

THE ROLE OF ZINC ATOMS IN MODIFICATION STABILIZATION IN Cu_2Se

Yu.G. ASADOV, Yu. I. ALIYEV, F.G. MAGERRAMOVA, A.G. BABAYEV

*G.M. Abdullayev Institute of Physics of National Academy of Sciences,**AZ-1143, Baku, H. Javid ave., 33*

The single crystals of Cu_2Se , $\text{Cu}_{1.80}\text{Zn}_{0.20}\text{Se}$ and $\text{Cu}_{1.75}\text{Zn}_{0.05}\text{Se}$ composition have been synthesized and grown up. The structural phase transformations in single crystals of the given compositions are investigated by high-temperature x-ray diffractometer method and it is shown that the orthorhombic modification at 407 K transforms into FCC modification in Cu_2Se . High-temperature FCC modification stabilizes at room temperature and low-temperature orthorhombic modification stabilizes at high-temperature in $\text{Cu}_{1.80}\text{Zn}_{0.20}\text{Se}$ crystal where definite part of Cu atoms is exchanged by Zn atoms. The polymorphous transformations are absent in two-phase crystals $\text{Cu}_{1.80}\text{Zn}_{0.20}\text{Se}$ in temperature interval from room one up to melting point.

Cu_2Se compound exists in 38.22 weight % Se [1] region in state diagram of cuprum-selenium system, melting point is $T_{mp} = 1390\text{K}$, molecular weight is 206.04 and density $\rho = 6.749 \text{ g/cm}^3$.

In work [2] it is shown that low-temperature orthorhombic modification with lattice parameters $a=4.119 \text{ \AA}$, $b=7.028 \text{ \AA}$, $c=20.390 \text{ \AA}$, $Z=12$ at 407 K transforms into high-temperature FCC modification with lattice parameters $a=5.837 \text{ \AA}$, $Z=4$ and space group $Fm\bar{3}m$. In work [3] the large single crystals are obtained by method of structural transformation after couple cycle of transformations and it is noted that the stresses and cracks accumulate in single crystal as a result of which it becomes the polycrystal if transformation cycle would be continued later. It is also shown that $\text{Cu}_2\text{Se} \rightarrow \text{Cu}_{2-x}\text{Se}$ ($x=0.20$) takes place in the dependence on transformation order, i.e. some cuprum atoms leave the lattice and crystal has FCC structure with $a=5.72 \text{ \AA}$ parameter and space group $F\bar{4}3m$, $Z=4$ at room temperature. This compound is stable in temperature interval from room one up to melting point.

In the given paper the role of zinc atoms in modification stabilization and structural aspects of polymorphous transformations in Cu_2Se is considered.

Table 1

Atom percentages of components being part of Cu_2Se , $\text{Cu}_{1.80}\text{Zn}_{0.20}\text{Se}$, $\text{Cu}_{1.75}\text{Zn}_{0.05}\text{Se}$ compositions.

Composition	Cu, at. %	Zn, at. %	Se, at. %
Cu_2Se	61.677	-	38.323
$\text{Cu}_{1.80}\text{Zn}_{0.20}\text{Se}$	55.458	6.162	38.380
$\text{Cu}_{1.75}\text{Zn}_{0.05}\text{Se}$	57.488	1.690	40.822

The method of direct synthesis, i.e. chemical interaction of initial components is used for obtaining of homogeneous samples of given compositions. The ampoules from high-quality quartz with internal diameter 1 cm and length 10 cm are applied for synthesized compositions in the capacity of reactor. The ampoules are filled by initial components Cu, Zn and Se in quantities which are necessary for each composition: Cu_2Se , $\text{Cu}_{1.80}\text{Zn}_{0.20}\text{Se}$ and $\text{Cu}_{1.75}\text{Zn}_{0.05}\text{Se}$, are evacuated up to pressure 1.3MPa, and later are sealed. The used initial components for synthesis have the following purifications: cuprum has electrolytic one, zinc and selenium are crystalline «04» one. The quantities of initial components which are necessary for synthesizing for each composition (by mass 5 g) separately are given in table 1.

