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STRUCTURAL TRANSITIONS IN $Cu_{1.85}S$ SINGLE CRYSTALS

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$Cu_{1.85}S$ is of significant current interest due to its complex crystal chemistry, wide homogeneity range, and unique physicochemical properties. These materials belong to the class of digenites and exhibit various structural transformations and reversible phase transitions that are highly sensitive to copper content. The synthesis, growth, and investigation of the structural behavior of $Cu_{1.85}S$ single crystals provide essential insights into phase stability and transformation mechanisms in the $Cu_{2-x}S$ system. Such knowledge is crucial for potential applications in semiconductor devices, catalysts, and energy conversion systems, where the crystal structure and phase composition directly influence material performance. This paper presents the results of the synthesis, growth of single crystals, and X-ray phase analysis of the nonstoichiometric compound $Cu_{1.85}S$, which belongs to the class of digenites. The single crystals were obtained by combining the Bridgman directional crystallization method with slow cooling. A comprehensive microstructural and X-ray analysis was carried out, including the use of Weissenberg photographs and temperature-dependent diffraction studies in the range from room temperature to 420°C. It was established that at room temperature, the $Cu_{1.85}S$ sample is biphasic and consists of orthorhombic (P_{nma}) and monoclinic ($P2_{1/n}$) phases. Upon heating, two structural transitions were observed: first to a tetragonal phase at approximately 93°C, and then to a high-temperature face-centered cubic (FCC) lattice at around 120°C. All transitions are reversible and occur via a single-crystal-to-single-crystal mechanism with well-defined orientational relationships between the lattices. The biphasic nature at room temperature is attributed to the accumulation of copper atoms in twin regions. This work contributes to understanding structural transformations in the $Cu_{1.85}S$ system and confirms the existence of stable interphase transitions that depend on copper content.

Keywords: *Crystal; Phase transitions; X-ray diffraction; Digenite; Lattice*
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1. INTRODUCTION

Compounds of the $Cu-S$ system are among the most complex materials in crystal chemistry due to their nonstoichiometric nature, broad homogeneity range, and diverse phase states. Particular attention is given to copper sulfides of the $Cu_{2-x}S$ composition, which belongs to the class of digenites. These compounds are characterized by a high level of lattice defects, a variety of structural transformations, and unique physicochemical properties. They offer potential applications in semiconductor devices, catalysis, and energy conversion systems.

An analysis of the literature reveals that no universal method exists for synthesizing nonstoichiometric compounds of the $Cu-S$ system. While some studies utilized natural crystals, others involved powdered mixtures of the starting components, subjected to prolonged heat treatment or the slow-cooling method [3, 13]. However, variations in sample preparation conditions lead to discrepancies in structural study results. Thus, developing synthesis methods that ensure the production of homogeneous, single-phase, and well-crystallized samples is crucial.

It is known that at room temperature, $Cu_{2-x}S$ compounds often exist as two-phase systems. The most characteristic phases include the orthorhombic modification of the anilite type ($Cu_{1.75}S$, space group P_{nma}) and the monoclinic modification of the yarrowite type ($Cu_{1.96}S$, space group $P2_{1/n}$). These phases are close in both composition and unit cell parameters, making their identification by microstructural methods particularly challenging. Additionally, many compositions exhibit a metastable high-temperature cubic (FCC) modification.

Previous studies have shown that phase transformations in $Cu_{1.75}S$, $Cu_{1.80}S$, and $Cu_{1.90}S$ compounds exhibit different characteristics. Even small variations in copper content led to changes in both transition temperatures and transformation sequences [1,3]. This highlights the high sensitivity of the crystal structure to defect concentration and confirms the complexity of the phase behavior in digenite.

In this context, systematically investigating structural transformations in $Cu_{1.85}S$, a composition lying between the previously studied phases, is of particular interest. This study will help refine the understanding of phase stability within the $Cu_{2-x}S$ system, trace regularities in structural variations with respect to copper content, and elucidate the mechanisms of reversible phase transitions.

