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X-RAY GRAPHIC STUDY OF STRUCTURAL TRANSFORMATIONS IN CRYSTALS OF $Cu_{2-x}Ni_{0.05}S$ $(x = 0.05, 0.25, 0.30)$

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Abstract. The article is devoted to the physico-chemical and structural phenomena that occur under the influence of the partial replacement of Cu atoms with Ni atoms in Cu2S crystals on the mechanism and nature of the phase transition. For this purpose, X-ray phase analysis of single crystals Cu_(2-x) Ni_0.05 S (x=0.05,0,25,0,30) was performed, which were synthesized and grown in the laboratory for the first time. A diffractogram of the crystal Cu_1.70 Ni_0.05 C, Cu_1.75 Ni_0.05 C, Cu_1.95 Ni_0.05 C was prepared at a room temperature. The results were analyzed. Thus, it was found that, unlike non-stoichiometric Cu_(2-x)S compounds having two and three phases at room temperature, the obtained crystals Cu_1.70 Ni_0.05s, Cu_1.75 Ni_0.05s and Cu_1.95 Ni_0.05s are single-phase. The reliability of the experimental results were confirmed by the theoretical calculations using the example of the fragment taken from the diffractogram of the Cu1.95Ni0.05S crystal (radiation: CuKa (λα=1.5418 A0), filter-Ni, mode: 35 kV, 10 mA).

Keywords: *polymorphic transformation, semiconductor, crystal, diffractogram, monocline.*

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1. Introduction

Modern semiconductor physics studies the various properties of semiconductor materials and their dependence on numerous external parameters (for example, temperature, pressure, strong electric field, etc.). The influence of these external parameters, various processes occur in matter. Examples of that process include structural changes in the crystal, decomposition of solid solutions, ordering and disordering, recrystallization, and so on can be shown (Nasirov & Abbasova, 2005; Solanki *et al*., 2023).

Among the mentioned materials, non-stoichiometric combinations of the $Cu - S$ system occupy a special place (Hashimov, 2023). When the composition of those system compounds is changed, structural transformations occur in the system under the influence of temperature and pressure. This transformation changes the concentration of charge carriers. For example, thermodynamic method, spectral analysis, microscopic method, X-ray method, etc. (Nasirov & Bairamov, 2020; Haziyeva *et al*., 2018).

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The x-ray graphic method is widely used to study structural transformations. So that, with the help of this method, it is possible to study not only optically transparent crystals, but also optically opaque crystals. Also, the X-ray diffraction method is an objective, accurate and universal method. Since the object of research in the presented article is opaque crystals, this method is more suitable for the purpose (Fedyna *et al*., 2005; Jafarov *et al*., 2014).

Considering the above, polymorphic transformations in $Cu_{2-x}Ni_{0.05}S$ ($x = 0.05, 0.25, 0.30$) crystals were studied by X-ray method and a comparative analysis of the obtained results with theoretical values was carried out.

2. Research objects and methods

2.1. Polymorphic transformation in $Cu_{1.70}Ni_{0.05}S$ crystal

To make this transformation the crystal samples were cut and shaped into a planar shape of 1x4x6 mm^3 size. X-ray studies were first performed at room temperature in the angular range $0° \leq 2\theta \leq 100°$. The studies were carried out in a DRON-3M X-ray diffractometer equipped with a URVT-2000 heater (Hashimov, 2023; Solanki *et al*., 2023).

10 diffraction reflections in the above-mentioned angular range were recorded from the polished face of $Cu_{1.70}Ni_{0.05}S$ at room temperature. Those reflections belonged to the monoclin lattice, the parameters of the lattice are $a = 26.897$ A^0, b $= 15.745$ A^0, c $= 13.56$ A^0, $\beta = 90^0 13'$. At temperature T $= 323$K, reflections from the (001) and (201) planes disappeared, and a new reflection appeared from the (0.10.2) plane. At that temperature, reflections are indexed in a monoclinic lattice. The parameters of this lattice are $a = 26.897$ A^0, b $= 15.745$ A^0, c $= 13.56$ A^0, $\beta = 90^0 13'$.

Table 1 shows the report of the diffractogram for the temperatures at which noticeable changes in the number and intensity of diffraction reflections occur in the $Cu_{1.70}Ni_{0.05}S$ crystal.

As can be seen from Table 1, structural changes occur in this crystal at the temperature T $= 423$ K. Thus, the monoclinic lattice becomes a face-centered cubic lattice. The face-centered cubic lattice parameter is $a = 5.596$ A^0. Seven diffraction reflections were observed in the face-centered cubic lattice, and the most intense one was reflected from the (222) plane.

Table 1. Report of the diffractogram of $Cu_{1.70}Ni_{0.05}S$ crystal
(Radiation: Cu Kα ($\lambda_\alpha = 1.5418$ A^0), filter-Ni, mode: 35kV, 10mA)

T , K	θ	İ/İ$_0$	d $_{reflection,}$ A^0	d$_{calculation,}$ A^0	hkl	Cage parameters
293	$3^0 16'$	10	13.525	13.5650	001	Monocline a $= 26.897$ A^0 b $= 15.745$ A^0 c $= 13.565$ A^0 $\beta = 90^0$ 13' z $= 8$ $\rho = 5.290$ q/sm^3 Space group: $P2_{1/n}$
	$4^0 48'$	30	9.210	9.5396	201	
	$13^0 47'$	20	3.236	3.2172	214	
	$15^0 02'$	10	2.9719	2.9711	350	
	$15^0 44'$	15	2.8426	2.8484	034	
	$16^0 14'$	40	2.7572	2.7496	740	
	$18^0 43'$	50	2.4023	2.4020	634	
	$19^0 31'$	30	2.3074	2.3076	054	
	$23^0 05'$	100	1.9666	1.9645	373	
	$24^0 19'$	60	1.8720	1.8716	282	
323	$13^0 45'$	20	3.245	3.2309	214	Monocline