All ampoules with corresponding compositions are put in furnace simultaneously so that they would be in furnace stable band for achieving of similar synthesis conditions.

Further furnace temperature is increased up to selenium melting point ($T_{mp}=493\text{K}$) and is kept at this temperature during 3 hours for which the total reaction selenium-cuprum and selenium-zinc takes place. Further furnace temperature is increased with rate 50K/hour up to temperature which is close to Cu_2Se melting point ($T_{mp}=1390\text{K}$). The furnace with rate 50K/hour is cooled up to 350K (below the temperature of polymorphous transformations) after two-hour keeping at this temperature and the annealing is carried out for total composition homogenization at this temperature during 200 hours.

The roentgen-phase analysis is carried out for individuality establishment of obtained compositions and also for definition of phase compositions. The samples in powder forms are produced from ingots of each synthesized material for definition of phase relations of composition. The powder of each composition is filled in glass capillary with internal diameter $\sim 0,8 \text{ mm}$ and the pressed powder in wire form appears from capillar one end at pressing-out by wire with diameter $\sim 0,7$ from another end. The powdergrams in RCD-57.3 camera on CuK_α radiation are taken from such sample at similar conditions. The powdergram calculations are given in the tables 2, 3 and 4. In these tables the interplanar spacings calculated from diffraction data and also interplanar spacings with corresponding indexes hkl calculated on computer on structural data are given.

As it is seen from table 2, Cu_2Se powdergrams are indicated in low-temperature orthorhombic structure with lattice parameters $a=4.118 \text{ \AA}$, $b=7.028 \text{ \AA}$, $c=20.360 \text{ \AA}$, $Z=12$.

All registered 24 diffraction reflections from $\text{Cu}_{1.80}\text{Zn}_{0.20}\text{Se}$ are explicitly indicated on the base of orthorhombic structure as Cu_2Se , but in this case the reflections from high-temperature FCC modification with (111), (220), (311) и (222) indexes collide on the reflections from planes (002), (00 10), (042) and (044) correspondingly (table 3).

As it is seen from the table 4 the powdergram of $\text{Cu}_{1.75}\text{Zn}_{0.05}\text{Se}$ composition is explicitly indicated on the basis of FCC lattice with parameter $a=5.7412\text{\AA}$ which corresponds to lattice parameter Cu_{2-x}Se ($x=0.20$).

The synthesized samples of Cu_2Se , $\text{Cu}_{1.80}\text{Zn}_{0.20}\text{Se}$ and $\text{Cu}_{1.75}\text{Zn}_{0.05}\text{Se}$ are put in ampoules from high-quality quartz tubes of length 10 cm and internal diameter 1 cm after roentgen-phase analysis carrying out. The ampoules evacuated up to pressure 1,3 MPa with corresponding compositions are moved inside furnace having three temperature zones with the help of special mechanism. The temperature on 50K higher than the compound melting point

is kept in upper furnace zone, the temperature on 50K below sharp end exceeds the compound melting point The ampoule is kept in the second zone. The crystal germ creates from the moves with rate 0,2 cm/h is suitable for growth of created side of least temperature when the temperature of ampoule germ.

Table 2

The calculation of Cu₂Se powdergram.
CuK_α is radiation ($\lambda_{\alpha}=1.5418 \text{ \AA}$), Ni is filter, regime: 35 kV, 8 mA, experiment continues 12 hours.

