

STUDY OF STRUCTURAL AND VIBRATIONAL PROPERTIES OF $\text{Cu}_2\text{In}_4\text{Se}_7$ BY ANALYTICAL METHODS

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The compound $\text{Cu}_2\text{In}_4\text{Se}_7$ was synthesized, the crystal structure and atomic dynamics were studied. The studies were carried out at room temperature and under normal conditions using XRD, Raman spectroscopy and FTIR spectroscopy. The obtained X-ray structural spectra were analyzed by the Rietveld method and various crystallographic parameters were determined. It was established that the crystal structure of this compound corresponds to tetragonal symmetry with the space group P-42c (112). As a result of the analysis of the Raman spectrum with the Gaussian function, it was established that in the $\text{Cu}_2\text{In}_4\text{Se}_7$ crystal in the frequency range $\nu = 0-800 \text{ cm}^{-1}$ 3 main vibrational modes are observed: $\nu_1 = 146 \text{ cm}^{-1}$, $\nu_2 = 171 \text{ cm}^{-1}$ and $\nu_3 = 229 \text{ cm}^{-1}$. It was found that these modes correspond to vibrations of InSe_4 tetrahedra formed by In-Se bonds. As a result of analysis of the FTIR spectrum, it was established that 3 main vibration modes are observed in the $\text{Cu}_2\text{In}_4\text{Se}_7$ crystal in the wavenumbers range $\nu = 400-4000 \text{ cm}^{-1}$. These modes are associated with water and carbon dioxide molecules in the sample.

Key words: Crystal structure; Chalcogen; Atomic dynamics; Crystallographic parameters

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1. INTRODUCTION.

The crystal structure and various physical properties of copper and silver chalcogenide semiconductors have long been studied by various methods. However, there are still a number of questions in this direction that require study. Compounds and solid solutions of the ABX_2 type (A – Cu, Ag; B – Fe, In, Ga; X – S, Se, Te) have been in the field of research for many years as promising electrically and optically sensitive materials. Studying the structure of these compounds, structural phase transitions and atomic dynamics is important for explaining their other physical properties. Therefore, extensive research has been carried out in this direction recently [1-5].

Copper chalcogenides have some advantages and disadvantages compared to other chalcogenides. The main advantage is that copper atoms, due to their variable valency, can form crystals of various configurations. These crystals differ in both electronic structure and crystal structure. The missing point is that two- and three-phase systems are often observed in these compositions. At high temperatures, the process of phase formation occurs and a single-phase system is formed [6-10].

In chalcogenide semiconductors, the effect of cation-cation substitutions is big. Because with substitutions, important changes occur in both the electronic structure and the crystal structure. At this time, chalcogenides exhibited interesting optical, electrical, and thermal properties. Therefore, extensive research is being carried out in this direction [11-13]. It has been established that the acquisition and study of single-phase systems with cation-cation substitution leads to the production of semiconductors with stable properties. In this work, a new compound $\text{Cu}_2\text{In}_4\text{Se}_7$ with $\text{Cu} \rightarrow \text{In}$ substitutions was synthesized. The structure and atomic dynamics of the resulting compound were studied by analytical methods.

2. EXPERIMENTAL PART

2.1. Synthesis. Polycrystalline sample of the $\text{Cu}_2\text{In}_4\text{Se}_7$ compound was synthesized by a standard method typical of chalcogenide semiconductors [14,15]. In the synthesis process, metal chalcogen elements Cu, In and Se with a purity of at least 99.98% were used. Based on the stoichiometry of the intended sample, the elements were weighed on a high-precision electronic balance, then a mixed mass weighing 5 g was poured into a synthesis ampoule and air ($\sim 10^{-2} \text{ Pa}$) was sucked into the ampoule). The oven temperature was previously raised to 700 K. For the synthesis process, the finished ampoule is placed in an inclined oven. After holding in this mode (700 K) for an hour, the furnace temperature was increased to 1200 K at a rate of 50 degrees/hour. The ampoule was shaken periodically and kept at this temperature for 1.5 hours. At the next stage, the oven temperature was again reduced to 750 K. To achieve sample homogeneity, long-term tabulation was carried out. During the heating process, the sample was kept at a temperature of 750 K for fifteen days. Upon opening the ampoule, it was noticed that the synthesized mass mainly consists of small single-crystalline tetrahedral grains.

