INVESTIGATION OF PHASE TRANSITION IN Cu$_4$Te$_{1.5}$Se$_{0.5}$ SOLID SOLUTION BY HIGH-TEMPERATURE ROENTGENOGRAPHY METHOD

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The solid solution of Cu$_4$Te$_{1.5}$Se$_{0.5}$ is synthesized. By roentgenographic method it is established that Cu$_4$Te$_{1.5}$Se$_{0.5}$ samples crystallize in trigonal structure with lattice periods in hexagonal establishment: a_h=8,2319(11) Å, c_h=21,4145(23) Å, V=1089,811(12) Å^3, sp.gr. P3m1, Z=22, ρ_x=7,33 gr/cm^3. By comparative roentgen-phase analysis of temperature diffraction data it is established that trigonal phase of Cu$_4$Te$_{1.5}$Se$_{0.5}$ at room temperature transits at T=750±3K into two-phase system consisting of hexagonal phase of Cu$_2$Te$_{0.5}$Se$_{0.5}$ composition with periods a=4,231 Å, c=7,223Å; sp.gr. P6$_3$/mmc and cubic phase of Cu$_2$Te composition with a = 6,049 Å periods. It is shown that near T=800K±5K the two-phase system transits into unique cubic phase with periods a=6.061 Å.

INTRODUCTION

It is known that the development of electron technique, energetic and radio electronics stimulates the search and investigation of physicochemical properties of perspective materials. In this relation the thermomagnetic and thermoelectric materials with small lattice thermal conductivity and high mobility of charge carriers has the wide region of application in the capacity of thermoelectric transformers [1-3]. Ag, Cu chalcogenides and based on them different solid solutions are to them. It is obvious that for effective use of these materials it is necessary to have experimental data on influence of external factors on structure and structural changes. Note that for above mentioned chalcogenides the presence of polymorphous transformations under temperature influence is the one of character properties [4-6]. The results of experimental investigations of synthesis and structural-phase transitions of Cu$_4$Te$_{1.5}$Se$_{0.5}$ in temperature interval 360-1250K are given in present work. Note that all roentgen-diffraction experiments are carried out on powder diffractometer "D8 ADVANCE Bruker (Germany) in regime: 40кV, 40mA, 05°≤2θ≤80°, CuK$_\alpha$ - radiation, λ=1.5406Å. The temperature investigations are carried out in HTK16 camera in vacuum 1.3 torr. The heating rate is 2°/min.

EXPERIMENTAL PART

Synthesis. The samples of Cu$_4$Te$_{1.5}$Se$_{0.5}$ solid solution are synthesized by the melting of initial elements Cu, Te, Se having the purity not less 99.998 in vacuum-processed quartz ampoule 10^{-2} Pa in one-zone furnace. The ampoule of length 20 cm with substance (5gr) is gradually put into furnace with temperature 1200K. After that the furnace is closed and ampoule is kept at this temperature during one hour. Further, the temperature into furnace is slowly decreased up to 750K and ampoule with substance is kept during 5 days for homogenization.

The investigation of phase transformations. For establishment of possible structural transformations in Cu$_4$Te$_{1.5}$Se$_{0.5}$ sample one can determine the crystallographic parameters of low-temperature phase.

Table 1.