θ	I/I_0	$d_{exp}, \text{ \AA}$	$d_{calc}, \text{ \AA}$	hkl	Lattice parameters
			Orthorhombic		
6°42'	30	6.614	6.6475	011	$a=4.119 \text{ \AA}$ $b=7.028 \text{ \AA}$ $c= 20.390 \text{ \AA}$ $Z=12$ $V=590.2565 \text{ \AA}^3$ $\rho= 6.749 \text{ g/cm}^3$
12°32'	20	3.553	3.3535	110	
12°51'	10	3.466	3.4648	021	
13°27'	70	3.316	3.3237	022	
18°18'	10	2.455	2.4551	116	
19°43'	20	2.285	2.2843	032	
20°06'	90	2.241	2.2358	125	
20°57'	10	2.156	2.1557	019	
21°59'	10	2.060	2.0590	200	
22°14'	100	2.038	2.0381	0 0 10	
23°49'	10	1.909	1.9090	204	
26°06'	60	1.753	1.7580	040	
30°45'	10	1.507	1.5083	233	
35°27'	20	1.330	1.3295	055	
40°33'	50	1.185	1.1845	330	
43°00'	10	1.131	1.1323	0 0 18	
45°24'	10	1.083	1.0819	340	
48°30'	10	1.030	1.0295	400	
51°33'	10	0.984	0.9834	422	

Table 3

The results of X-ray investigation of Cu_{1.80}Zn_{0.20}Se.
CuK_α is radiation ($\lambda_{\alpha}=1.5418 \text{ \AA}$), Ni is filter, regime: 35 kV, 8 mA, experiment continues 12 hours.

θ	I/I_0	$d_{exp}, \text{ \AA}$	$d_{calc}, \text{ \AA}$	hkl	$d_{calc}, \text{ \AA}$	hkl	Lattice parameters			
			Orthorhombic		FCC					
6°39'	30	6.6571	6.6522	001	$a=4.1169 \text{ \AA}$ $b=7.0288 \text{ \AA}$ $c= 20.3932 \text{ \AA}$ $Z=12$ $\rho= 6.9675 \text{ g/sm}^3$					
11°39'	70	3.8182	3.8175	102						
12°32'	20	3.5525	3.5536	110						
13°06'	10	3.4005	3.3990	006						
13°24'	70	3.3271	3.3261	022			3.3255	111		
18°18'	10	2.4551	2.4563	116						
19°54'	20	2.2647	2.2660	009			2.0365	220		
20°10'	90	2.2358	2.2367	125						
21°00'	10	2.1509	2.1569	019						
21°51'	60	2.0712	2.0714	118						
22°14'	100	2.0378	2.0381	0.0.10						
23°49'	10	1.9091	1.9051	029						
24°58'	10	1.8263	1.8275	1.0.10						
26°01'	60	1.7572	1.7592	040						
26°24'	36	1.7327	1.7336	042					1.7367	311
26°56'	8	1.7019	1.7031	043						
27°37'	5	1.6629	1.6630	044	1.6627	222				
30°48'	10	1.5057	1.5060	047						
31°55'	80	1.4584	1.4567	0.0.14						
35°26'	20	1.3296	1.3303	055						
40°36'	50	1.1845	1.1845	330						
42°54'	10	1.1325	1.1330	0.0.18						
45°24'	10	1.0827	1.0821	340						
48°35'	10	1.0279	1.0279	401						
51°24'	10	0.9867	0.9867	421						

The results of X-ray investigation of Cu_{1.75}Zn_{0.05}Se.
 CuK_α is radiation ($\lambda_{\alpha}=1.5418 \text{ \AA}$), Ni is filter, regime: 35 kV, 8 mA, experiment continues 12 hours.

θ	I/I_0	$d_{exp}, \text{ \AA}$	$d_{calc}, \text{ \AA}$	hkl	Lattice parameters
			FCC		
13°27'	100	3.3147	3.3147	111	$a=5.7412 \text{ \AA}$ $Z=4$ $V=189.2379 \text{ \AA}^3$ $\rho=6.7869 \text{ g/cm}^3$
15°35'	10	2.8706	2.8706	200	
22°19'	95	2.0298	2.0298	220	
26°27'	25	1.7310	1.7310	311	
27°43'	20	1.6573	1.6573	222	
32°29'	35	1.4353	1.4353	400	
35°49'	20	1.3171	1.3171	331	
41°08'	50	1.1719	1.1719	422	
44°14'	15	1.1049	1.1049	511, 333	
49°26'	10	1.0149	1.0149	440	
52°36'	30	0.9704	0.9704	531	
58°07'	25	0.9078	0.9078	620	
61°42'	15	0.8755	0.8755	533	
68°29'	10	0.8287	0.8287	444	