2.2. XRD analysis. The crystal structure of the chalcogenide compound $\text{Cu}_2\text{In}_4\text{Se}_7$ was studied by X-ray diffraction. X-ray diffraction experiments of the synthesized sample were carried out on a modern D8 ADVANCE diffractometer. Diffractometer parameters: with $\text{CuK}\alpha$ irradiation, $\lambda = 1.5406 \text{ \AA}$, 40 kV, 40 mA. The synthesized polycrystal was ground in a mortar, and then structural studies were carried out. The X-ray phase spectrum obtained at room temperature and under normal conditions for the $\text{Cu}_2\text{In}_4\text{Se}_7$ compound was analyzed by the Rietveld method in the Mag2Pol program and the crystallographic parameters were determined.

2.3. Raman spectroscopy. Vibrational properties of the samples were studied by Raman spectroscopy method. The experiments were carried out on the Nanofinder 30 Raman spectrometer at room-temperature. Nd:YAG laser with a wavelength $\lambda = 532 \text{ nm}$ and a maximum power of 10 mW was used as an excitation source. The obtained spectra were analyzed by the Gaussian function.

2.4. FTIR spectroscopy. The sample for the FTIR (Fourier transforms infrared spectroscopy) experiment was prepared from cylindrical $\text{Cu}_2\text{In}_4\text{Se}_7$ compounds. The infrared spectrum was obtained at room temperature in the wavenumber range $\nu = 400\text{--}4000 \text{ cm}^{-1}$ using a Varian 640 FT-IR instrument.

3. RESULTS AND DISCUSSIONS

The X-ray diffraction spectrum of the chalcogenide compound $\text{Cu}_2\text{In}_4\text{Se}_7$ obtained at room temperature is shown in Figure 1.

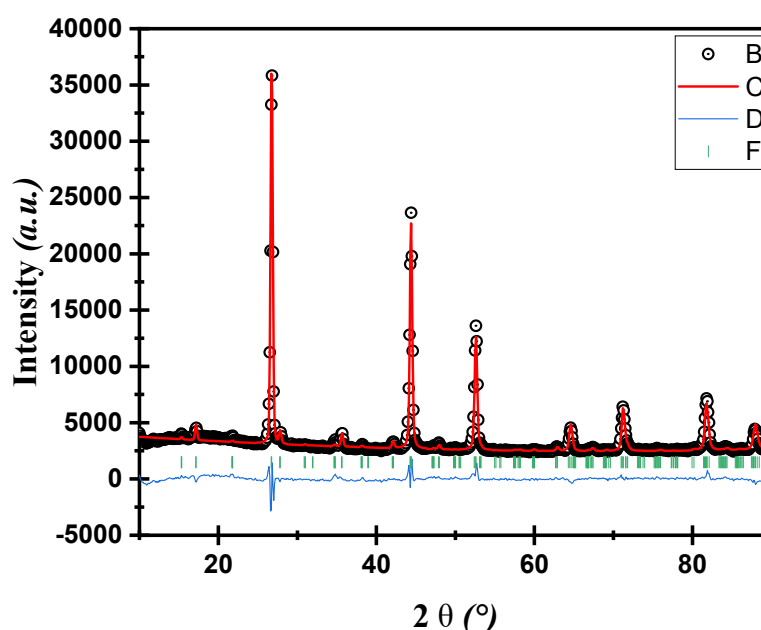


Figure 1. X-ray diffraction spectrum of $\text{Cu}_2\text{In}_4\text{Se}_7$ compound

B – experimental points, C – calculated curve, D – difference between experimental and calculated curves, F – atomic planes.