	$15^0\,00'$	10	2.979	2.9775	350	$a = 26.897\ A^0$ $b = 15.745\ A^0$ $c = 13.565\ A^0$ $\beta = 90^0\ 13'$ $z = 8$ $\rho = 5.290\ q/sm^3$ Space group: $P2_{1/n}$
	$15^0\,41'$	15	2.852	2.756	034	
	$16^0\,12'$	40	2.763	2.7629	740	
	$18^0\,40'$	50	2.409	2.4140	634	
	$19^0\,28'$	30	2.313	2.3131	054	
	$23^0\,02'$	100	1.971	1.9697	373	
	$24^0\,16'$	60	1.876	1.8755	282	
	$30^0\,09'$	30	1.535	1.5365	0.10.2	
423	$13^0\,48'$	60	3.231	3.2323	111	Face-centered cubic lattice $a = 5.596\ A^0$ $\rho = 5.419\ q/sm^3$ Space group: Fm3m
	$16^0\,00'$	10	2.798	2.7972	200	
	$22^0\,56'$	60	1.979	1.9785	220	
	$27^0\,11'$	50	1.687	1.6876	311	
	$28^0\,30'$	100	1.615	1.6154	222	
	$33^0\,26'$	20	1.399	1.3991	400	
	$38^0\,02'$	30	1.251	1.2513	420	

The picture of the diffractogram taken from the $Cu_{1.70}Ni_{0.05}S$ crystal is given in Figure 1. As is seen the picture of diffraction reflections in the sample viewed at temperature $T > 423K$ changes completely. So, a structural transformation occurs in this crystal.

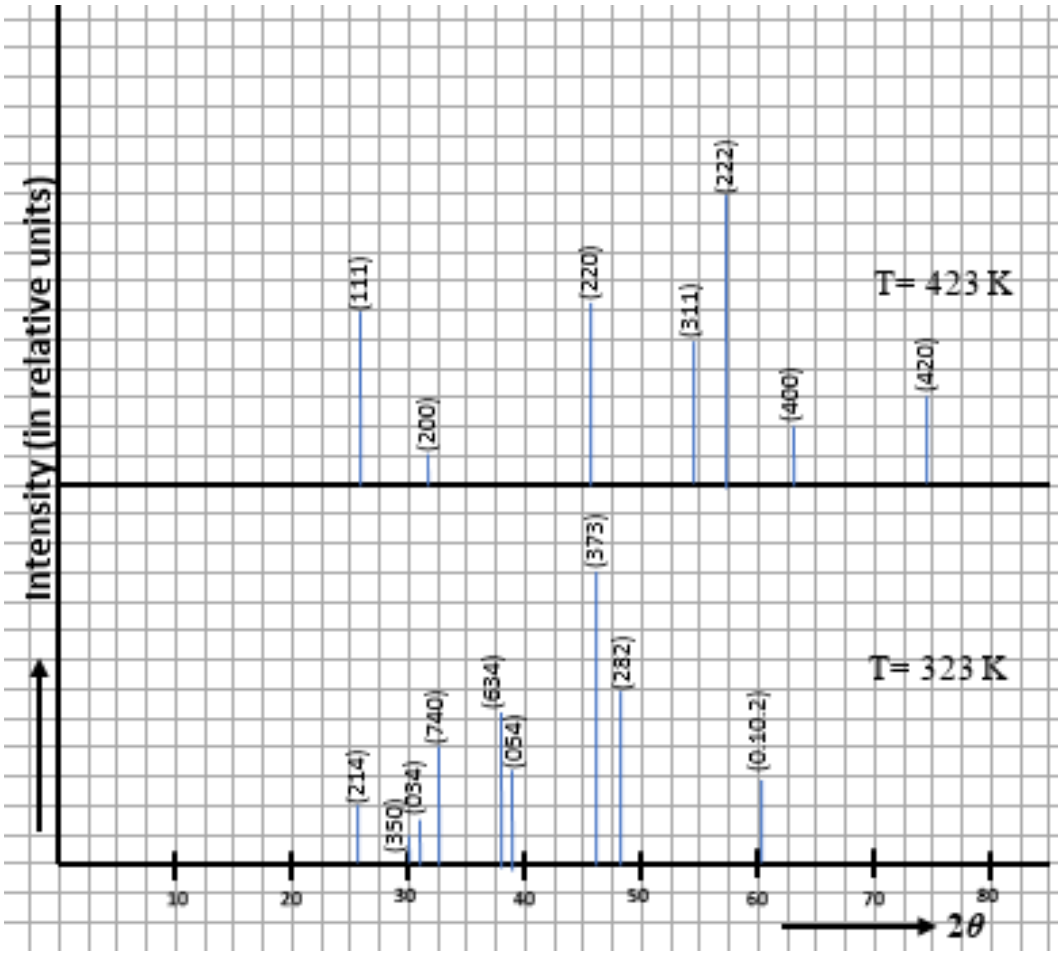

Figure 1. Diffractogram of $Cu_{1.70}Ni_{0.05}S$ crystal

As a result of the conducted research, it can be concluded that structural transformations in the $Cu_{1.70}Ni_{0.05}S$ crystal follow the following scheme (Figure. 2).

