STRUCTURAL PHASE TRANSITIONS IN $Cu_3Ni_{0.5}Se_2$ CRYSTALS

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The compound of magnetic semiconductor of $Cu_3Ni_{0.5}Se_2$ composition is synthesized. The parameters of low-temperature phase are determined and the structural-phase transitions are investigated by high-temperature X-ray diffraction method. It is established that synthesized $Cu_3Ni_{0.5}Se_2$ is two-phase one at room temperature and it consists of rhombohedral and cubic phases with parameters a=4,321Å, c=20,620Å and a=11,841Å correspondingly. It is determined that the rhombohedral phase disappears and cubic superlatice saves in temperature interval 293<T<773 K at T=462±3K in two-phase system. At temperature T=665K the cubic superlatice transforms into cubic subcell with parameters a=5,94 Å,V=209.58 Å^3, sp.gr. Fm$\overline{3}$m, Z=4.

Keywords: crystalls, structure, phase transitions, modifications.
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INTRODUCTION

It is known that thermomagnetic and thermoelectric materials with small lattice thermal conduction and high mobility of charge carrier have the wide field of use [1 – 4]. The so-called superion chalcogenides Ag, Cu and different solid solutions on their base belong to number of such materials [5 – 7]. It is obvious that the presence of experimental data on external factor influence on their structure is necessary for effective use of these materials. Note that for the given materials the polymorphous transformations under temperature influence is the one of the character properties. Indeed, the determination of equilibrium temperature between possible polymorphous modifications, temperature interval existence and structures of these phases has the big scientific and practical value.

The investigation results of structural-phase transitions of $Cu_3Ni_{0.5}Se_2$ composition solid solution in temperature interval 293-800K are given in present work.

EXPERIMENTAL PART

The physico-chemical characteristics of natural and synthetic umangite Cu_3Se_2 described in works [8 – 10] is the stimulus for $Cu_3Ni_{0.5}Se_2$ synthesis. It is seen that in such recording of chemical composition the valency balance isn't carried out and open composition should be in the form $Cu_2^{+1}Cu^{+2}$Se. For explanation of this statement we have made the attempt to obtain the full-valent solid solution by the way of implantation of Ni atom into Cu_3Se_2 composition. $Cu_3Ni_{0.5}Se_2$ is synthesized from Cu, Ni and Se elements the purity of which isn't less than 99.999 in evacuated ~ 10^{-4} millimeter of mercury in quartz ampoules in inclined furnace (~15^0). Ampoule of length ~20 cm with substance (5 gr.) is gradually put into furnace the temperature of which is previously established in point 1250K. After total immersion of the ampoule the furnace temperature is increased up to T=1370 K and it is endured at the given temperature during 2,5 hours. Further the furnace temperature is decreased up to 700K and the ampoule is endured at this temperature during six days for homogenization. The synthesized and annealed sample is the compact alloy of dark grey color and its powder has black color.

INVESTIGATION OF PHASET RANSFORMATIONS

All temperature experiments on revealing of structural-phase transitions in crystal of $Cu_3Ni_{0.5}Se_2$ composition are carried out in Institute of Physics of ANAS on powder diffractometer «D8 ADVANCE» («Bruker») in vacuum (10^{-2} torr) in temperature interval 293<T<700K at mode 40 кV, 40 мA, CuK_α-λ=1.5406Å, 10<2θ<80^0.

For this purpose, from the synthesized sample $Cu_3Ni_{0.5}Se_2$ the fine-dispersed powders are prepared and the diffractogram at temperature 300K (Fig.1) is obtained.

The treatment of the obtained diffraction picture, i.e. the indicating of interplanar spaces (d) with the use of calculative program TOPAS 4.2 shows that synthesized material at room temperature is the two-phase one and it consists of rhombohedral phase with lattice periods on hexagonal axes a_h=4.32 Å, c_h=20.60 sp.gr. $R\overline{3}m$, Z=9 and cubic phase with parameter a=11,841 Å, sp.gr. Pa-3, Z=32. The obtained X-ray diffraction data are given in Table 1, where ▲is rhombohedral phase and ■ is cubic phase.

After definition of the main crystallographic parameters of low-temperature phase, we carry out the high-temperature investigations of the same sample in the mode of low-temperature variant. Whole investigation process is regulated in automatic mode. X-ray diffraction pictures at temperatures 293, 400, 500, 600, 700 K are obtained. At give temperatures the sample is endured during 25 minutes and the picture is taken after it.

The visual comparison of obtained temperature diffraction pictures and the treatment of separate peaks and whole diffractograms using TOPAS and EVA programs shows that the essential changes aren't observed in $Cu_3Ni_{0.5}Se_2$ structure in temperature interval 293-500K besides the decrease of initial peak intensity. The essential changes in sample diffraction picture is observed in point 500K. If we compare the

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diffraction spectra in the given temperature, then it is revealed that at T= 500K the initial peak intensity 2θ=13,125^0 increases and reflections of double peak 2θ=26,20^0 and 26,53^0, 43,35^0, 44,00^0 peaks of low-temperature phase damp. Simultaneously, the intensities of new reflections at 2θ=26,68^0 and 44,02^0 strong increase.

The given experimental facts evidence that the structural change takes place in the sample near T=500K. By treatment of these diffraction pictures using the above mentioned programs it is established that the picture observable near 500K shows that all images of rhombohedral phase in the given temperature disappear and the system transforms into one-phase state with primitive cubic structure (Table 2). The lattice parameters of this phase are following: a ≈11,8684 Å, sp.gr.-$Pa\bar{3}$, Z=32.