The diffraction spectrum obtained for the $\text{Cu}_2\text{In}_4\text{Se}_7$ compound in the diffraction angle range $10^\circ \leq 2\theta \leq 90^\circ$ was analyzed by the Rietveld method in the Mag2Pol program. As a result of the analysis, it was established that the crystal structure of this compound corresponds to a tetragonal system with space group P-42c(112). Values of lattice parameters: $a = b = 5.7624 \text{ \AA}$, $c = 11.5432 \text{ \AA}$, $V = 383.295 \text{ \AA}^3$, $\rho = 4.9697 \text{ g/cm}^3$, $Z = 2$. As a result of spectrum analysis, the coordinates of Cu, In and Se located in different crystallographic positions (Table 1).

Table 1. Atomic coordinates of the $\text{Cu}_2\text{In}_4\text{Se}_7$ compound.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	Occ
In1	0.00000	0.50000	0.25000	0.930
In2	0.50000	0.50000	0.00000	0.600
In3	0.50000	0.00000	0.25000	0.400
Se	0.25345	0.22727	0.12586	0.875
Cu	0.00000	0.00000	0.00000	1.000

It has been established that the crystal structure of the $\text{Cu}_2\text{In}_4\text{Se}_7$ compound consists of Cu atoms located at lattice sites, In atoms distributed throughout the lattice volume, and Se atoms forming tetrahedra by combining with In atoms. The three-dimensional crystal structure obtained in the Diamond 3.2 program, corresponding to tetragonal symmetry, is presented in Figure 2.

From the structure presented in Figure 2, it is clear that indium atoms combine with selenium atoms, forming InSe_4 tetrahedra. Although the indium atoms occupy three different positions, they are all monovalent, and all the polyhedra they form with the chalcogen atoms are tetrahedra. It is known that copper atoms form monovalent and divalent covalent

bonds in crystals. In the $\text{Cu}_2\text{In}_4\text{Se}_7$ compound, the copper atoms are located in the same crystallographic position and are in the monovalent state. Therefore, the crystal structure has a fairly simple form. It is known that copper atoms form monovalent and divalent covalent bonds in crystals. Interatomic distances were determined depending on the atomic coordinates and ionic radii. The obtained values are shown in Table 2.

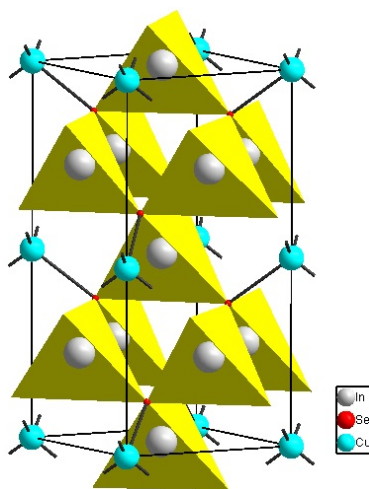


Figure 2. Crystal structure of the $\text{Cu}_2\text{In}_4\text{Se}_7$ compound

Table 2. Interatomic distances in the $\text{Cu}_2\text{In}_4\text{Se}_7$ compound

Atoms	Interatomic distances
In1 - Se	2.5800
In2 - Se	2.5689
In3 - Se	2.4056
Cu - Se	2.4411

Crystals with a polyhedral structure exhibit interesting atomic dynamic. Vibrations corresponding to both metal-chalcogen-metal bonds and vibrations of polyhedra are observed. From the structure shown in Fig. 2, it is clear that the $\text{Cu}_2\text{In}_4\text{Se}_7$ compound also forms a structure consisting of polyhedra. This predicts the observation of interesting vibrational properties in this compound. Therefore, the atomic dynamics of the $\text{Cu}_2\text{In}_4\text{Se}_7$ compound was studied using Raman spectroscopy. The Raman spectrum obtained in the wavenumbers range $\nu = 0\text{-}800\text{ cm}^{-1}$ at room temperature is shown in Figure 3.