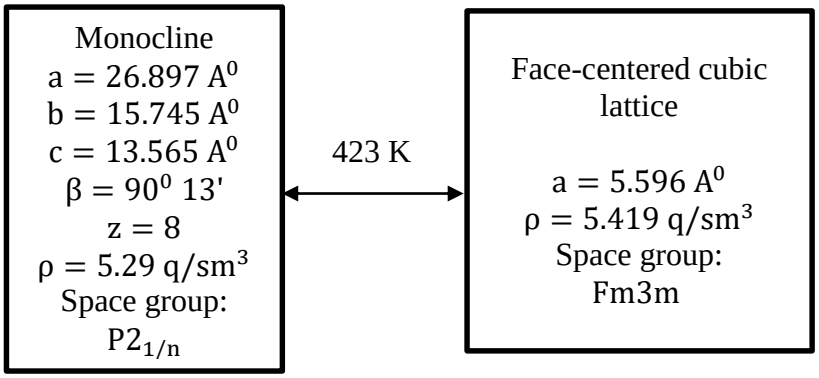

Figure 2. Structural transformations in $Cu_{1.70}Ni_{0.05}S$ crystal

For comparison, the scheme of structural transformations in Cu_2S has the following form (Hashimov, 2023; Alsén, 1931).

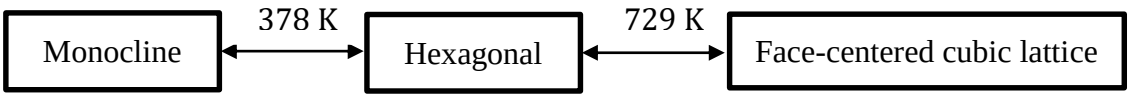

Figure 3. Structural transformations in Cu_2S crystal

As can be seen, unlike Cu_2S, the monoclinic lattice in the $Cu_{1.70}Ni_{0.05}S$ crystal directly transforms into a face-centered cubic lattice at $T = 423K$.

It should be noted that the distance between planes and lattice parameters in the crystal lattice are calculated by the following formulas known to science (Nasirov *et al.*, 2012).

For monoclinic lattice:

$$\frac{1}{d^2_{(hkl)}} = \frac{h^2}{a^2 sin^2\beta} + \frac{k^2}{b^2} + \frac{l^2}{c^2 sin^2\beta} - \frac{2hlcos\beta}{ac\, sin^2\beta}. \quad (1)$$

For a hexagonal lattice:

$$\frac{1}{d^2_{(hkl)}} = \frac{4(h^2+k^2+hk)}{3a^2} + \frac{l^2}{c^2} \quad \text{and} \quad sin^2\theta = \frac{\lambda^2}{4}\left[\frac{4(h^2+k^2+hk)}{3a^2} + \frac{l^2}{c^2}\right]. \quad (2)$$

For cubic lattice:

$$\frac{1}{d^2_{(hkl)}} = \frac{h^2+k^2+l^2}{a^2}. \quad (3)$$

The observed transformation is enantiotropic, face-centered cubic→monoclinic, when $T < T_0$, and monoclinic→face-centered cubic transition occurs, when $T > T_0$. Here T_0 is the equilibrium temperature of modifications.

2.2. Polymorphic transformation in $Cu_{1.75}Ni_{0.05}S$ crystal

Using the above-mentioned method, diffractometric studies were carried out on the $Cu_{1.75}Ni_{0.05}S$ crystal in the angle range $0^0 \leq 2\theta \leq 100^0$ on the 1x4x6 mm^3 crystal.

As a result of shooting at room temperature, it was found that 10 diffraction reflections are observed from the studied sample. Maximum intensity refers to reflection from the (180) plane. The diffraction reflections are indexed in a monoclinic lattice and the lattice constants are $a = 26.847\ A^0$, $b = 15.745\ A^0$, $c = 13.565\ A^0$, $\beta = 90^0 13'$. The lattice space group is $P2_{1/n}$.

At the next stage, the crystal was heated and a diffractogram was recorded every 10 Kelvin. Diffraction reflections were observed at temperature $T = 323$ K, and these reflections were also indexed in the monoclinic lattice. The parameter of this lattice is $a = 26.9830\ A^0$, $b = 15.7867\ A^0$, $c = 13.5926\ A^0$, $\beta = 90^0 13'$. The reflection from the (001) plane disappeared at the considered temperature.