Roentgen-diffraction data for Cu$_4$Te$_{1.50}$Se$_{0.50}$ at 300K

№	2θ	$d_{экс}$	I/I_0	hkl
1	12.398	7.13387	22.2	100
2	21.558	4.11874	3.2	110
3	24.943	3.56694	100	200, 006
4	26.372	3.37680	3	202
5	28.272	3.15405	14.1	203
6	29.237	3.05213	7.6	007
7	33.199	2.69635	13.7	008
8	35.831	2.50414	12.4	206
9	36.616	2.45222	8.5	213
10	40.172	2.24298	4.7	207
11	42.054	2.14684	20	00.10
12	42.887	2.10704	33	208
13	43.931	2.05937	81.7	222
14	45.824	1.97858	77.6	223
15	47.735	1.90375	3.5	224
16	51.178	1.78347	32.9	00.12
17	51.968	1.75820	2.3	226
18	52.943	1.72808	1.2	402
19	53.067	1.72435	3.6	403
20	53.645	1.70712	1.1	404
21	55.917	1.64301	2.7	00.13
22	58.478	1.57703	4.7	406
23	60.631	1.52607		00.14
24	63.072	1.47276	5.5	408
25	65.135	1.43100	4.9	00.15
26	65.352	1.42677	10.61	500
27	66.031	1.41374	1	409
28	66.875	1.39793	4.4	503
29	66.982	1.39596	2.6	501
30	68.047	1.37668	8.3	420
31	68.26	1.37291	1.6	421
32	69.691	1.34817	5.8	423
33	70.96	1.32714	3.7	00.16

To this purpose the small powder from synthesized sample is prepared and made the diffractograms in vacuum. On the base of the calculative analysis of obtained diffracted data with the help of "TOPAS" program is determined that synthesized sample crystallizes in hexagonal lattice with parameters a_h=8.2319Å, c_h=21,4145, V=1089,811Å, sp.gr P31c, Z=4, ρ_x=8.11gr/cm^3 at 300K. The diffractogram of $Cu_4Te_{1.5}Se_{0.5}$ phase at room temperature is shown in fig.1a, and calculated crystallographic data 2θ, $\dot{I}$, d, reflextion indexes (hkl) are given in table 1.The high-temperature investigations are carried out after obtaining of above mentioned main crystallographic parameters of phase $Cu_4Te_{1.5}Se_{0.5}$ at room temperature. To this purpose the necessary diffractometric photos for different temperatures with step 50K are obtained. The sample is kept in each temperature point of photoradiography at the given temperature during 25 minutes for temperature stabilization in whole camera volume with investigated sample. Further, the comparative analysis of obtained temperature diffractograms is carried out.

The carried comparative analysis shows that in temperature interval 300<T<1250K the essential diffraction changes corresponding to possible structural transitions take place near temperatures T=770K and T=850K. In other words, the trigonal α-phase up to temperature 750K keeps own structure.

Note that the treatment of obtained diffraction experiments shows that the structural change process begins as a result of gradually temperature increase in trigonal structure of α-phase of $Cu_4Te_{1.5}Se_{0.5}$ at $T\approx$723K.

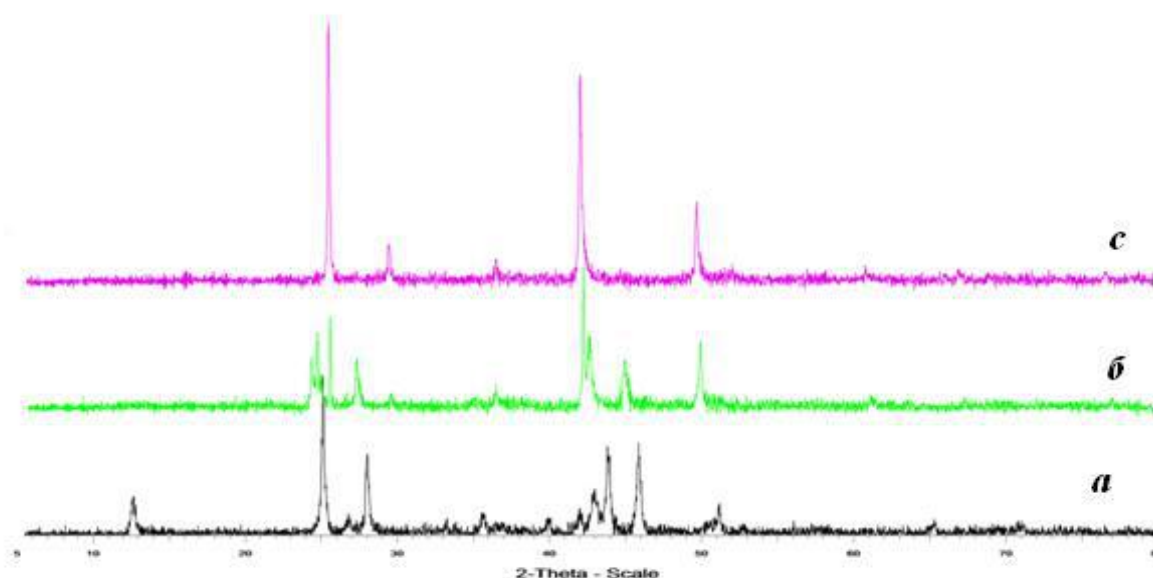*Fig.1.* $Cu_4Te_{1.5}Se_{0.5}$ diffractograms at different temperatures: 1-300K, 2-770K, 3-900K .