The ampoule, containing the crystals of high-temperature FCC modification at further shift achieves the third furnace zone where transformation of FCC modification into low-temperature orthorhombic modification takes place. In this furnace zone the ampoule with crystals is annealed during 50 hours. The single crystals obtained by such way are the objects of high-temperature-roentgen-diffractometer investigations. The experiments are carried out on diffractometer DRON-3M (CuK_α is radiation, $\lambda_{\alpha}=1.5418 \text{ \AA}$, Ni is filter) with high-temperature attachment URVT-2000 providing the vacuum 10^{-2} Pa , the record angular resolution is $\approx 0.1^\circ$, error of angle of reflection definition doesn't exceed $\Delta\theta=\pm 0.02^\circ$.

1. Cu₂Se. The obtained single crystals Cu₂Se easily shear in [011] direction. The six clear diffraction peaks with (011), (022), (027), (040), (055) and (0.0.18) indexes are fixed from such crystals at room temperature in angle interval $10^\circ \leq 2\theta \leq 90^\circ$. Not changing this crystal orientation, the furnace is switched on and records are taken at 323, 373, 405 and 413K temperatures. The temperature before each record is supported constant during 30 minutes.

The record taken at 423K is related to high-temperature FCC modification. Moreover all diffraction reflections belonging to low-temperature orthorhombic modification disappear and diffraction reflections with (111), (222) and (333) indexes belonging to high-temperature FCC modification with lattice parameter $a=5.8356 \text{ \AA}$ are fixed in previous angle interval.

The counter is fixed on maximum of one from diffraction reflections of low-temperature modifications $2\theta=40^\circ 12'$ (027) which disappears after transformation and appears at inverse transformation for detail definition of equilibrium temperature between modifications. Heating the low-temperature modification from 393K with rate 2 K/h it is defined that equilibrium temperature between modifications $T_0=407\pm 1\text{K}$.

The parameters of elementary orthorhombic cell are calculated at temperatures 298, 323, 373, 405K and parameters of FCC modification are calculated at temperatures 423, 473, 523, 573K. The results are given in tables 5,6 and graphically on the fig.1.

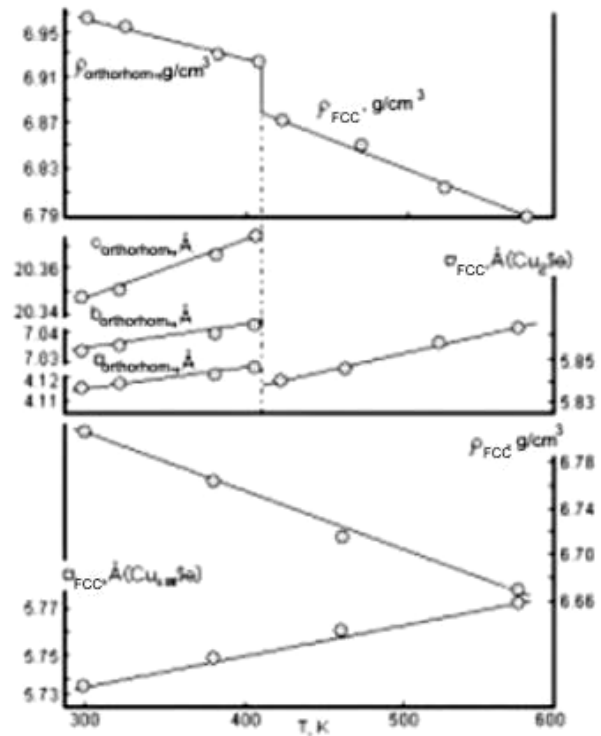


Fig.1. The temperature dependences of lattice parameters and densities of low-temperature orthorhombic and high-temperature FCC modifications Cu₂Se and lattice parameter and Cu_{1.80}Se crystal density.