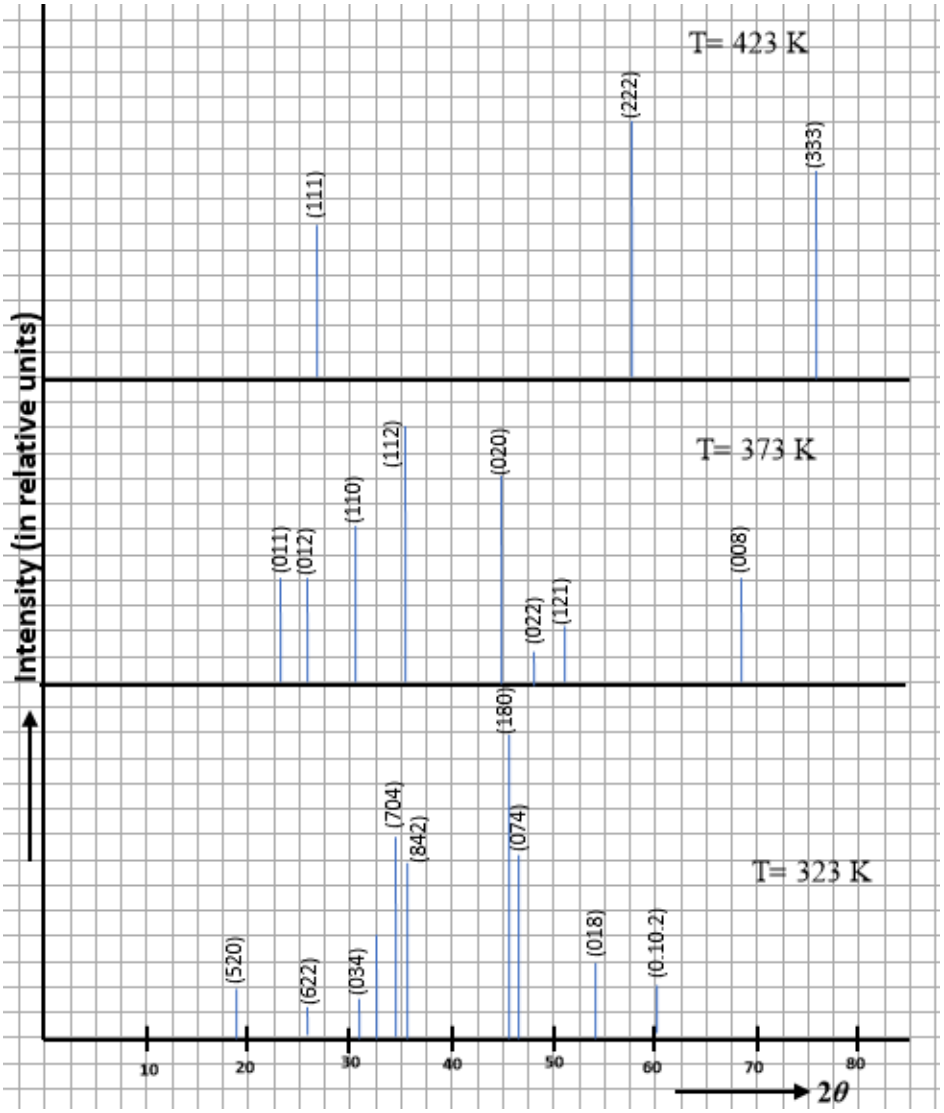

Figure 4. Diffractogram of $Cu_{1.75}Ni_{0.05}S$ crystal

At the temperature $T = 373$ K, 8 diffraction reflections were observed and these reflections were indexed in the tetragonal lattice. More precisely, at $T > 373$ K, the monoclinic lattice is transformed into a tetragonal lattice. That is, a polymorphic transformation has occurred in the crystal. The parameters of the tetragonal lattice are $a = 4.008\ A^0$, $c = 11.268\ A^0$, $z = 4$. The maximum intensity reflection belongs to the (112) plane.

Another structural transformation occurred in the sample viewed at temperature $T = 423$ K. Thus, at that temperature, 3 diffraction reflections were observed and these reflections were indexed in a face-centered cubic lattice. The parameters of that lattice are $a = 5.580\ A^0$, $z = 4$, space group is Fm3m.

Figure 4 shows a diffractogram taken from a $Cu_{1.75}Ni_{0.05}S$ crystal. The report of the diffractogram taken on the $Cu_{1.75}Ni_{0.05}S$ crystal is given in Table 2.

Table 2. The diffractogram of $Cu_{1.75}Ni_{0.05}S$ crystal
(Radiation: Cu Kα ($\lambda_\alpha = 1.5418\ A^0$), filter-Ni, mode: 35kV, 10mA)

T , K	θ	I/I_0	$d_{reflection,}$ A^0	$d_{calculation,}$ A^0	hkl	Cage parameters
293	$3^0\,30'$	10	12.638	13.5650	001	Monocline $a = 26.897\ A^0$ $b = 15.745\ A^0$ $c = 13.565\ A^0$ $\beta = 90^0\ 13'$ $z = 8$ $\rho = 5.29\ q/sm^3$ Space group: $P2_{1/n}$
	$10^0\,01'$	20	4.433	4.4415	520	
	$13^0\,13'$	10	3.371	3.3751	622	
	$17^0\,43'$	15	2.846	2.8484	034	
	$17^0\,40'$	60	2.541	2.5397	704	
	$18^0\,49'$	50	2.390	2.3908	842	
	$23^0\,09'$	100	1.961	1.9629	180	
	$24^0\,16'$	50	1.876	1.8745	074	
	$27^0\,10'$	30	1.688	1.6859	018	
	$30^0\,11'$	20	1.534	1.5337	0.10.2	
323	$9^0\,57'$	20	4.461	4.4588	520	Monocline $a = 26.983\ A^0$ $b = 15.7867A^0$ $c = 13.5926A^0$ $\beta = 90^0\ 13'$ $z = 8$ $\rho = 5.29\ q/sm^3$ Space group: $P2_{1/n}$
	$13^0\,10'$	10	3.384	3.3884	622	
	$15^0\,40'$	15	2.855	2.8548	034	
	$17^0\,36'$	60	2.549	2.5491	704	
	$18^0\,46'$	50	2.396	2.3987	842	
	$23^0\,06'$	100	1.965	1.9680	180	
	$24^0\,13'$	50	1.879	1.8791	074	
	$27^0\,06'$	30	1.692	1.6893	018	
	$30^0\,08'$	20	1.536	1.5377	0.10.2	
373	$11^0\,49'$	40	3.766	3.7642	011	Tetragonal $a = 5.580\ A^0$ $c = 11.268\ A^0$ $\rho = 5.829\ q/sm^3$ $Z = 4$
	$13^0\,47'$	40	3.240	3.2402	012	
	$15^0\,47'$	60	2.834	2.8341	110	
	$17^0\,49'$	100	2.519	2.5193	112	
	$22^0\,37'$	80	2.004	2.0044	020	
	$24^0\,10'$	10	1.883	1.8831	022	
	$25^0\,50'$	20	1.769	1.7693	121	
	$34^0\,041'$	40	1.376	1.3763	008	
423	$13^0\,50'$	60	3.224	3.2217	111	Face-centered cubic lattice $a = 5.580\ A^0$ $Z = 4$ $\rho = 6.073\ q/sm^3$ Space group: Fm3m
	$28^0\,36'$	100	1.610	1.6109	222	
	$45^0\,52'$	800	1.074	1.0739	333	

A comparison of the obtained diffractograms (Figure 1, Figure 4) shows that structural transformations in the $Cu_{1.75}Ni_{0.05}S$ crystal follow the following scheme (Figure 5).