The objective of this work is to synthesize and grow $Cu_{1.85}S$ single crystals, perform comprehensive microstructural and X-ray phase analyses, and investigate temperature-dependent structural transformations from room temperature to 420°C.

MATERIALS AND METHODS

Synthesis of nonstoichiometric $Cu_{2-x}S$ compounds. Synthesis of nonstoichiometric $Cu_{2-x}S$ compounds. There is no single method reported in the literature for the synthesis of nonstoichiometric compounds of the $Cu-S$ system.

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Some authors used natural crystals, whereas in [4,5,6] samples of the desired phases with various compositions were obtained by mixing the individual components in powder form and then heat-treating. In one case, ampoules containing the corresponding components were held at 593–743 K for 7 days [4]; in another, Cu and S components in the desired stoichiometric ratios were heated to 773–873 K for 24 hours [5]; and in a third case, powdered Cu and S were maintained in an evacuated Pyrex ampoule for 7 days at 723 K [6].

In [3], pressed powders of Cu_2S and CuS were placed in an open glass ampoule and annealed for 12 hours at 383 K. In [10,11,12], samples of some nonstoichiometric $Cu-S$ compositions were obtained using the slow-cooling method.

An analysis of these studies shows that the existing discrepancies in structural investigations are primarily determined by the different conditions used to prepare various nonstoichiometric $Cu-S$ samples.

To obtain homogeneous samples of composition $Cu_{1.85}S$, we employed the direct synthesis method, i.e., the chemical reaction of the starting components. Double-walled ampoules made of high-quality quartz, possessing high thermal stability, were used as reactors. The main ampoules, with an inner diameter of 1.5 cm and a length of 10 cm, were filled with the starting materials – Cu (electrolytic) and S (grade "Ultra-pure") in the required amounts for each composition – and evacuated to a pressure of 10^{-5} mmHg.

All ampoules containing the respective compositions were placed in the stable zone of the furnace. The furnace temperature was raised to the melting point of sulfur ($393\ K$) and maintained at this temperature for 3 hours to ensure thorough interaction of molten sulfur with copper and to prevent ampoule rupture. The temperature was then increased at a rate of 50 K per hour up to the melting point of Cu_2S ($1403\ K$) with cyclic vibration. After a two-hour dwell at this temperature, the ampoules containing the samples were slowly cooled to $373\ K$ and annealed at this temperature for 300 hours to achieve homogenization, while the phase composition was monitored using microstructural and X-ray phase analyses.

Growth of $Cu_{1.85}S$ Single crystals. Given that nonstoichiometric $Cu_{2-x}S$ compounds are defect-containing crystals, the optimal method for obtaining single crystals of the desired $Cu_{1.85}S$ composition was determined experimentally to be a combination of the Bridgman method and slow cooling.

The synthesized $Cu_{1.85}S$ compositions were placed in specially designed high-quality quartz ampoules tailored for the Bridgman technique (length: 10 cm, inner diameter: 1 cm). The ampoules were evacuated to a pressure of 10^{-5} mmHg and subsequently placed in a two-zone furnace, where a temperature controller maintained the desired temperature. The furnace temperature was gradually increased above the melting point of Cu_2S. Following a three-hour dwell at this temperature, an electric motor was activated to lower the ampoule at a rate of 6 mm/h. Once the ampoule reached the lower zone of the furnace, it was transferred to an electric furnace and annealed at 573 K for 3 weeks. This annealing process corresponds to the lower zone of the two-zone furnace.

The samples obtained via this method were high-quality single crystals, exhibiting well-defined structural properties suitable for subsequent analysis.

Microstructural analysis. To reveal the microstructures, samples were prepared from each of the synthesized $Cu_{1.85}S$ composition. The surfaces of all samples were washed, degreased with ethanol, and dried after grinding and polishing. Experimentally, an etchant consisting of $50\%\ HNO_3\ +\ 50\%\ H_2O$, with the addition of 5% acetic acid to prevent oxidation was selected.