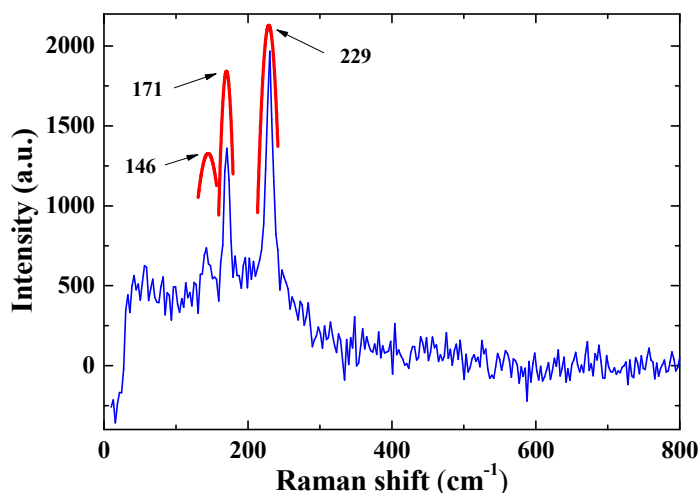


Figure 3. Raman spectrum of the $\text{Cu}_2\text{In}_4\text{Se}_7$ compound

From Figure 3 it can be seen that 3 main vibration modes are observed in the $\text{Cu}_2\text{In}_4\text{Se}_7$ crystal. These vibrational modes were interpreted using a Gaussian function. It has been established that these vibration modes correspond to the following wavenumbers: $\nu_1 = 146\text{ cm}^{-1}$, $\nu_2 = 171\text{ cm}^{-1}$ and $\nu_3 = 229\text{ cm}^{-1}$. It is known that in the wavenumbers range $\nu = 0\text{-}100\text{ cm}^{-1}$ vibrations of bonds formed by heavy elements are observed. At higher wavenumbers, vibrations of bonds formed by atoms of light elements such as H, C and O are observed. The main reason for the absence of such vibrations in the Raman spectrum obtained for the $\text{Cu}_2\text{In}_4\text{Se}_7$ crystal is that the sample was obtained with high purity. Consequently,

the obtained vibration modes correspond only to the frequencies of the bonds formed by the chemical elements included in the composition. It has been established that these modes correspond to In – Se bonds and vibrations of InSe_4 octahedra formed by these bonds. From the Raman spectrum it is clear that vibration modes are not observed at wavenumbers $\nu > 250 \text{ cm}^{-1}$. Vibration modes that occur at higher wavenumbers are observed mainly in bonds formed by atoms of light elements, such as H, C, O. It is known that there are no atoms of light elements in the $\text{Cu}_2\text{In}_4\text{Se}_7$ compound. However, in real crystals, due to contact with molecules of water and carbon dioxide in the air, it becomes possible to form bonds under the influence of atoms of light elements. FTIR spectroscopy studies were carried out to determine such connections. In Figure 4 shows the Fourier transform IR spectrum obtained for a $\text{Cu}_2\text{In}_4\text{Se}_7$ crystal under normal conditions and at room temperature.

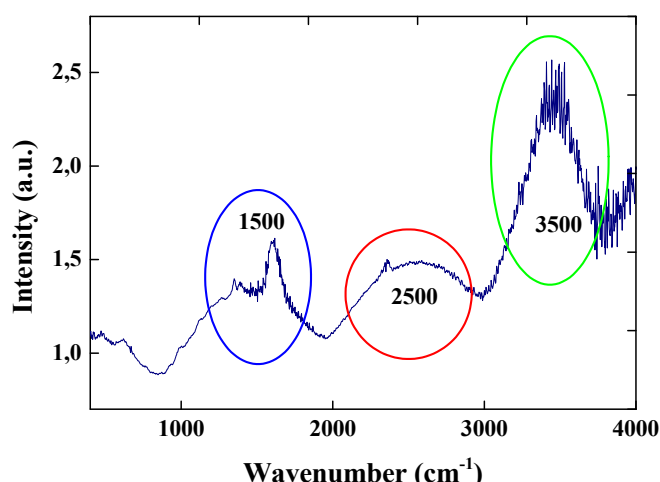


Figure 4. FTIR spectrum of the compound $\text{Cu}_2\text{In}_4\text{Se}_7$

From the spectrum shown in Figure 4, it is clear that in the wavenumbers range $\nu = 400\text{--}4000 \text{ cm}^{-1}$ three main maxima are observed. These maxima correspond to the values $\nu_1 = 1500$, $\nu_2 = 2500$ and $\nu_3 = 3500 \text{ cm}^{-1}$. In previous studies, it was found that vibrations with a wavenumber of $\nu \sim 1500 \text{ cm}^{-1}$ are carbon and oxygen, vibrations with a wavenumber of $\nu \sim 2500 \text{ cm}^{-1}$ are carbon, oxygen and hydrogen, and vibrations with a wavenumber of $\nu \sim 3500 \text{ cm}^{-1}$ are vibrations of bonds formed by oxygen and hydrogen atoms correspond to [16].