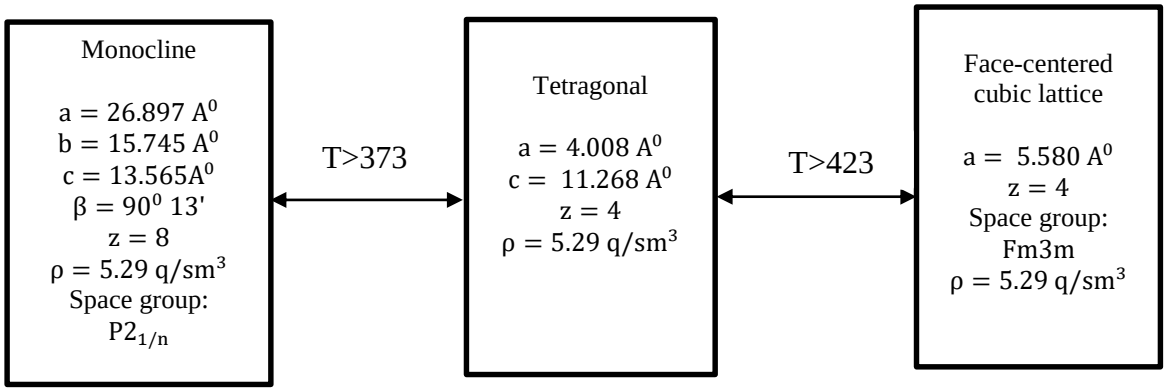

Figure 5. Structural transformations in $Cu_{1.75}Ni_{0.05}S$ crystal

In fact, 9 diffraction reflections are observed at the temperature $T = 323$ K, 8 diffraction reflections at the temperature T=373 K, and finally 3 diffraction reflections at the temperature $T = 423$ K. Thus, the change in the number of diffraction reflections and their corresponding diffraction angles in the report of the diffractogram indicates that a structural transformation has occurred in the observed crystal.

2.3. Polymorphic transformation in $Cu_{1.95}Ni_{0.05}S$ crystal

Accordingly, the 1x4x6 mm^3 sample was cut from the $Cu_{1.95}Ni_{0.05}S$ crystal and diffractometric studies were conducted in the angle interval $0^0 \leq 2\theta \leq 100^0$.

During the shooting at room temperature, 15 diffraction reflections were observed. The maximum intensity reflection was in the plane (10.3.2). The received diffraction reflections were indexed in a monoclinic lattice and the lattice parameters were $a = 26.897$ A^0, $b = 15.745$A^0, $c = 13.565$ A^0, $\beta = 90^0 13'$, $Z = 8$, the space group is $P2_{1/n}$.

It should be noted that 10 diffraction reflections were recorded during the shooting at temperature $T = 423$ K and that that diffraction pattern is indexed in a monoclinic lattice. The parameters of that lattice are $a = 27.630$ A^0 , $b = 15.284$ A^0, $c = 14.90$ A^0, $\beta = 90^0 13'$. The space group is $P2_{1/n}$, $z = 8$.

At temperature $T = 473$ K, the monoclinic lattice turns into a hexagonal lattice. At this time, 7 diffraction reflections were recorded. So, at the considered temperature, the monoclinic lattice has turned into a hexagonal lattice.

At temperature $T = 738$ K, the hexagonal lattice turns into a face-centered cube, and 7 diffraction reflections are observed at this time. Of these diffraction reflections, the one with the maximum intensity is the reflection from the (222) plane. The observed hexagonal lattice parameters are $a = 3.961$ A^0, $c = 6.790$ A^0, $z = 8$, space group $P6_{3/mmm}$. The parameter of the face-centered cube is $a = 5.725$ A^0 , $z = 4$, space group is Fm3m.

Figure 6. shows a diffractogram taken from a $Cu_{1.95}Ni_{0.05}S$ crystal. The report of the diffractometric studies conducted on the considered samples is given in table 3. Both from the graph given in figure 6 and from the results given in table 3, it can be seen that

two structural transformations occur in the $Cu_{1.95}Ni_{0.05}S$ crystal from room temperature to the melting temperature of that crystal. During these structural transformations, the relatively low-symmetry monoclinic lattice transforms into a hexagonal lattice, and then the same hexagonal lattice transforms into a higher-symmetry face-centered cubic lattice.