The density dependence of orthorhombic and FCC modifications on temperature shows that density at equilibrium temperature of modifications $T_0=407\text{K}$ is changed by jump on 0.062 g/cm^3 . It is necessary to note that concentration change takes place in the dependence on transformation order, i.e. the transition Cu₂Se into Cu_{2-x}Se ($x=0.20$) with cuprum extraction on Cu_{2-x}Se block boundaries. This non-stoichiometric composition also has FCC lattice with parameter $a=5.740\text{ \AA}$. This compound is stable in temperature interval from room one up to melting point.

Table 5

The temperature dependence of crystal lattice periods of orthorhombic phase Cu₂Se.

T_{exp} , K	Orthorhombic				V , Å ³	ρ , g/cm ³
	a , Å	b , Å	c , Å	Z		
298	4.1168	7.0320	20.3472	12	589.038	6.968
323	4.1180	7.0336	20.3508	12	589.4480	6.963
373	4.1212	7.0384	20.3670	12	590.7785	6.947
405	4.1248	7.0416	20.3796	12	591.9293	6.934

Table 6

The temperature dependence of crystal lattice periods and thermal expansion of FCC phase Cu₂Se.

T_{exp} , K	a , Å	Z	V , Å ³	ρ , g/cm ³	T_{exo} , K	$\alpha_{[100]} \times 10^{-6} K^{-1}$
423	5.8391	4	199.0846	6.872	423-473	17.47
473	5.8442	4	199.6067	6.854	423-523	27.74
523	5.8553	4	200.7463	6.815	423-573	26.37
573	5.8622	4	201.4568	6.791		

The thermal expansion on main crystallographic directions of orthorhombic and FCC modifications Cu₂Se is given in tables 6 and 7, and FCC modifications Cu_{2-x}Se is given in table 8.

Table 7

Thermal expansion of orthorhombic phase Cu₂Se.

T_{exp} , K	Thermal expansion coefficients $\times 10^{-6} K^{-1}$			
	$\alpha_{[100]}$	$\alpha_{[010]}$	$\alpha_{[001]}$	$\bar{\alpha} = \frac{\alpha_{[100]} + \alpha_{[010]} + \alpha_{[001]}}{3}$
298-323	11.66	9.10	7.08	9.28
298-373	14.25	12.14	12.97	13.12
298-405	18.16	12.76	14.88	15.27

Table 8

Temperature dependence of crystal lattice periods and thermal expansion of FCC phases Cu_{1.80}Se.

T_{exp} , K	a , Å	Z	V , Å ³	ρ , g/cm ³	T_{exp} , K	$\alpha_{[100]} \times 10^{-6} K^{-1}$
298	5.7356	4	188.625	6.804	298	-
383	5.7480	4	189.911	6.760	298-383	25.74
473	5.7610	4	191.910	6.714	298-473	32.57
573	5.7746	4	192.559	6.667	298-573	24.82

2. Cu_{1.80}Zn_{0.20}Se. Cu_{1.80}Zn_{0.20}Se single crystals also easily shear on plane (011). The plate samples with sizes 4×4×1 mm which are suitable for diffractometer investigation are separated from crystalline ingot for temperature investigation. The six diffraction reflections fixed from such

samples at room temperatures in angle intervals $30^0 \leq 2\theta \leq 70^0$ are indicated in the same way as powder diffractogram Cu_{1.80}Zn_{0.20}Se on the basis of parameters of orthorhombic and FCC modifications which stabilize at room temperature (table 9).

Table 9

The crystal lattice periods of existing phases Cu_{1.80}Zn_{0.20}Se at 290-870K.