Microstructural analysis. To reveal the microstructures of the synthesized $Cu_{1.85}S$ compositions, samples were carefully prepared by grinding and polishing the surfaces of each specimen. Once polished, the samples were washed, then degraded with ethanol to remove surface contaminants, and finally dried. To reveal the structural details, an etching solution was applied to the samples. The etching solution consisted of 50% nitric acid (HNO_3) and 50% distilled water (H_2O), with 5% acetic acid added to prevent oxidation of the sample surface during etching.

This microstructural preparation method ensured the samples were adequately prepared for further analysis. The etchant enabled the identification of key microstructural features, including grain boundaries, phase distribution, and lattice defects, providing important insights into the overall quality and homogeneity of the synthesized $Cu_{1.85}S$ single crystals.

Debye-Scherrer patterns for all synthesized compositions were obtained using Cu Kα radiation under identical conditions. The calculations and indexing of interplanar spacings (see Tables 1-3) indicated that in $Cu_{1.85}S$ crystals, a second phase appears at room temperature. The amount in this second phase decreases as copper deficiency increases. Furthermore, in all $Cu_{1.85}S$ crystals, a metastable high-temperature face-centered cubic (FCC) phase also exists at room temperature.

The first phase in these compositions corresponds to anilite ($Cu_{1.75}S$), which crystallizes in an orthorhombic structure with unit cell parameters: $a = 7.89$ Å, $b = 7.84$ Å, and $c = 11.01$ Å, belonging to the space group Pnma, with $Z = 4$ formula units per unit cell. The second phase corresponds to yarrowite ($Cu_{1.96}S$), which crystallizes in a monoclinic structure with unit cell parameters: $a = 26.897$ Å, $b = 15.745$ Å, $c = 13.565$ Å, $\beta = 90.13°$, and space group $P2_1/n$. The unit cell contains 8 $Cu_{31}S_{16}$ formula units.

Due to the close composition and similar unit cell parameters of these two phases, distinguishing them in micrographs is practically impossible. However, their identification is essential as the two-phase nature of $Cu_{1.85}S$ at room temperature significantly influences the material's structural properties.

For the study of structural transformations, flat-parallel crystals were cleaved from the two-phase sample along the (111) cleavage plane, which corresponds to the high-temperature FCC phase. Diffraction measurements were taken from crystals mounted on a temperature-controlled stage of the diffractometer. At room temperature, nine diffraction peaks were recorded (see Table 3). These diffraction peaks are consistent with the existence of both phases.

Upon heating the crystal without changing its orientation, subsequent diffraction recordings were made at various temperatures. At higher temperatures, four of the nine diffraction peaks transitioned to tetragonal symmetry, indicating the formation of an intermediate phase. The equilibrium temperature between these phases, determined according to the method described in, corresponds to the transformation temperature from the low-temperature yarrowite phase to the intermediate tetragonal phase.

RESULTS AND DISCUSSION

Structural transitions in $Cu_{2-x}S$ crystals ($x = 0.10, 0.20$, and 0.25) were studied in detail in [1]. It was shown that at room temperature, these samples consist of two phases. One of them crystallizes in an orthorhombic lattice with unit cell parameters $a = 7.89$ Å, $b = 7.84$ Å, $c = 11.01$ Å; space group P_{nma}, $Z = 4$ [2]. The second phase has a monoclinic lattice with parameters $a = 26.897$ Å, $b = 15.745$ Å, $c = 13.565$ Å, $\beta = 90° 08'$, $Z = 8$ $Cu_{31}S_{16}$; space group $P2_{1/n}$, corresponding to the yarrowite ($Cu_{1.96}S$) lattice described in the literature [3].

For the samples of the specified compositions, the structural data and transformation temperatures are presented in Table 1. As in Table 1, the sequence of structural transformations in $Cu_{1.75}S$ and $Cu_{1.80}S$ samples is identical, whereas the transitions in $Cu_{1.90}S$ occur according to a different sequence. In the $Cu_{1.75}S$ and $Cu_{1.80}S$ samples, the first phase (α_1) corresponds to the tetragonal phase, followed by a transformation to a second phase (α_2) at a higher temperature. The sequence of transformations for these samples is consistent, with α_1 transforming to α_2 at 116°C and 104°C, respectively. In contrast, the $Cu_{1.90}S$ sample exhibits a distinct transformation pattern, with its first phase (α_1) remaining stable until a much higher transition temperature is reached.