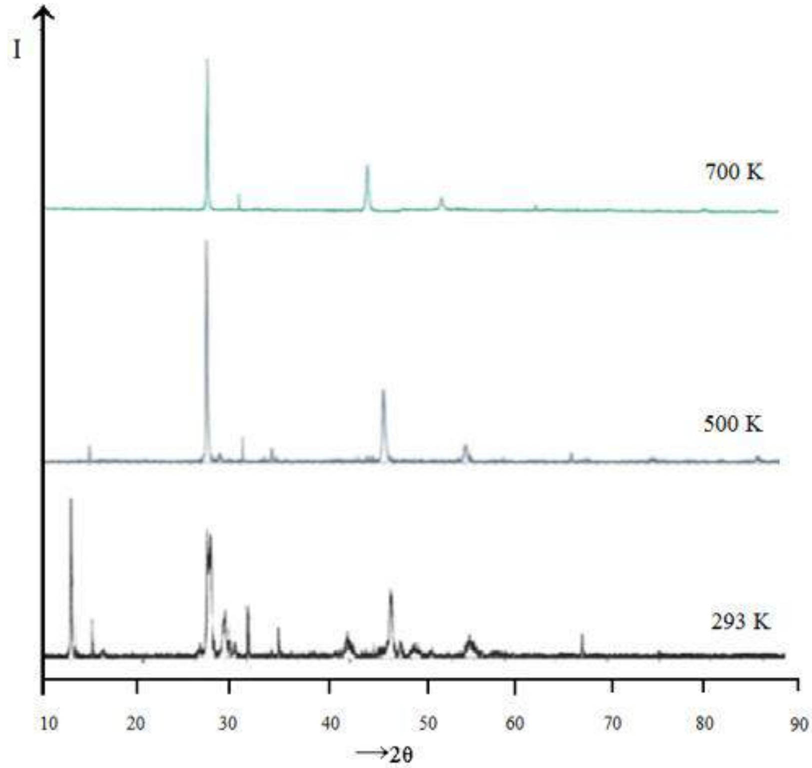

Fig. 1. $Cu_3Ni_{0.5}Se_2$ diffractograms in different temperatures 293K, 500K, 700K.

Table 1.
X-ray diffraction data of $Cu_3Ni_{0.5}Se_2$ at temperature 293K.

№	d	I/I0	hkl
1	6.77348	20	003▲
2	5.90905	1.5	200■
3	5.51234	10	100▲
4	3.51229	2	311■
5	3.39444	100	006▲
6	3.19555	17	312■
7	2.96211	3	400■
8	2.77339	6	330▲
9	2.70852	4	331■
10	2.26410	14	009▲
11	2.06174	60	440■
12	2.02388	11	441■
13	1.95728	7	600■
14	1.90273	3	611■
15	1.76240	11	200▲

▲is rhombohedral phase with lattice parameter a=4.32 Å
■ is cubic phase with lattice parameter a=11,841 Å

Table 2.
X-ray diffraction data of $Cu_3Ni_{0.5}Se_2$ at temperature 500K.

№	d	I/I0	hkl
1	5,8984	18	200
2	3,3451	100	222
3	3,1989	7	321
4	2,9612	20	400
5	2,7102	10	330
6	2,0527	36	440
7	1,7519	12	622
8	1,6467	3	710
9	1,4639	7	800
10	1,3332	5	554
11	1,1188	5	910

The diffraction picture in comparison with intermediate cubic phase is significantly simplified with further temperature increase up to 700K. The part of weak reflections disappears and the intensities of neogenic peaks increase. By treatment and definition by auto-indicating program TOPAS of this phase diffraction data it is established that the primitive cubic superlatice with parameter a=11.684 Å at T=700K transforms into face-centered cubic (FCC) phase with parameters a=5,96 Å, sp.gr. $Fm\overline{3}m$, Z=4 (Table 3).

Table 3.
X-ray diffraction data of $Cu_3Ni_{0.5}Se_2$ at temperature 700K.

№	*d*	*I/I₀*	*hkl*
1	3,34862	100	111
2	2,05061	43,5	220
3	1,74876	9,6	311
4	1,67431	0,6	222
5	1,45000	0,5	400
6	1,33061	1,5	331
7	1,29692	1	420

Correcting the equilibrium temperature between polymorpous modifications by extinction method and appearance of diffraction reflections (at increase and decrease of the temperature) it is established that rhombohedral α-phase of $Cu_3Ni_{0.5}Se_2$ at T=560±3K room-temperature two-phase system transforms into cubic β-phase (a=11.8844 Å) of $Pa\overline{3}$ symmetry.

CONCLUSION

As it is mentioned above, authors [5] show that Cu_3Se_2 umangite forms at interaction of $Cu_{2-x}Se$ and CuSe at temperature 408K. It decomposites on $Cu_{2-x}Se$ и CuSe at heating higher T=408K. Note that results of the given investigation of phase transitions show that implantation of Ni atoms into umangite increases $Cu_3Ni_{0.5}Se_2$ stability and it is stable up to T=567 K. Higher this temperature the cubic superlatice transforms into FCC lattice with parameter a=5,96 Å. One can suppose that the implantation of Ni bivalent atoms in umangite composition prevents the oxidation of Cu atoms up to bivalent state.

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