The diffractogram "b" fig.1 shows that the process of structural transformation near T=770K is seemed to be finished as at given temperature almost all reflections of α-phase disappear, but the new system of reflections appears, on the base of which one can propose that the structural phase transformations takes place.

That's why for definition of equilibrium temperature of the given transition we begin to observe the change of the positions of diffraction reflections by decrease of heating step. To this purpose we observe for reflection position changes beginning from T=725K in each 10K. It is observed that at T=755K almost all diffraction peaks of α-phase disappear and we obtain the observable diffractograms at T-770K as a result of observation for process of reflection position changes. The process temperature decrease from 755K up to 745K with step 5K shows that the system returns to previous structure, i.e. to α-phase at T=745K. Thus, it is established that transition temperature of low-temperature α-phase in new phase is 750±3K.

In the next investigation stage one should define the crystallographic parameters and lattice symmetry obtained by phase transformation of room temperature trigonal α-phase $Cu_4Te_{1.5}Se_{0.5}$.

Note that multiple attempts of lattice constant obtaining of investigated substance from diffractogram found at temperature 750K using the structural program TOPAS doesn't give us the expected results. That's why we suppose that obserable diffraction change at T=770K isn't the phase transformation but sample decomposition under temperature influence. The fact of diffraction change higher than T=800K contradicts to above mentioned version. As it is seen from "c" diffractogram of fig.1, the sample diffraction picture at the given temperature is simpler than one obtained at T=770K. Moreover, the comparison of these two diffractograms shows that all peaks observable on diffractogram T=850 K is the exact repeating of part of reflections taking place on diffractograms at T=770K, namely in interval T=750-850 K the investigated substance is in mixture state of two lattices differentiating by structure (see table 2-3).

The treatment of diffraction data obtained at $T=850K$ using TOPAS program shows that sample at this temperature is to cubic phase with lattice periods 6,061Å, $V=223.3Å^3$, $Z=4$, sp.gr.Pa-3. Taking off the list the two-phase diffraction data of the cubic phase reflections the rest reflections of diffractogram at $T=770K$ are indentified by TOPAS program. The process of reflection indication shows that second phase crystallizes in hexagonal syngony with periods: $a=4,231$ Å, $c=7,223$ Å, $V=112,0527$, sp.gr $P6_3/mmc$, $Z=2$. This is the structure by β-Cu_2S type. We suppose that investigated sample desintegrates in two equal parts at $T=770K$ by $Cu_4Te_{1.5}Se_{0.5} \rightarrow Cu_2Te+Cu_2(SeTe)_{0.5}$ reaction. Near $T=800K$ both these phases joining with each other transforms into one unique cubic phase which is above mentioned.

Table 2.
Roentgen-diffraction data for $Cu_4Te_{1.50}Se_{0.50}$ at 773K.

№	2θ	$d_{экс}$	I/I_0	hkl
1	24.28	3.6633	24	1 0 0♦
2	24.64	3.6017	20	0 0 2♦
3	25.48	3.4929	80	1 1 1□
4	27.28	3.2664	20	1 0 1♦
5	29.51	3.0251	14	2 0 0□
6	36.35	2.4603	8	2 1 1□
7	42.28	2.1395	100	2 2 0□
8	42.72	2.1150	14	1 1 0♦
9	44.91	2.0178	10	1 0 3♦
10	49.96	1.8267	27	3 1 1□
11	52.34	1.7488	2	2 2 2□
12	61.23	1.5174	3	4 0 0□
13	64.42	1.3879	3	3 3 1□
14	73.15	1.2925	5	2 1 2♦
15	77.18	1.2386	5	4 2 2□

♦ is Hexagonal phase $a=4,231$ Å , $c=7,223$ Å .$P6_3/mmc$
□ is Cubic phase K $a=6,061$Å, $V=223.3Å^3$, $Z=4$, sp.gr.Pa-3.

