PHASE TRANSITIONS IN $CuAgS_{0.5}Se_{0.5}$

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$CuAgS_{0.5}Se_{0.5}$ monocrystals were synthesized and grown. Phase transitions were investigated by high temperature x-ray analysis. It's been shown, that at room temperature crystals have two phases, and one of the phases has structure of $Cu_{1.96}S$ and the other of CuAgSe. Both phases at 695 K turn to single FCC lattice with parameter a=6.356 Å.

In [1] it has been determined that CuAgS crystals at room temperature are crystallized into orthorhombic structure with lattice parameters a=4.06 Å, b=6.66 Å, c=7.99 Å, space group D^{17}_{2h} – Cmcm, Z=4, ρ=6.4 г/см^3. The only thing about polymorphism mentioned in [1], is that at 366 K low temperature orthorhombic modification turns to hexagonal one that is identical to β-Cu_2S (a=4.005 Å, c=6.806 Å, Z=2, space group $P6_3/mmm$)[2].

In [3] phase transitions in CuAgS were investigated. It has been shown that low temperature orthorhombic modification at 400 K turns to hexagonal and the hexagonal one in its part turns at 705 K to high temperature FCC with a=5.7288Å. Crystal turns back to its initial state when cooled.

Partial replacement of 50% Se atoms by Te atoms and its influence on phase transitions in $CuAgS_{0.5}Te_{0.5}$ were also investigated in [3]. It has been shown that at room temperature $CuAgS_{0.5}Te_{0.5}$ consist of three phases, one of them identical, as regards lattice size, to low temperature monocline $Cu_{1.96}S$ [4], another one has lattice of low temperature orthorhombic phase of Cu_2Te [5] and the last one has lattice of low temperature orthorhombic CuAgS [1]. $CuAgS_{0.5}Te_{0.5}$ consist of three phases and at 720±1 K turns to single FCC phase with lattice parameter a=6.531 Å.

In present paper the influence of partial replacement of 50% of S atoms by Se atoms on structure and temperatures of phase transitions in $CuAgS_{0.5}Se_{0.5}$ has been investigated. The conditions of crystal synthesis and growth did not differ from those of CuAgS and $CuAgS_{0.5}Te_{0.5}$ [3].

An X-ray diffractometric temperature investigation was conducted in a "DRON-3M" diffractometer with a temperature attachment URVT-2000 in vacuum (10^{-1} Pa). Angular resolution was ≈0.1°. Diffraction angles were measured with an accuracy $\Delta\theta$=±0.02°.

Table 1

XRD data for $CuAgS_{0.5}Se_{0.5}$ (Fe-filtered, CoK_α radiation, λ_α=1.7902 Å, 55kV, 12mA).

