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STRUCTURAL PHASE TRANSFORMATION IN $\text{Cu}_{1,80}\text{Ni}_{0,2}\text{S}$ CRYSTAL**V.I.Nasirov, A.G.Rzayeva, G.B.Ibrahimov**

(Presented by Academician of ANAS B.H.Tagiev)

The structural phase transformation of the composition $\text{Cu}_{1,80}\text{Ni}_{0,2}\text{S}$ in the solid solution was synthesized and investigated by the method of DTA and x-ray diffraction. It was determined that the achieved crystal has rhombic lattice which is transferred into hexagonal form at the temperature 379K and in its turn the hexagonal modification is turned into the cubic form at 1079K. This transfer concerns to the enantiotropic type.

Keywords: polymorphism, modification, enantiotropic, transformation

Introduction

One of the interesting phenomenon occurred in solid bodies depending on changes of external thermodynamic conditions is the structural phase transformation. The investigation of the mechanism of structural transformations, determination of the temperature of equilibrium of the phase presents in the most degree the basis of modern material science, partially, technical application of materials—as every polymorphous phase presents new separate object with different physicochemical features.

The investigation of the structural transformations in semiconductor combinations, mainly, in chalcogenides of copper has not only scientific, but also great practical values. Having great ionic conduction with high coefficient of diffusion of chalcogenides of copper, it is widely used in preparation of super conductors, transformer of energy, electrolytic sensors, registrar and other devices [1-4].

It is necessary to investigate the effect of temperature and introduction of atoms of different metals, for example Ni in the crystal lattice on the mechanism of phase transformations and the structures of polymorphous modifications for the purpose of improvement and management of the features of chalcogenides of copper.

It is known that there are three individual phases at the system Cu–S (5, 6): Cu_2S –chalcosis, $\text{Cu}_{1,87}\text{S}$ –digenet and CuS –covellite.

But, having investigated the natural minerals, a lot of authors [7-12] discovered additional three nonstoichiometric phases of the composition existing stably in the nature: $\text{Cu}_{1,96}\text{S}$ –djurlite,

$35\text{Cu}_{1,8}\text{S}$ –digenet, $\text{Cu}_{1,75}\text{S}$ –anilite and $\text{Cu}_{1,50}\text{S}$ –umangite.

Different solid solutions which were the materials with high thermoelectric efficiency [12, 14] were achieved by substitution of the atoms of copper with different metals at chalcogenides of the type Cu_2X (where X= S, Se, Te). In connection with aforementioned, we consider it necessary to synthesize the solid solution in the composition $\text{Cu}_{2-x}\text{M}_x\text{S}$ (where M=Ni x=0.5).

According to the data [7, 8] there are three polymorphous modifications in Cu_2S : orthorhombic α –modification stable to 376,5 K with the parameters of crystal lattice $a=14.90\text{\AA}$, $b=27.28\text{\AA}$, $c=13.41\text{\AA}$ Abm2, hexagonal β modification, resistant at the interval of temperature $376,5\div 708\text{K}$ with the parameter of crystal lattice $a=3.89$, $c=6.68\text{\AA}$, cubic with the period of lattice $a=14.90\text{\AA}$, Fm $\bar{3}$ m existing at the temperature more than 780 K.

According to the author [14], the orthorhombic modification Cu_2S has the following parameters of the crystal lattice: $a=1.80\text{\AA}$, $b=27.20$, $c=22.70\text{\AA}$. According to the data [14], Cu_2S has monoclinic lattice with the parameters $a=15.246\text{\AA}$, $b=11.884\text{\AA}$, $c=13.494\text{\AA}$, $\beta=116^\circ 35$, pr.gr. $\text{P}2_{1/c}$ at the room temperature.

Experimental part

The initial elements of the following clearance are used for the synthesis of $\text{Cu}_{1,80}\text{Ni}_{0,2}\text{S}$: Cu–99,998, Ni–99,990 and S mark OSC. The quartz vessel was filled with the initial substances at the quantity necessary for the present composition and was evacuated till the tension 0.193 Pa.