It is known that copper atoms are a metal of variable valence. The lengths of the bonds formed by chemical elements with variable valence are also different. Therefore, these systems have a complex structure. In the $\text{Cu}_2\text{In}_4\text{Se}_7$ compound, each of the Cu, In and Se atoms is in a stable divalent state. Therefore, such crystals have a simple structure. Such structures can be used as model objects to explain the structural aspects of certain physical properties. In recent years, crystal structures have begun to be used for theoretical and practical modeling of a number of processes [17,18]. From this point of view, the structural data obtained for the $\text{Cu}_2\text{In}_4\text{Se}_7$ compound may be useful for various purposes in the future. The results obtained can be used to study the electrical, optical, thermal and other physical properties of this crystal.

4. CONCLUSIONS

In the course of studying the crystal structure and atomic dynamics of the $\text{Cu}_2\text{In}_4\text{Se}_7$ compound, the following main results were obtained:

1. It has been established that the compound under study, $\text{Cu}_2\text{In}_4\text{Se}_7$, crystallizes in tetragonal systems and its crystallographic parameters are: $a = b = 5.7624 \text{ \AA}$, $c = 11.5432 \text{ \AA}$, $V = 383.295 \text{ \AA}^3$, $\rho = 4.9697 \text{ g/cm}^3$, $Z = 2$ and $P-42c(112)$, corresponding to their values.
2. When studying the atomic dynamics of the $\text{Cu}_2\text{In}_4\text{Se}_7$ compound, it was found that the vibration modes corresponding to the wavenumbers $\nu_1 = 146 \text{ cm}^{-1}$, $\nu_2 = 171 \text{ cm}^{-1}$ and $\nu_3 = 229 \text{ cm}^{-1}$ belong to In – Se bonds and vibrations of polyhedra formed by these bonds. The vibration modes observed at higher wavenumbers correspond to water and carbon dioxide molecules in the sample.

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ДОСЛІДЖЕННЯ СТРУКТУРНИХ ТА КОЛИВАЛЬНИХ ВЛАСТИВОСТЕЙ $\text{Cu}_2\text{In}_4\text{Se}_7$ АНАЛІТИЧНИМИ МЕТОДАМИ

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Синтезовано сполуку $\text{Cu}_2\text{In}_4\text{Se}_7$, досліджено кристалічну структуру та атомну динаміку. Дослідження проводили при кімнатній температурі та звичайних умовах із застосуванням XRD, рамановської спектроскопії та FTIR-спектроскопії. Отримані рентгенівські структурні спектри аналізували методом Рітвельда та визначали різні кристалографічні параметри. Встановлено, що кристалічна структура цієї сполуки відповідає тетрагональній симетрії з просторовою групою $P-42c$ (112). В результаті аналізу КР спектра з функцією Гаусса встановлено, що в кристалі $\text{Cu}_2\text{In}_4\text{Se}_7$ в діапазоні частот $\nu = 0-800 \text{ cm}^{-1}$ спостерігаються 3 основні коливальні моди: $\nu_1 = 146 \text{ cm}^{-1}$, $\nu_2 = 171 \text{ cm}^{-1}$ і $\nu_3 = 229 \text{ cm}^{-1}$. Встановлено, що ці моди відповідають коливанням тетрадрів InSe_4 , утворених зв'язками In-Se . В результаті аналізу спектру FTIR встановлено, що в кристалі $\text{Cu}_2\text{In}_4\text{Se}_7$ спостерігаються 3 основні моди коливань в діапазоні хвильових чисел $\nu = 400-4000 \text{ cm}^{-1}$. Ці режими пов'язані з молекулами води і вуглекислого газу в зразку.

Ключові слова: кристалічна структура; халькоген; атомна динаміка; кристалографічні параметри