T_{exp} , K	Syngony	a , Å	b , Å	c , Å	Z	Sp.gr.	V , Å ³	ρ , g/cm ³
290	Orthorhombic	4.1274	7.0327	20.3618	14	-	591.0372	6.957
	FCC	5.7560	-	-	-	Fm3m	190.7051	7.187
370	Orthorhombic	4.1310	7.0491	20.4085	12	-	591.2921	6.919
	FCC	5.7651	-	-	4	Fm3m	191.6110	7.153
470	Orthorhombic	4.1486	7.0535	20.4390	12	-	598.0831	6.875
	FCC	5.7724	-	-	4	Fm3m	192.3398	7.126
570	Orthorhombic	4.1559	7.0700	20.4705	12	-	601.4686	6.836
	FCC	5.7818	-	-	4	Fm3m	193.2810	7.091
670	Orthorhombic	4.1667	7.0877	20.5055	12	-	605.5750	6.790
	FCC	5.7931	-	-	4	Fm3m	194.4165	7.050
770	Orthorhombic	4.1885	7.0892	20.5168	12	-	609.277	6.749
	FCC	5.8019	-	-	4	Fm3m	195.3038	7.018
870	Orthorhombic	4.1959	7.1015	20.5352	12	-	611.8911	6.720
	FCC	5.8110	-	-	4	Fm3m	196.2242	6.985

The control diffraction recordings are carried out saving crystal orientation in temperature interval 290-900K in each 100K. The temperature before each record is kept constant during 30 minutes. It is necessary to note that the essential changes of intensity values aren't observed in the given temperature intervals.

The parameters of elementary cell of orthorhombic modifications are calculated from reflections with (009), (0010), (1.0.10), (042), (043), (044) indexes which are given in table 10, and FCC parameter of modification is calculated from reflections with (220), (311) and (222) indexes, its results are also given in table 10.

Table 10

Thermal expansion of elementary cell parameters of orthorhombic phase Cu_{1.80}Zn_{0.20}Se in temperature interval 290-870K.

T_{exp}, K	Thermal expansion coefficients $\times 10^{-6} K^{-1}$			
	$\alpha_{[100]}$	$\alpha_{[010]}$	$\alpha_{[001]}$	$\bar{\alpha} = \frac{\alpha_{[100]} + \alpha_{[010]} + \alpha_{[001]}}{3}$
290-370	10.90	29.15	28.67	22.91
290-470	28.54	16.56	21.12	22.07
290-570	24.66	18.94	19.07	20.89
290-670	25.22	20.58	18.57	21.46
290-770	31.64	16.14	15.86	21.21
290-870	29.35	16.87	14.68	20.30

290-370	20.63
290-470	11.00
290-570	17.25
290-670	18.10
290-770	17.55
290-870	16.44

The temperature dependences of elementary cell parameters of orthorhombic and FCC modifications are graphically given on the fig.2.

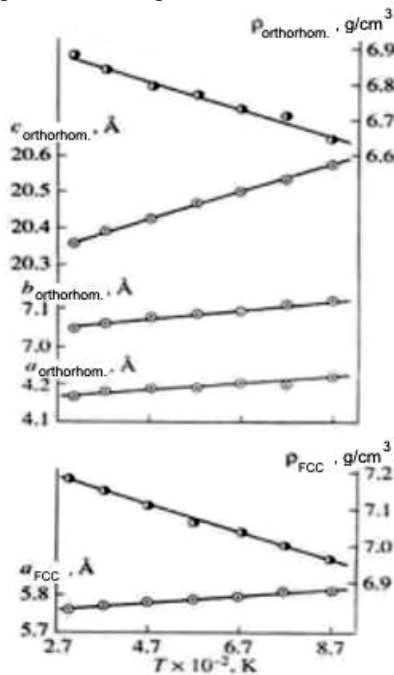


Fig.2. The temperature dependences of elementary cell parameters of orthorhombic and FCC phase Cu_{1.80}Zn_{0.20}Se.

As it is seen from fig.2 the values of elementary cell parameters of orthorhombic and FCC modifications in temperature function increase linearly. The linear increase of lattice parameters of both modifications shows that both modifications stably exist in considered temperature interval, i.e. low-temperature orthorhombic modification metastably exists at high temperatures, and high-temperature FCC modification exist at room temperature.