T, K	Θ	$I/I_\circ$	$D_{exp.}$Å	CuAgSe		Ag_2Se		Lattice Parameters, Å
				$d_{calc.}$Å	hkl	$d_{calc.}$Å	Hkl	
1	2	3	4	5	6	7	8	9
293	18° 00'	30	2.897	2.898	243	2.890	150	$Cu_{1.96}S$ Monocline a=26.897 b=15.515 c=13.585 Z=8 S.G. $P2_{1/n}$ ρ_x=5.870 g/cm^3
	19° 30'	80	2.682	2.690	10 0 0	2.681	042	
	20° 24'	100	2.568	2.569	044			
	21° 36'	50	2.432	2.437	162			
	23° 30'	70	2.245	2.245	942			
	25° 06'	40	2.110	2.111	326			
	25° 36'	50	2.072	2.073	11 2 3			
	26° 36'	60	1.999	1.998	645	2.012	220	
	28° 24'	90	1.882	1.882	027	1.890	191	
	31° 24'	40	1.718	1.717	275, 390	1.710	0 10 2	CuAgSe Orthorhombic a=4.086 b=20.533 c=6.275 S.G. D^7_{2h} – P4/nmm Z=10 ρ_x=7.895 g/cm^3
	33° 42'	50	1.163	1.614	038			
	37° 24'	10	1.474	1.473	908, 286			
	39° 06'	30	1.419	1.419	938	1.411	243	
	41° 24'	10	1.354	1.354	078, 1 0 10			
	45° 54'	10	1.247	1.246	0 5 10	1.247	0 10 4	
	48° 00'	20	1.205	1.205	0 6 10	1.204	115	
373	17° 55'	30	2.909	2.910	243	2.909	150	$Cu_{1.96}S$ a=26.859 b=15.811 c=13.608 ρ_x=5.759 g/cm^3
	19° 28'	80	2.686	2.686	10 0 0	2.684	042	
	20° 19'	100	2.578	2.579	044			
	21° 27'	45	2.448	2.447	132			
	23° 28'	70	2.248	2.248	942			
	25° 00'	40	2.118	2.118	326			
	25° 33'	50	2.075	2.074	11 2 3			
	26° 32'	60	2.004	2.004	645	2.014	220	CuAgSe a=4.107 b=20.664 c=6.374 ρ_x=7.683 g/cm^3
	28° 18'	90	1.888	1.888	027	1.906	191	
	31° 17'	35	1.724	1.724	275, 390	1.724	0 10 2	
	33° 34'	45	1.619	1.619	038			
	37° 17'	10	1.478	1.478	908			
	38° 59'	25	1.423	1.423	938	1.411	243	

	41° 12'	10	1.359	1.359	1 0 10		
	45° 44'	10	1.250	1.250	0 5 10	1.250	0 10 4
	47° 46'	20	1.209	1.209	0 6 10	1.201	115
473	17° 49'	30	2.925	2.926	243	2.925	150
	19° 26'	75	2.691	2.691	10 0 0	2.712	042
	20° 10'	100	2.596	2.597	044		
	21° 22'	50	2.456	2.456	162		
	23° 24'	70	2.254	2.255	942		
	24° 45'	40	2.138	2.138	326		
	25° 27'	50	2.083	2.082	11 2 3		
	26° 30'	60	2.006	2.006	645	2.030	220
	28° 00'	90	1.907	1.908	027	1.915	191
	31° 05'	40	1.734	1.734	275, 390	1.734	0 10 2
	33° 12'	50	1.635	1.635	038		
	36° 55'	10	1.490	1.490	908, 286		
	38° 37'	30	1.434	1.434	938	1.425	243
	40° 39'	10	1.374	1.374	078, 1 0 10		
	45° 11'	10	1.262	1.262	0 5 10	1.262	0 10 4
	47° 12'	20	1.220	1.221	0 6 10	1.216	115
573	17° 47'	30	2.931	2.931	243	1.931	150
	19° 24'	80	2.694	2.964	10 0 0	1.716	042
	20° 07'	100	2.602	2.602	044		
	21° 20'	45	2.460	2.460	162		
	23° 22'	70	2.257	2.258	942		
	24° 42'	40	2.142	2.142	326		
	25° 25'	50	2.086	2.085	11 2 5		
	26° 17'	60	2.022	2.021	645	2.039	220
	27° 56'	90	1.911	1.910	027	1.923	191
	31° 02'	35	1.736	1.737	275	1.741	0 10 2
	33° 08'	45	1.638	1.638	038		
	36° 51'	10	1.493	1.493	908		
	38° 32'	25	1.437	1.437	938	1.430	243
	40° 35'	10	1.376	1.376	1 0 10		
	45° 06'	10	1.264	1.264	0 5 10	1.266	0 10 4
	47° 06'	20	1.222	1.222	0 6 10	1.218	115
673	17° 44'	30	2.939	2.937	243	2.939	150
	19° 23'	80	2.697	2.696	10 0 0	2.720	042
	20° 05'	100	2.606	2.606	044		
	21° 15'	50	2.466	2.467	162		
	23° 20'	70	2.260	1.260	942		
	24° 40'	40	2.145	1.145	326		
	25° 24'	50	2.087	2.087	11 2 3		
	26° 15'	60	2.024	2.024	645	2.039	220
	27° 54'	90	1.913	1.913	027	1.923	191
	30° 57'	40	1.740	1.740	275	1.741	0 10 2
	33° 05'	50	1.640	1.640	038		
	36° 48'	10	1.494	1.494	908		
	38° 29'	30	1.438	1.438	938	1.430	243
	40° 32'	10	1.377	1.377	1 0 10		
	45° 01'	10	1.266	1.266	0 5 10	1.266	0 10 4
	47° 00'	20	1.224	1.244	0 6 10	1.220	115
773	16° 19'	40	3.176	3.185	200		
	23° 30'	65	2.246	2.245	220		
	27° 52'	100	1.915	1.915	311		
	29° 12'	70	1.834	1.835	222		
	34° 19'	30	1.588	1.588	400		
	37° 54'	80	1.457	1.458	331		
	39° 04'	30	1.420	1.420	420		
	43° 39'	50	1.297	1.297	422		
	47° 04'	90	1.222	1.223	333, 511		
873	16° 16'	40	3.196	1.182	200		
	23° 27'	65	2.250	1.250	220		
	27° 49'	100	1.918	1.919	311		
	29° 10'	70	1.837	1.837	222		
	34° 16'	30	1.590	1.591	400		
	37° 51'	80	1.459	1.460	331		
	39° 02'	30	1.422	1.423	420		