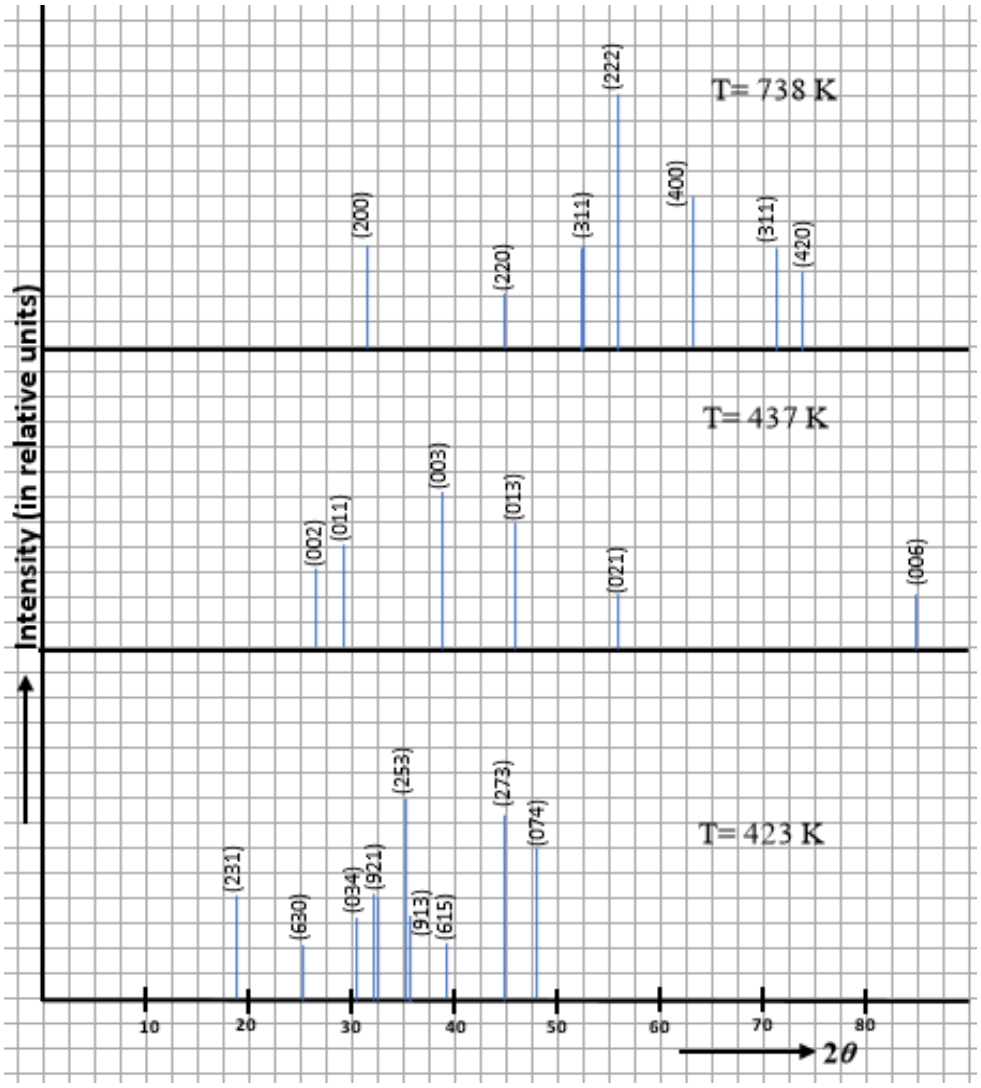

Figure 6. Diffractogram of $Cu_{1.95}Ni_{0.05}S$ crystal

Table 3. Report of the diffractogram of $Cu_{1.95}Ni_{0.05}S$ crystal
(Radiation: Cu Kα ($\lambda_\alpha = 1.5418\ A^0$), filter-Ni, mode: 35kV, 10mA)

T , K	θ	I/I_0	$d_{reflection}$, A^0	$d_{calculation}$, A^0	hkl	Cage parameters
293	$3^0\,16'$	10	13.525	13.5650	001	Monocline $a = 26.897\ A^0$ $b = 15.745\ A^0$ $c = 13.565\ A^0$ $\beta = 90^0\ 13'$ $z = 8$ $\rho = 5.877\ q/sm^3$ Space group:
	$4^0\,55'$	25	8.995	8.9656	300	
	$9^0\,30'$	40	4.672	4.5984	231	
	$13^0\,04'$	10	3.410	3.4087	630	
	$15^0\,49'$	30	2.846	2.8484	034	
	$16^0\,21'$	20	2.739	2.7354	921	

	$17^0\,42'$	80	2.536	2.5371	253	$P2_{1/n}$
	$17^0\,53'$	15	2.510	2.5140	405	
	$18^0\,16'$	30	2.460	2.4600	913	
	$18^0\,51'$	10	2.386	2.3849	804	
	$19^0\,38'$	20	2.294	2.2940	615	
	$20^0\,00'$	100	2.254	2.2558	10.3.2	
	$22^0\,46'$	10	1.992	1.9914	273	
	$23^0\,04'$	70	1.968	1.9645	373	
	$24^0\,16'$	60	1.876	1.8745	074	
423	$4^0\,48'$	25	9.210	9.2103	300	Monocline a=27.630 A^0 b=15.289 A^0 c=14.907 A^0 $\beta=90^0\,13'$ z=8 ρ=5.362 q/sm^3 Space group: $P2_{1/n}$
	$18^0\,16'$	40	4.738	4.7382	231	
	$9^0\,22'$	10	3.438	3.4384	630	
	$12^0\,57'$	15	2.849	2.8489	034	
	$15^0\,42'$	20	2.763	2.7631	921	
	$16^0\,12'$	80	2.549	2.5493	253	
	$17^0\,36'$	30	2.479	2.4732	913	
	$19^0\,31'$	20	2.307	2.3074	615	
	$22^0\,38'$	70	2.003	2.0034	273	
	$24^0\,09'$	60	1.884	1.8844	074	
473	$13^0\,07'$	30	3.395	3.3950	002	Hexagonal $a = 3.961\ A^0$ $c = 6.790\ A^0$ $\rho = 5.718\ q/sm^3$ $Z = 2$ Space group: $P6_{3/mmm}$
	$14^0\,35'$	40	3.061	3.0612	011	
	$19^0\,55'$	60	2.263	2.2633	003	
	$24^0\,05'$	50	1.889	1.8890	013	
	$27^0\,38'$	20	1.663	1.6625	021	
	$42^0\,56'$	10	1.132	1.1317	006	
738	$15^0\,37'$	40	2.864	2.8635	200	Face-centered cubic lattice $a = 5.725\ A^0$ $Z = 4$ $\rho = 5.623\ q/sm^3$ Space group: Fm3m
	$22^0\,21'$	10	2.024	2.0241	220	
	$26^0\,31'$	20	1.727	1.7266	311	
	$27^0\,48'$	100	1.653	1.6527	222	
	$32^0\,34'$	60	1.431	1.4313	400	
	$35^0\,56'$	40	1.313	1.3134	311	
	$37^0\,021'$	30	1.280	1.2802	420	

The X-ray images showed that the transition from the $Cu_{1.95}Ni_{0.05}S$ crystal is monocrystalline→monocrystalline, and when the temperature is lowered, the face-centered cubic→hexagonal→monoclinic transition occurs (Figure 6). In other words, the conversion in the considered samples is enantiotropic (Figure 7)