Table 1. Structural and temperature transformations in $Cu_{2-x}S$ [1-3].

Composition	Phase	Transformation temperature, °C	Intermediate phases	Temperature of the intermediate transformation, °C	Lattice parameters of the high-temperature phase
$Cu_{1.75}S$	α_1	35	Tetragonal	116	(FCC) ($a = 5.5$)
	α_2	80			
$Cu_{1.80}S$	α_1	38	»	118	(FCC) ($a = 5.58$ Å)
	α_2	83			
$Cu_{1.90}S$	α_1	-	Orthorhombic + Hexagonal Close-Packed (HCP) ($a_{hex} = 3.97$ Å; $c_{hex} = 6.69$ Å)	157	(FCC) ($a = 5.62$ Å)
	α_2	104			

It was of interest to investigate how the structure and the sequence of structural transformations vary with the composition, specifically from $Cu_{1.80}S$ to $Cu_{1.90}S$, as demonstrated by the X-ray study of structural transformations in these compounds.

The main X-ray measurements were carried out using an "Enraf-Nonius" goniometer and a D8 ADVANCE diffractometer (Cu Kα radiation; $5^{\circ} \leq 2\theta \leq 100^{\circ}$), operating in the temperature range from room temperature to $420\ °C$, with the use of the EVA and Topas 4.2 software packages supplied with the diffractometer.

To determine the unit cell parameters and the crystal system of the $Cu_{1.85}S$ single crystal at room temperature, a Weissenberg photograph of the zero-layer line along the $(1\bar{1}0)$ direction [1] and a powder pattern were recorded, the calculation of which is presented in Table 2 (diffraction lines of the α_2-phase were indexed based on a pseudo-monoclinic crystal system).

Table 2. Recording of the $Cu_{1.85}S$ debaegram (sample radius – 0.8 mm; Cu Kα radiation, Ni filter)

No. lines	d_{exsp}, Å		α_1 - phase		α_2- phase	
		I/I	$d_{theoretical}$, Å	hkl	$d_{theoretical}$, Å	hkl
1	3.334	2	3.3239	013	3.3183	233
2	3.209	8	3.2066	202	3.2172	214
3	2.960	1	2.9600	122	2.9505	143
4	2.770	1	2.7807	220	2.7855	234
5	2.681	4	2.6870	203	2.6736	015
6	2.540	3	2.5368	123	2.5371	253(704)
7	2.417	1	2.4201	131	2.4202	505
8	2.365	6	2.3731	302	2.3714	235
9	2.260	4	2.2617	132	2.2608	006
10	2.172	1	2.1692	214	2.1701	316(026)
11	2.132	5	2.1372	231	2.1349	072(470)
12	2.023	10	2.0258	232	2.0219	336(255)
13	1.866	8	1.8654	215	1.8675	407(265)
14	1.821	1	1.8280	331	1.8193	482(256)
15	1.743	2	1.7426	116	1.7425	483
16	1.690	1	1.6963	413	1.6956	008
17	1.670	9	1.6723	242	1.6720	384(218)
18	1.652	1	1.6505	315	1.6512	547(057)
19	1.600	1	1.6033	404	1.6016	457(238)

No. lines	d_{exsp}, Å		α_1 **- phase**		α_2**- phase**	
		I/I	$d_{theoretical}$, Å	hkl	$d_{theoretical}$, Å	hkl
20	1.551	2	1.5506	325	1.5510	476(3.10.0)
21	1.442	2	1.4419	0.53	14400	239(748)
22	1.385	4	-	-	1.3836	3.11.2(096)
23	1.305	3	1.3067	0.60	1.3045	3.11.4(0.12.1)
24	1.287	1	1.2878	254	1.2878	4.12.0
25	1.265	2	1.2644	353	1.2651	4.12.2
26	1.204	1	1.2049	318	1.2037	4.12.4
27	1.140	6	1.1411	256	1.1406	0.13.4(5.13.3)
28	1.119	3	1.1188	633	1.1188	4.12.6
29	1.087	2	1.0867	641	1.0873	6.14.1(5.14.2)
30	1.072	3	1.0721	455	1.0723	4.12.7
31	0.989	5	0.9893	636(800)	0.9896	5.14.6(0.12.9)
32	0.947	7	0.9462	654	0.9465	5.16.3(3.15.6)