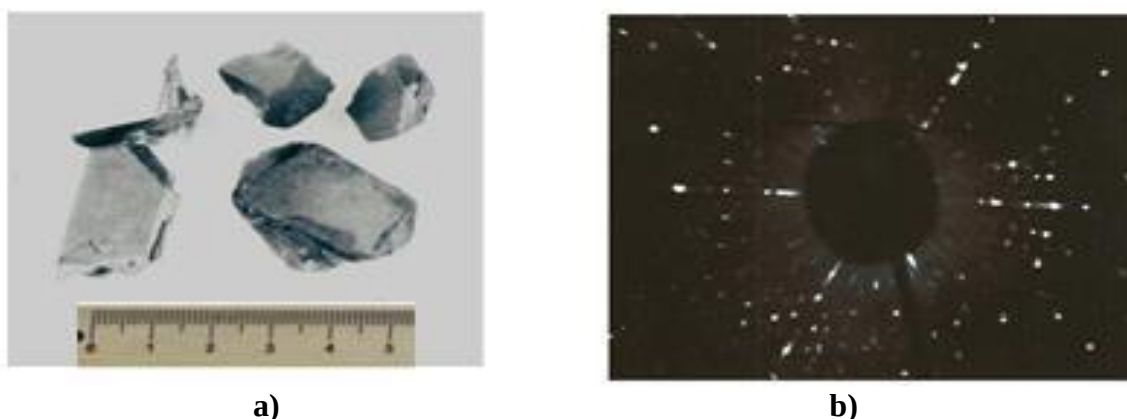


Fig. 1. External form and Laue pattern of the monocrystal $\text{Cu}_{1.80}\text{Ni}_{0.2}\text{S}$ at room temperature

The synthesis was held at the interval of the temperature 800-1150°C. The synthesized sample was kept under the temperature 800°C within 100 hours for homogenizing. The combination of the methods of slow cooling and Bridgman method was used for receiving the monocrystal $\text{Cu}_{1.80}\text{Ni}_{0.2}\text{S}$. The external form of received monocrystals and Laue pattern, the quality showing them is given in fig. 1(a,b).

The x-ray examination was implemented on the diffractometer DPOH-3M ($\text{CuK}\alpha$, $\lambda=1.5418\text{\AA}$) equipped with high temperature attachment YBД 2000 at the atmosphere. The sample was heated till the fixed temperature and recording was implemented under the isometric conditions.

The differential thermic analysis of the

sample was held at the device "Perkin Elmer" STA 6000 (USA). The sample was heated with the speed 5°C/minute. The nitric gas was taken as the working gas and its speed was 20 ml/minute.

Results and their discussion

The obtained sample $\text{Cu}_{1.80}\text{Ni}_{0.2}\text{S}$ was washed in the powder for the diffractometer investigation. The diffractometer investigation held at the interval of the corners $10^\circ \leq 2\theta \leq 100^\circ$ shows that $\text{Cu}_{1.80}\text{Ni}_{0.2}\text{S}$ has rhombic α -modification with the parameters of crystal lattice $a=29.91\text{\AA}$, $b=15.72\text{\AA}$, $c=13.5\text{\AA}$ Abm2 at room temperature ($T=300\text{K}$). The calculation of the diffraction pattern of α -modification of the investigated crystal at the temperature 300K is given in table 1.

Table 1

Calculation of the diffraction pattern of $\text{Cu}_{1.80}\text{Ni}_{0.2}\text{S}$ at the temperature 300K, emission $\text{CuK}\alpha$ ($\lambda=1.5418\text{\AA}$), regime 35kB, 10mA

T, K	d, $\text{\AA}$	I/I ₀	hkl	Parameters of the crystal lattice
300	6,182	86	410	$a=29.91\text{\AA}$, $b=15.72\text{\AA}$, $c=13.5\text{\AA}$ Abm2
	4,291	54	113	
	3,763	70	223	
	3,592	65	323	
	3,284	75	532	
	3,043	65	151	
	3,012	100	802	
	2,869	70	504	
	2,709	60	642	
	2,516	52	534	
	2,203	52	245	
	2,106	48	662	
	1,958	51	835	
	1,870	53	12.04	
	1,693	55	955	
	1,644	42	408	

Table 2

Calculation of the diffraction pattern of $\text{Cu}_{1,80}\text{Ni}_{0,2}\text{S}$ at the temperature 379K