Table 3.
Roentgen-diffraction data for $Cu_4Te_{1.50}Se_{0.50}$ at 900K.

№	2θ	$d_{экс}$	I/I_0	hkl
1	25.471	3.4951	100	1 1 1
2	29.445	3.0261	14	2 0 0
3	36.355	2.4711	8	2 1 1
4	42.21	2.1431	70	2 2 0
5	49.545	1.8341	28	3 1 1

In conclusion note that the different low-temperature structures form in $Cu_4Se_{1-x}Te_x$ ($x=0.25$; 0,50; 0,75) solid solutions in dependence on atom processes Se/Te [7] and therefore, their structural transitions occur on different scheme. For example, the trigonal α-phase with $Cu_4Se_{1.5}Te_{0.5}$ periods: $a_h=4,162$Å, $c_h=20.660$Å in temperature interval 300-1250K has the only one phase transition. At $T=558K$ α-phase transits into cubic structure with period $a=5,899$Å [8]. For solid solutions of Cu_4SeTe and $Cu_4Te_{1.5}Se_{0.5}$ compositions the trigonal structure with lattice periods $a_h=4,1880$Å, $c_h=41,8531$Å [9] and $a_h=8,2319$Å, $c_h=21,4145$Å[10] correspondingly is established. These phases aren't isostructural ones. Their structures differ from each other. The first structure is the structure polytype form of $NaCu_6Se_4$ type structure [11] and second phase is ordered structure of $Cu_{1.75}Te$ type [12]. The processes of the structural transformation are also different for them. In Cu_4SeTe and $Cu_4Se_{0.5}Te_{1.5}$ in temperature interval $T=300\sim1250K$ the phase transformation process is accompanied by composition desintegration. For Cu_4SeTe at $T=573K$ the sample decomposes in $Cu_2Se_{0.5}Te_{0.5}$ having structure of Novotny phase type [13] with space group P6/mmm and Cu_2Te having cubic structure. The next transition corresponds to temperature $T=673K$. At this temperature the situation is similar as one at $T=573K$. The two-phase state keeps but hexagonal phase of $Cu_2Se_{0.5}Te_{0.5}$ composition transits into to structure with sp.gr. $P6_3/mmc$ of β-Cu_2S type [14]. The further heating at $T=735K$ shows that these both phases transit into unique cubic phase with period $a=6,05$Å.

As it is above mentioned the sample of composition decomposes in two phases at $T\cong750K$. Moreover, the process is identical with the one at $T=673K$ observed for $Cu_4S_{0.5}Te_{0.5}$. In given case the two-phase state higher $T=800K$ transits into unique cubic phase $a=6,06$Å.

CONCLUSION

1. The solid solution of $Cu_4Te_{1.5}Se_{0.5}$ composition is synthesized and it is defined by roentgenophase analysis that it crystallizes in trigonal syngony with lattice periods $a_h=8,2319(11)$ Å, $c_h=21,4145(23)$ Å, $V=1089,811(12)$ Å^3, sp.gr. P3m1, $Z=22$, $\rho_x=7,33$ gr/cm^3.

2. By high-temperature roentgen-diffraction method it is established that in $300<T<1250K$ temperature interval the substance at $750\pm5K$ decomposes in hexagonal and cubic phases of $Cu_2Se_{0.5}Te_{0.5}$ and Cu_2Te compositions with lattice periods $a_h=4,231$ Å, $c_h=7,223$ Å and $a=6,049$ Å correspondingly.

3. It is observed that in further heating the two-phase system higher 850K transits into unique cubic phase.

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