The calculated values of ρ (g/cm³) orthorhombic and FCC modifications given in table 9 are also graphically shown on the fig.2. As it is seen from the figure the density of both modifications is linearly decreases and FCC modification density is bigger than density of orthorhombic one, i.e. $\Delta\rho = \rho_{\kappa} - \rho_{\text{ортром}} = 0.25 \text{ g/cm}^3$.

The crystal thermal expansion of orthorhombic and FCC modifications are given in table 10.

3. Cu_{1.75}Zn_{0.05}Se. The plane samples with sizes 5×4×2 mm (of undefined crystallographic orientation) are taken for temperature-diffractometer investigations. The reflections from (111), (200), (220), (311) and (400) planes which are enough for calculation of elementary cell parameter are fixed at room temperature in angle interval $20^{\circ} \leq 2\theta \leq 70^{\circ}$. The investigation is carried out in temperature interval 290-670K.

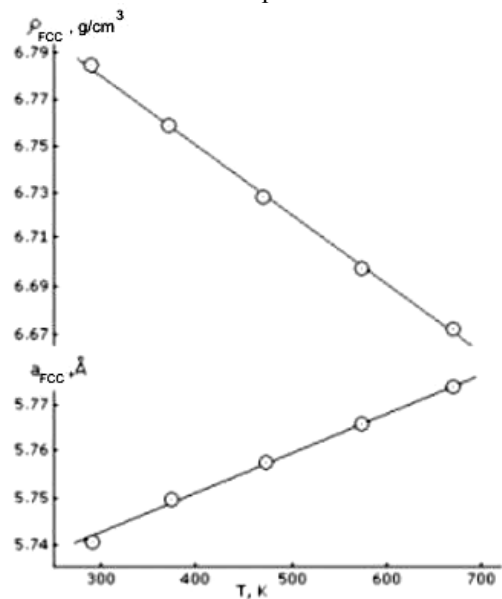


Fig.3. The temperature dependence of elementary cell parameters of FCC phase Cu_{1.75}Zn_{0.05}Se.

The results of these investigations and also thermal expansion are given in the table 11. As it is seen on the fig.3a elementary cell parameter in temperature function linearly increases, and density linearly decreases.

Table 11

The temperature dependence of crystal lattice periods and thermal expansion of FCC phase $Cu_{1.75}Zn_{0.05}Se$.

T_{exp}, K	FCC		Sp. gr.	$V, \text{Å}^3$	$\rho, g/cm^3$	T_{exp}, K	$\alpha_{[100]} \times 10^{-6} K^{-1}$
	$a, \text{Å}$	Z					
290	5.7412	4	Fm3m	189.2379	6.787	290-370	17.42
370	5.7492	4	Fm3m	190.0300	6.759	290-470	16.06
470	5.7578	4	Fm3m	190.8841	6.728	290-570	15.68
570	5.7664	4	Fm3m	191.7407	6.698	290-670	14.90
670	5.7737	4	Fm3m	192.4698	6.673		

Finally note that Cu_2Se lattice carcass belongs to Se^{2-} atoms (ion radius is 1.93 Å), Cu atoms are statistically situated between them. There are defects with empty cuprum knots in crystal lattice. The cuprum atoms can easily move from one crystal region to another one. The atom oscillation in lattice increases with temperature increase and lattice becomes unstable one at given temperature. As a result the structural transformations take place.