Analysis of the Debye and Weissenberg patterns reveals that, as in the case of $Cu_{1.75}S$, $Cu_{1.80}S$, and $Cu_{1.90}S$, two systems of reflections are observed. One of these corresponds to the $Cu_{1.85}S$ sample, which possesses an orthorhombic lattice with unit cell parameters: α = 7.94 Å, b = 7.86 Å, c = 11.12 Å, and space group Pbnm, while the other corresponds to variscite.

For the study of structural transformations, flat-parallel $Cu_{1.85}S$ crystals were cleaved from the two-phase sample along the cleavage plane (111), which belongs to the high-temperature FCC phase. From a crystal mounted on the diffractometer's temperature stage, nine diffraction peaks were recorded at room temperature (see Table 3).

Table 3. Calculations of the $Cu_{1.85}S$ Diffractogram; Cu Kα Radiation

$No.$ lines	$\theta,°$	d, Å	$hkl\ (\alpha_1)$	$hkl\ (\alpha_2)$	Unit Cell Parameters	$t, °C$
1	13°22'	3.334	013	233	α_1 - Phase ($a = 7.84;\ b = 7.89;\ c = 11.01$ Å)	22
2	13°53'	3.209	202	214		
3	16°43'	2.680	203	015		
4	26°15'	1.743	116	483		
5	27°20'	1.679	242	384	α_2- Phase ($a = 26.864$ Å; $b = 15.759$ Å; $c = 13.565$ Å; $\beta = 90.13°$)	
6	28°40'	1.607	404	457		
7	43°33'	1.119	633	4.12.6		
8	45°10'	1.087	641	6.14.1		
9	45°58'	1.072	455	4.12.7		
1	13°50'	3.224	102		Tetragonal ($a = 4.00;\ c = 11.18$ Å)	100
2	26°16'	1.742	203			
3	28°34'	1.612	204 (007)			
4	45°46'	1.076	323			
1	13°48'	3.232	111		FCC ($a = 5.603$ Å)	150
2	28°27'	1.618	222			
3	45°37'	1.079	333			

Then, without changing the crystal orientation, control recordings were performed every $10\ °C$ to observe changes in the diffraction pattern. Only at $100\ °C$ were four out of nine diffraction peaks recorded (see Table 3), which can be indexed on the basis of a tetragonal symmetry. The equilibrium temperature between the phases, $t = (93 \pm 1)\ °C$ (determined according to the method described in [4]), corresponds to the transformation temperature of the low-temperature yarrowite phase into the intermediate phase.

The intermediate tetragonal phase in $Cu_{1.85}S$ transforms into a phase with a face-centered cubic (FCC) lattice at $(120 \pm 1)\ °C$ (see Table 3). A series of temperature-dependent diffractometric recordings and Laue photographs taken before and after each transformation showed that all structural transitions in the $Cu_{1.85}S$ single crystal are reversible, with rigid orientational relationships between the lattices of the modifications, and that the transitions occur via a single-crystal-to-single-crystal mechanism.

Once the temperatures and the number of structural phase transitions were determined, Weissenberg photographs of each phase were taken at $t_1 > 93\ °C$ and $t_2 > 120\ °C$.

Zero-layer line projections were obtained by rotating the crystal around the direction that, at temperatures above $120\ °C$, corresponds to the $(1\bar{1}0)$ direction of the FCC lattice.

The Weissenberg photograph recorded at room temperature contains two systems of reflections, corresponding to the α_1 (orthorhombic) and α_2 (monoclinic) lattices, which merge into a single tetragonal lattice in the Weissenberg photograph obtained at $t_1 > 90\ °C$. The Weissenberg photograph was recorded at $t_2 > 120\ °C$ corresponds to the FCC lattice.

