpha = \frac{1}{V_0} \cdot \frac{dV}{dx}$. It has been determined that the decrease in volume in the interval $x = 0.1\text{-}0.3$ occurred with the coefficient $\alpha = -0.125$.

CONCLUSION

In the Cu2Se compound, Cu → Tm cation-cation substitutions have been used to synthesize $Cu_{1.9}Tm_{0.1}Se$, $Cu_{1.8}Tm_{0.2}Se$, and $Cu_{1.7}Tm_{0.3}Se$ compounds, and their structures have been investigated. It has been determined that as the concentration of Tm atoms increases, the symmetry of the crystals increases and a more ordered arrangement occurs. Depending on the concentration, changes in lattice parameters have been observed, and it has been determined that the changes mainly occur along the c-axis. The volume change mechanism has been calculated depending on the concentration, and it has been determined that it occurs with an $\alpha = -0.125$ coefficient.

ORCID

Y.I. Aliyev, https://orcid.org/0000-0001-8896-2180; **R.E. Huseynov,** https://orcid.org/0000-0003-0636-3948

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ВПЛИВ КАТИОН-КАТІОННИХ ЗАМІЩЕНЬ Cu → Tm НА СТРУКТУРНІ ВЛАСТИВОСТІ Cu_2Se

Ю.І. Алієв[a,b], А.О. Дащеміров[a], Т.М. Ільяслі[c], С.Р. Азімова[d], М.Е. Алієв[e], Г.Дж. Гусейнов[d]
[a]*Азербайджанський державний педагогічний університет, Баку, AZ-1000, Азербайджан*
[b]*Західно-Каспійський університет, Баку, AZ-1001, Азербайджан*
[c]*Бакинський державний університет, Баку, AZ-1148, Азербайджан*
[d]*Інститут фізики, Міністерство науки і освіти, Баку, AZ-1143, Азербайджан*
[e]*Нахчиванський державний університет, Нахічевань, AZ-7012, Азербайджан*

Синтезовано сполуки системи $Cu_{2-x}Tm_xSe$ ($x = 0.1$, 0.2, 0.3) та вивчено їх структурні властивості. Дослідження проводилися методом рентгенівської дифракції за кімнатної температури. Було встановлено, що кристалічна структура цих сполук відповідає ромбоедричній симетрії з просторовою групою R-3m(166). Для кожної сполуки було визначено параметри кристалічної решітки та атомні координати. Різниця між кристалографічними параметрами сполук $Cu_{1.9}Tm_{0.1}Se$, $Cu_{1.7}Tm_{0.3}Se$ та $Cu_{1.5}Tm_{0.5}Se$ була пояснена різницею між іонними радіусами атомів Cu та Tm.

Ключові слова: *Cu_2Se; рідкісноземельний елемент; халькогенід; рентгенівська дифракція*