Usually cuprum atoms in cuprum chalcogenides in lattices of stoichiometric compounds participate in two different valent states, i.e. $Cu^+(0.98)$ and $Cu^{++}(0.80)$. This is the main existence reason of non-stoichiometric compounds $Cu_{2-x}Se$, $Cu_{2-x}Te$ и $Cu_{2-x}S$ where $0 \leq x \leq 25$ and excess of structural transformations. The obtained crystals

$Cu_{1.80}Zn_{0.20}Se$ at room temperature in $Cu_{2-x}Se$ at isomorphous exchange of definite cuprum atom quantity by $Zn^+(0.83)$ atoms become two-phase ones, i.e. high-temperature FCC modification stabilizes at room temperature and low-temperature orthorhombic modification stabilizes at high temperature. $Cu_{1.75}Zn_{0.05}Se$ crystals at all considered temperatures are one-phase and have FCC structure. Zn^{++} atoms in $Cu_{1.80}Zn_{0.20}Se$ and $Cu_{1.75}Zn_{0.05}Se$ crystal structures take Cu^{++} places in tetrahedral empty spaces. The mobility of Zn^{++} atoms in $Cu_{1.80}Zn_{0.20}Se$ and $Cu_{1.75}Zn_{0.05}Se$ lattices and Zn-Se and Zn-Cu bonds differ from mobility of Cu atoms in $Cu_{2-x}Se$, and also from Cu-Se and Cu-Cu bonds which are the reason of modification stabilization in $Cu_{1.80}Zn_{0.20}Se$ and $Cu_{1.75}Zn_{0.05}Se$.

[1] M. Khansen, K. Anderko. *Struktura dvoynikh splavov*. 1962, tom 1. (in Russian)
 [2] Yu G. Asadov, G.A. Jabrailova, V.I. Nasirov. *Izv. AN SSSR, Neorganicheskie materialy*. 1972, t.8, №6, s.1144. (in Russian)

[3] Yu G. Asadov, G.B. Gasimov, G.A. Jabrailova. *Izv. AN SSSR, Neorganicheskie materialy*. 1972, №12, s.2208.

Y.Q. Əsədov, Y.İ. Alıyev, F.Q. Məhərrəmovə, Ə.Q. Babayev

Cu_2Se BİRLƏŞMƏLƏRİNDƏKİ MODİFİKASİYALARIN STABİLLƏŞMƏSİNDƏ Zn ATOMLARININ ROLU

Cu_2Se , $Cu_{1.80}Zn_{0.20}Se$ və $Cu_{1.75}Zn_{0.05}Se$ birləşmələri sintez edilmiş və monokristalları göyərdilmişdir. Yüksəktemperatur rentgendifraktometrik metodla qeyd olunan monokristallarda struktur faza keçidləri tədqiq edilmiş və göstərilmişdir ki, Cu_2Se -də ortorombik modifikasiya 407K temperaturda ÜMK modifikasiyaya keçir, Cu atomlarının müəyyən hissəsi Zn atomları ilə əvəz olunmuş $Cu_{1.80}Zn_{0.20}Se$ birləşməsində isə yüksəktemperatur ÜMK modifikasiyası otaq temperaturunda ortorombik modifikasiya ilə stabilləşir. İkifazlı $Cu_{1.80}Zn_{0.20}Se$ kristalında otaq temperaturundan ərimə temperaturuna qədər intervalda polimorf çevrilmə baş verir.

Ю.Г. Асадов, Ю.И. Алыев, Ф.Г. Магеррамова, А.Г. Бабаев

РОЛЬ АТОМОВ ЦИНКА В СТАБИЛИЗАЦИИ МОДИФИКАЦИЙ В Cu_2Se

Синтезированы и выращены монокристаллы состава Cu_2Se , $Cu_{1.80}Zn_{0.20}Se$ и $Cu_{1.75}Zn_{0.05}Se$. Высокотемпературным рентгendifрактометрическим методом исследовались структурные фазовые превращения в монокристаллах указанных составов и показано, что в Cu_2Se орторомбическая модификация при 407К превращается в ГЦК модификацию. В кристалле $Cu_{1.80}Zn_{0.20}Se$, где определенная часть атомов Cu заменена атомами Zn, высокотемпературная ГЦК модификация стабилизируется при комнатной температуре, а низкотемпературная орторомбическая модификация стабилизируется при высокой температуре. В двухфазных кристаллах $Cu_{1.80}Zn_{0.20}Se$ в интервале от комнатной температуры до температуры плавления полиморфные превращения отсутствуют.

Received: 17.03.08