It should be noted that, unlike the first α_1 phase, the α_2 phase is characterized by twins, where each main reflection from the crystal on the radiograph corresponds to a weaker spot arising from rotation of the sample by precisely fixed angles of $70°12'$ and $109°48'$ (angles between the body diagonals of the cube). As in the $Cu_{1.75}S$ and $Cu_{1.80}S$ samples, for the high-temperature form of $Cu_{1.85}S$, the twin lattice nodes can be obtained by mirror reflection in four noncoplanar

(111) planes of the primary cubic lattice or by rotation around the $(1\bar{1}0)$ axes. The elements of twinning are the (111) plane and the $(11\bar{2}\ )$ direction – typical for FCC metals [5].

Upon cooling the sample to room temperature, the diffraction pattern is completely restored in reverse sequence; that is, the single FCC phase passes through the intermediate tetragonal phase and transforms into a mixture of monoclinic and orthorhombic phases. The formation of two phases at room temperature is explained as follows. The anion lattice is fully occupied by sulfur atoms, while the copper atom positions are nonequivalent. Therefore, during the transition from the intermediate phase to the low-temperature phase, some copper atoms can accumulate in the twin regions, where a structure closer to the stoichiometric composition, i.e., $Cu_{1.96}S$, is formed. The amount of the $Cu_{1.96}S$ phase is minimal for $Cu_{1.75}S$ and increases as the alloy's copper deficiency decreases.

From this, it follows that digenite and yarrowite occupy different concentration ranges.

CONCLUSIONS

1. The $Cu_{1.85}S$ single crystal at room temperature consists of two coexisting phases: an orthorhombic (Pnma) phase and a monoclinic ($P2_1/n$) phase. This biphasic nature is attributed to the non-uniform distribution of copper atoms, which accumulate in twin regions, thereby contributing to the material's structural complexity.
2. X-ray phase analysis demonstrated the occurrence of two consecutive, reversible phase transitions in $Cu_{1.85}S$. The first transition occurs from the orthorhombic phase to an intermediate tetragonal phase at approximately 93°C, followed by a transformation to a high-temperature face-centered cubic (FCC) lattice at around 120°C. These transitions are well-defined and occur via a single-crystal-to-single-crystal mechanism.
3. The phase transitions in $Cu_{1.85}S$ are characterized by preserved orientational relationships between the lattices, indicating high structural order. The transitions are reversible and exhibit stable interphase transitions, with their behavior strongly influenced by the copper content, confirming the sensitivity of the material's structural properties to composition variations.