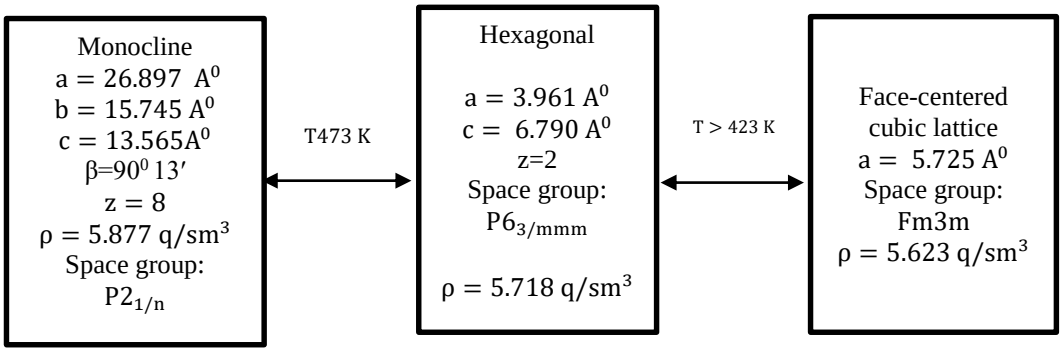

Figure 7. Structural transformations in $Cu_{1.95}Ni_{0.05}S$ crystal

3. Results and its discussion

The study of structural transformations in $Cu_{2-x}Ni_{0.05}S$ crystals shows that these transformations have certain characteristics. First of all, let's note that the X-ray diffractometric studies conducted on those samples at different temperatures in order to study the structural transformations showed that the lattice parameters of the crystals also change with the increase in temperature. That change is shown in table 4.

Table 4. Temperature dependence of low-temperature phase lattice parameters of $Cu_{2-x}Ni_{0.05}S$ crystals

Crystal	Cage parameters			Temperature
	a, A^0	b, A^0	c, A^0	T, K
$Cu_{1.70}Ni_{0.05}S$	26.897	15.745	13.565	293
	27.104	15.772	13.608	323
$Cu_{1.75}Ni_{0.05}S$	26.897	15.745	13.565	293
	26.983	15.7867	13.5926	323
$Cu_{1.95}Ni_{0.05}S$	26.897	15.745	13.565	293
	27.630	15.284	14.907	423

It is known that (Morimoto *et al*., 1969) $Cu_{1.75}S$ is two-phase at room temperature and these phases belong to monoclinic and rhombic lattices. At temperature $T = (308 \pm 1)$ K, rhombic phase turns into cubic phase. Also, at the temperature $T = (389 \pm 1)$ K, the monoclinic phase turns into a cubic phase (Nasirov *et al*., 2020; Hashimov, 2023). The $Cu_{1.70}Ni_{0.05}S$ crystal obtained by partial replacement of copper atoms with Ni atoms in $Cu_{1.75}S$ crystals is single-phase, and this modification has a monoclinic lattice. At temperature $T = 423$ K, that monoclinic structure turns into a face-centered cubic structure.

$Cu_{1.80}S$ crystals are also two-phase (Ralfs, 1936; Evans & Krist, 1970). Those phases belong to the rhombic and monoclinic lattice. The high temperature modification is a face-centered cube. Thus, at the temperature $T = (311 \pm 1)$ K, the rhombic lattice turns into a face-centered cubic lattice, and at the temperature $T = (391 \pm 1)$ K, the monoclinic lattice turns into a face-centered cubic lattice. Our studies have shown that the $Cu_{1.75}Ni_{0.05}S$ crystal is single-phase at room temperature, and that phase turns into a high-temperature phase at $T > T_{transformation}$ temperature.

In Cu_2S crystals, it becomes monoclinic→hexagonal at 378 K temperature, and hexagonal→face-centered cubic lattice at 729 K temperature. Apparently, this crystal is single-phase at room temperature.

In general, the analysis of the results mentioned in the article shows that the non-stoichiometric compounds of the Cu-S system are mainly two- and three-phase. However, the modifications obtained as a result of partially isomorphic replacement of copper atoms with nickel atoms in those compounds are single-phase. In addition, two structural transformations occur in $Cu_{1.95}Ni_{0.05}S$ and $Cu_{1.75}Ni_{0.05}S$. The first structural transformations occur at 473 K and 738 K, and the second at 373 K and 423 K, respectively. Comparison of the obtained results shows that as the amount of copper atoms in the considered compound increases, so does the temperature of structural transformations.

The sample with the least amount of copper atoms has a structural transformation and its temperature is 423 K. The redistribution of copper atoms in different crystal lattices as a result of polymorphic transformations probably caused the change of the scheme of structural transformations in $Cu_{1.70}Ni_{0.05}S$.

The obtained results show that in the $Cu_{1.70}Ni_{0.05}S$ crystal, the (214), (740) planes of the monoclinic lattice coincide with the (111), (200) planes of the cubic lattice. In the $Cu_{1.75}Ni_{0.05}S$ crystal, the planes of the monoclinic lattice (622), (034), (704), (074) coincide with the planes of the tetragonal lattice (012), (110), (112), (022), and the monoclinic and (622) and (012) planes of the tetragonal lattice coincide with the (111) plane of the face-centered cubic lattice.