T, K	d, Å	I/I ₀	hkl	Parameters of the crystal lattice
379	3,327	30	002	Hexagonal a=3,429Å, c=6.714Å P6 ₃ /mmc
	3,057	40	011	
	2,250	65	003	
	1,844	45	013	
	1,689	35	021	
	1,119	20	006	

Table 3

The calculation of the diffraction pattern of $\text{Cu}_{1,80}\text{Ni}_{0,2}\text{S}$ at temperature T=1079 K

T, K	d, Å	I/I ₀	hkl	Parameters of the crystal lattice
1079	2,813	30	200	a=5.626Å, Fm $\bar{3}$ m
	2,007	15	220	
	1,688	40	311	
	1,610	100	222	

Afterwards, the diffraction patterns were taken every 20K. Before beginning the recording the sample was taken at the given temperature within 30 minutes. There was no change at the number and intensiveness of diffraction images at heating till 379K. Only at 379K the all diffraction images concerning the rhombic crystal system are disappeared and 6 images concerning hexagonal β modification are fixed at the interval of corners $10^\circ \leq 2\theta \leq 100^\circ$. The parameters of the crystal lattice of β hexagonal modification are the following: a=3,429 Å, c=6.714 Å, P6₃/mmc. The calculation of the diffraction pattern of $\text{Cu}_{1,80}\text{Ni}_{0,2}\text{S}$ is given at schedule 2.

The diffraction image is changed totally continuing the heating of the investigated sample at temperature T=1079K, i.e., only 4 dif-

fraction images are discovered instead of 6 which are indicated well at HCC of the lattice.

Thereby, the hexagonal modification is turned into high temperature HCC modification with the parameters of the crystal lattice a=5.626 Å, Fm $\bar{3}$ m.

The calculation of the diffraction pattern of $\text{Cu}_{1,80}\text{Ni}_{0,2}\text{S}$ at temperature 1079 is given at table 3.

The structural transformation isn't observed at further heating of $\text{Cu}_{1,80}\text{Ni}_{0,2}\text{S}$ till the melting temperature ($T_{\text{melting}}=1410\text{K}$), i.e., the number of diffraction images from γ crystal remains unchanged.

Endoeffects obtained by differential thermic analysis of the crystal $\text{Cu}_{1,80}\text{Ni}_{0,2}\text{S}$ certifies the x-ray diffraction results obtained by us (fig. 2).

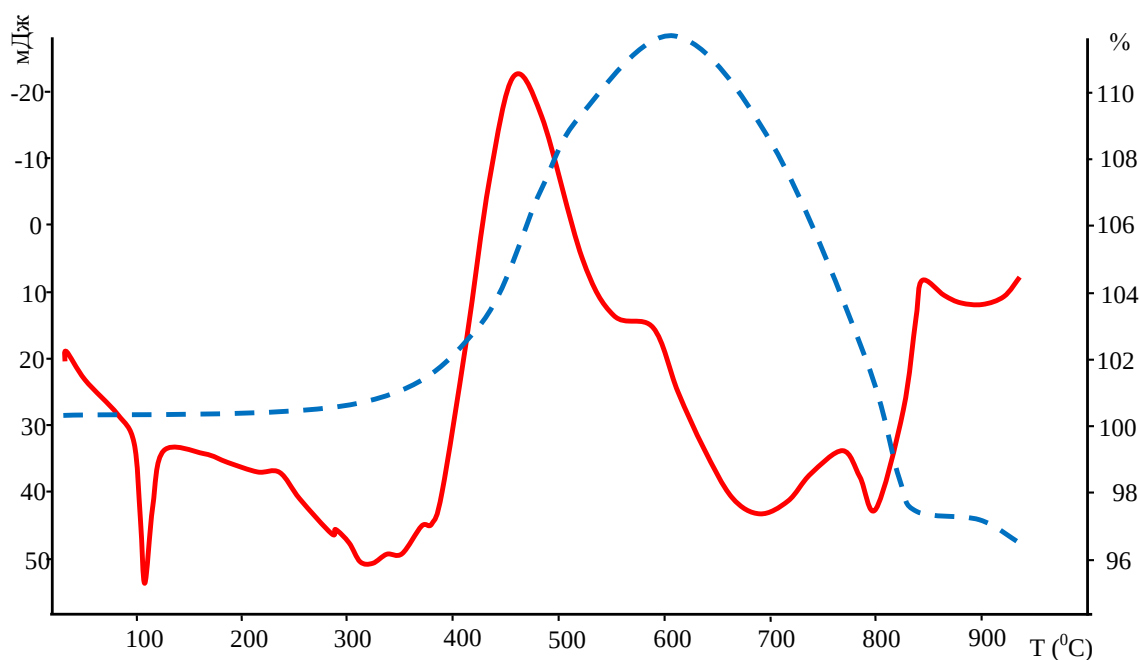
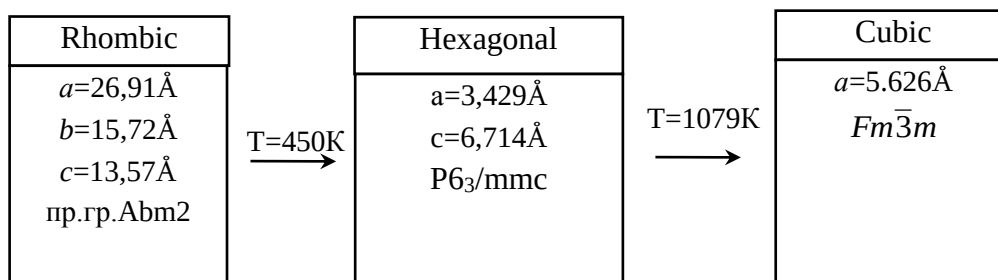