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REFERENCES

[1] N. Alsen, "Über Kristallstrukturen von Covelline (CuS) und Kupferglanz (Cu_2S)," Geologiska Föreningens I. Stockholm Förhandlingar, **53**, 111–120 (1931).
[2] P. Rahlfs, "Über die kubischen Hochtemperaturmodifikationen der Sulfide, Selenide und Telluride des Silbers und des einwertigen Kupfers," Zeitschrift für Physikalische Chemie, (B), **31**, 157–194 (1936).
[3] M.J. Buerger, aand N.W. Buerger, "Low Chalcocite and High Chalcocite," American Mineralogist, **29**(1–2), 55–65 (1944).
[4] S. Djurle, "An X-ray Study on the System Cu-S," Acta Chemica Scandinavica, **12**(7), 1415–1427 (1958). https://doi.org/10.3891/acta.chem.scand.12-1415
[5] E.H. Roseboom, "An Investigation of the System Cu-S and Some Natural Copper Sulfides between 25 and 700°C," Economic Geology, **61**(1), 641–672 (1966). https://doi.org/10.2113/gsecongeo.61.4.641
[6] O. Kimihiko, and K. Shichie, "Electrical Conduction and Phase Transformation of Copper Sulfides," Journal of the Physical Society of Japan, **16**(8), 1130–1138 (1973).
[7] W. Kurz, "Chemisch-röntgenographische Untersuchungen an Kuban Kupferglanz," Zeitschrift für Kristallographie - Crystalline Materials, **92**(1-6), 408–434 (1935). https://doi.org/10.1524/zkri.1935.92.1.408
[8] Kh.Kh. Hashimov, and N. Suleymanov, "Diffractometric Study of Structural Phase Transformations in $Cu_{2-x}S$ and $Cu_{2-x}Fe_{0.05}S$ Crystals," Advanced Physical Research, **7**(1), 123-132 (2025). https://doi.org/10.62476/apr.71123
[9] T. Howard, and I. Evans, "The crystal structures of low chalcocite and djurleite," Zeitschrift für Kristallografie, **150**, 299–320 (1979). https://doi.org/10.1524/zkri.1979.150.14.299
[10] Hashimov Kh.Kh. T.M. Isayeva, "X-ray Graphic Study of Structural Transformations in Crystals of Cu_2–x$Ni_{0.05}S$ (x = 0.05, 0.25, 0.30)," New Materials Compounds and Applications, **8**(1), 121-134 (2024). https://doi.org/10.62476/nmca8121
[11] Kh.Kh. Hashimov, "Synthesis of $Cu_{2-x}Ni_{0.5}S$ (x = 0.05, 0.25, 0.30) Compounds and Study of Single Crystals", Asian Journal of Physical and Chemical Sciences, **11**(3), 45-51 (2023). https://doi.org/10.9734/AJOPACS/2023/v11i3205
[12] Kh.Kh. Hashimov, "Investigation of Crystal Structure and Polymorphic Transformations of Cu-S System Compounds," in: *V International Scientific and Practical Conference "Modern Science: Actual Problems*", (Manchester, UK, 2023), pp. 55-59. https://doi.org/10.5281/zenodo.7950997
[13] Kh.Kh. Hashimov, "Investigation of Polymer Transformations in Crystals," in: *International Scientific-Practical Conference on Mathematical Methods and Mechatronic Systems in Engineering*, (2023), pp.25–27.

СТРУКТУРНІ ПЕРЕХОДИ В МОНОКРИСТАЛАХ $Cu_{1,85}S$

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$Cu_{1,85}S$ представляє значний сучасний інтерес завдяки своїй складній кристалохімії, широкому діапазону однорідності та унікальним фізико-хімічним властивостям. Ці матеріали належать до класу дигенітів і демонструють різні структурні перетворення та оборотні фазові переходи, які є дуже чутливими до вмісту міді. Синтез, вирощування та дослідження структурної поведінки монокристалів $Cu_{1,85}S$ дають важливе розуміння фазової стабільності та механізмів перетворення в системі $Cu_{2-x}S$. Такі знання є вирішальними для потенційного застосування в напівпровідникових пристроях, каталізаторах та системах перетворення енергії, де кристалічна структура та фазовий склад безпосередньо впливають на характеристики матеріалу. У цій статті представлені результати синтезу, вирощування монокристалів та рентгенофазового аналізу нестехіометричної сполуки $Cu_{1.85}S$, яка належить до класу дигенітів. Монокристали були отримані шляхом поєднання методу спрямованої кристалізації Бріджмена з повільним охолодженням. Було проведено комплексний мікроструктурний та рентгеноструктурний аналіз, включаючи використання фотографій Вайсенберга та температурно-залежних дифракційних досліджень в діапазоні від кімнатної температури до 420°C. Було встановлено, що за кімнатної температури зразок $Cu_{1,85}S$ є двофазним і складається з орторомбічної (Pnma) та моноклінної $P2_{1/n}$ фаз. При нагріванні спостерігалися два структурні переходи: спочатку до тетрагональної фази приблизно при 93°C, а потім до високотемпературної гранецентрованої кубічної (ГЦК) решітки приблизно при 120°C. Усі переходи є оборотними та відбуваються за механізмом від монокристала до монокристала з чітко визначеними орієнтаційними зв'язками між гратками. Двофазний характер за кімнатної температури пояснюється накопиченням атомів міді в двійникових областях. Ця робота сприяє розумінню структурних перетворень у системі $Cu_{1.85}S$ та підтверджує існування стабільних міжфазних переходів, залежних від вмісту міді.

Ключові слова: *кристал; фазові переходи; рентгенівська дифракція; дигеніт; ґратка*