In the $Cu_{1.95}Ni_{0.05}S$ crystal, the planes of the monoclinic lattice (630), (615) coincide with the planes of the hexagonal lattice (002), (003). The planes of the monoclinic lattice (034), (273) coincide with the face-centered cubic lattice (200), (220). The plane of the hexagonal lattice (021) coincides with the plane of the face-centered cubic lattice (222)

These obtained results show that the crystallographic direction relationships are preserved in the considered samples during structural transformations. This gives us reason to say that the disassembly of the mother crystal and the formation of a new phase occur from the same and also defective part of the crystal. So, that defect is thermally stable and does not leave the crystal after transformation. This allows us to say that the defect is "inherited", that is, the initial defects are stored in the crystal. Indeed, if the embryo of a new phase arises in such defects, then the spatial orientation of the crystal lattice can be repeated during successive transformations. One of the characteristic cases for the studied crystals is that the transformation is enantiotropic, and the other is that it is monocrystalline→monocrystalline type.

It is necessary to once again note the great importance of the experimental data presented in Tables 1-3. Given that the obtained results are sufficient, using identification methods, it is possible to determine mathematical formulas that show the regularity of changes in some parameters depending on others.

In particular, let us consider the experimental data for the values of the parameters given in Table 3 and located within the fragment, determined on the one hand by the temperature 473 K, on the other hand by the hexagonal structure (Table 5).

Table 5. A fragment from table 3. Report of the diffractogram of Cu1.95Ni0.05S crystal (Radiation: Cu Kα (λα=1.5418 A0), filter-Ni, mode: 35kV, 10mA)

T , K	θ	İ/İ$_0$	d $_{reflection,}$ A^0	d$_{calculation,}$ A^0	hkl	Cage parameters
473	13^0 07′	30	3.395	3.3950	002	Hexagonal a=3.961 A^0 c=6.790 A^0 ρ=5.718 q/sm^3 Z=2 Space group: P6$_{3/mmm}$
	14^0 35′	40	3.061	3.0612	011	
	19^0 55′	60	2.263	2.2633	003	
	24^0 05′	50	1.889	1.8890	013	
	27^0 38′	20	1.663	1.6625	021	
	42^0 56′	10	1.132	1.1317	006	

Now let's try to verify their validity using formula (2).
For the hexagonal lattice is valid

$$\theta = arcsin\left(\frac{\lambda^2}{2}\sqrt{\left[\frac{4(h^2+k^2+hk)}{3a^2}+\frac{l^2}{c^2}\right]}\right). \quad (4)$$

Table 6 is compiled in the Excel software environment using mathematical formulas for calculations. These calculations compare the values of the angles. At the first column of the table, the values that have already been presented in Table 3, in the specified fragment, are shown. In the next columns, the same angles obtained by formula (2) are given. Finally, at the last column, differences in relative units of the compared values are presented.

Thus, the differences in the compared values of the angle θ in percentage terms are so small that they can be ignored. In other words, it can be argued with great conviction that the experimental results are sufficiently reliable

Table 6. Comparison of tabular and calculated angle values *θ*

θ Tabular values		*h*	*k*	*l*	*a, A^0*	*c, A^0*	*λ, A^0*	*θ* Calculated values	Comparison errors
13^0 07′	13.1167	0	0	2	3.96	6.79	1.542	13.131	0.11113%
14^0 35′	14.5833	0	1	1	3.96	6.79	1.542	14.590	0.04823%
19^0 55′	19.9167	0	0	3	3.96	6.79	1.542	19.924	0.03565%
24^0 05′	24.0833	0	1	3	3.96	6.79	1.542	24.095	0.05006%
27^0 38′	27.6333	0	2	1	3.96	6.79	1.542	27.632	-0.00364%
13^0 07′	42.9333	0	0	6	3.96	6.79	1.542	42.960	0.06180%

4. Conclusions

As a result of the X-ray phase analysis, it was determined that at the temperature $T = 423$ K, a structural transformation occurs in the $Cu_{1.70}Ni_{0.05}S$ crystal, and the monoclinic lattice turns into a face-centered cubic lattice. In the $Cu_{1.75}Ni_{0.05}S$ crystal, the monoclinic→tetragonal transformation occurs at $T = 373$ K, and the tetragonal lattice transforms into a face-centered cubic lattice at $T = 423$ K. In the $Cu_{1.95}Ni_{0.05}S$ crystal, at

$T = 423$ K, the monoclinic lattice turns into a hexagonal lattice, and at $T = 738$ K, the hexagonal lattice turns into a face-centered cubic lattice. It was shown that the transformation in all three investigated samples is reversible, i.e. enantiotropic, monocrystalline←→monocrystalline type.

It was determined that the planes of the monoclinic lattice (214), (740) in the $Cu_{1.70}Ni_{0.05}S$ crystal coincide with the planes of the face-centered cubic lattice (111), (200). The (622), (034), (704), (074) planes of the monoclinic lattice of the $Cu_{1.75}Ni_{0.05}S$ crystal coincide with the planes of the tetragonal lattice (012), (110), (112), (022). The (622) and (012) planes of the monoclinic and tetragonal lattices coincide with the (111) plane of the face-centered cubic lattice. In the $Cu_{1.95}Ni_{0.05}S$ crystal, the planes of the monoclinic lattice (630), (615) coincide with the planes of the hexagonal lattice (002), (003). The (034), (273) planes of the monoclinic lattice coincide with (200), (220) of the face-centered cubic lattice. The plane of the hexagonal lattice (021) coincides with the plane of the face-centered cubic lattice (222). This means that there are rigid crystallographic directional relationships between the crystal lattices of the interconverting modifications.

It was determined that lattice parameters in $Cu_{1.70}Ni_{0.05}S$ and $Cu_{1.75}Ni_{0.05}S$ crystals increase as the temperature increases. however, as the temperature increases in the $Cu_{1.95}Ni_{0.05}S$ crystal, the a and c parameters of the monoclinic lattice increase, while the b parameter decreases.

From the comparative analysis of the results obtained at the temperature of 473 k of the $Cu_{1.95}Ni_{0.05}S$ crystal, it can be seen that there is a slight difference between the experimental results and the theoretical values. Comparative analysis proves that the experiment was very successful.

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