Fig. 2. Thermogram of heating of the crystal $\text{Cu}_{1,80}\text{Ni}_{0,2}\text{S}$

Two endoeffects are discovered which the central peaks coincide with the temperature 106°C and 803°C while changing the temperature from the room temperature to melting temperature. Accordingly, 1955,49 mJ, 5563,63 mJ and 3,61 mJ/g, 38,74 mJ/g were achieved for energy and enthalpy coinciding with the temperature 106°C (379K) and 803°C (1079K).

Increase of mass till ~11% is observed at the interval of temperature $230\div 606^{\circ}\text{C}$ upon the curve TG. It can be related with oxidation of the sample.

It was determined by such method of x-ray and DTA that the structural changes happens at the crystals $\text{Cu}_{1,80}\text{Ni}_{0,2}\text{S}$ at the temperature interval 300-1400K upon the following schema:



The analysis of obtained experimental data shows that partial substitution of atoms Cu with atoms Ni contributes to increase of the temperature area of existence of hexagonal modification nearly at 350K. This substitution doesn't impact the temperature area of rhombic α modification. The revealed polymorphism has enantiotropic character at the investigated crystal $\text{Cu}_{1,80}\text{Ni}_{0,2}\text{S}$.

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Cu_{1,80}Ni_{0,2}S KRİSTALINDA QURULUŞ FAZA ÇEVİRİLMƏLƏRİ

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Cu_{1,80}Ni_{0,2}S tərkibli bərk məhlul sintez olunaraq onda rentgenoqrafik və diferensial termik analiz üsulları ilə quruluş faza çevrilmələri tədqiq olunmuşdur. Müəyyən edilmişdir ki, sintez olunmuş nümunə otaq temperaturunda rombik qəfəsə malik olub, 379K temperaturda heksaqonal qəfəsə, 1079K-də isə heksaqonal qəfəs öz növbəsində kubik qəfəsə çevrilir. Tədqiq olunan nümunədə çevirmə prosesi enantiotropdur.

Açar sözlər: polimorfizm, modifikasiya, enantiotrop, çevirmə, kristal qəfəsi

СТРУКТУРНЫЕ ФАЗОВЫЕ ПРЕВРАЩЕНИЯ В КРИСТАЛЛЕ Cu_{1,80}Ni_{0,2}S

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Синтезированы методами ДТА и рентгеновской дифракции, исследованы структурные фазовые превращения в твердом растворе состава Cu_{1,80}Ni_{0,2}S. Установлено, что полученный кристалл при комнатной температуре имеет ромбическую решетку, которая при температуре 379K превращается в гексагональную, а при 1079 K, в свою очередь, гексагональная модификация превращается в кубическую. Эти превращения относятся к типу энантиотропных.

Ключевые слова: полиморфизм, модификация, энантиотропный, превращения