$Cu_{1.96}S$
a=26.905
b=15.852
c=13.753
ρ_x=5.673 g/cm^3

CuAgSe
a=4.142
b=20.664
c=6.374
ρ_x=7.619 g/cm^3

$Cu_{1.96}S$
a=26.936
b=15.893
c=13.775
ρ_x=5.643 g/cm^3

CuAgSe
a=4.152
b=20.695
c=6.383
ρ_x=7.578 g/cm^3

$Cu_{1.96}S$
a=26.936
b=15.893
c=13.775
ρ_x=5.620 g/cm^3

CuAgSe
a=4.152
b=20.695
c=6.383
ρ_x=7.536 g/cm^3

FCC
a=6.356
S.G. Fm3m
Z=4
ρ_x=6.376 g/cm^3

FCC
a=6.363
ρ_x=6.355 g/cm^3

	43° 36'	50	1.298	1.299	422		
	47° 01'	40	1.224	1.225	333		
973	16° 13'	40	3.205	1.186	200		FCC a=6.372 ρ_x=6.328 g/cm^3
	23° 24'	65	2.254	1.253	220		
	27° 46'	100	1.921	1.921	311		
	29° 07'	70	1.840	1.840	222		
	34° 13'	30	1.592	1.593	400		
	37° 49'	80	1.460	1.462	331		
	39° 00'	30	1.422	1.425	420		
	43° 33'	50	1.299	1.301	422		
	46° 58'	90	1.225	1.226	333		

At 293 K the XRD patterns from 5×5×1 mm arbitrary oriented $AgCuS_{0.5}Se_{0.5}$ single-crystal showed 16 diffraction peaks. Indexing of patterns confirms existence of two phases, the first is identical to monocline $Cu_{1.96}S$ [4], the second – to low temperature orthorhombic CuAgSe [6].

All 16 diffraction peaks (Table 1) can be indexed on the basis of lattice parameters of orthorhombic $Cu_{1.96}S$, 8 of them also can be indexed on the basis of orthorhombic CuAgSe.

After the patterns were recorded at room temperature, the furnace was turned on and reference recordings were taken every 100 K without disturbing the original crystal orientation. The sample temperature prior to every record was kept constant for 40 minutes.

At 773K 9 peaks were recorded that belong to high temperature FCC modification with a=6.356 Å, Z=4, space group Fm3m. The transition temperature was determined from disappeared peaks when both phases turn to FCC at T_t=695±2 K.

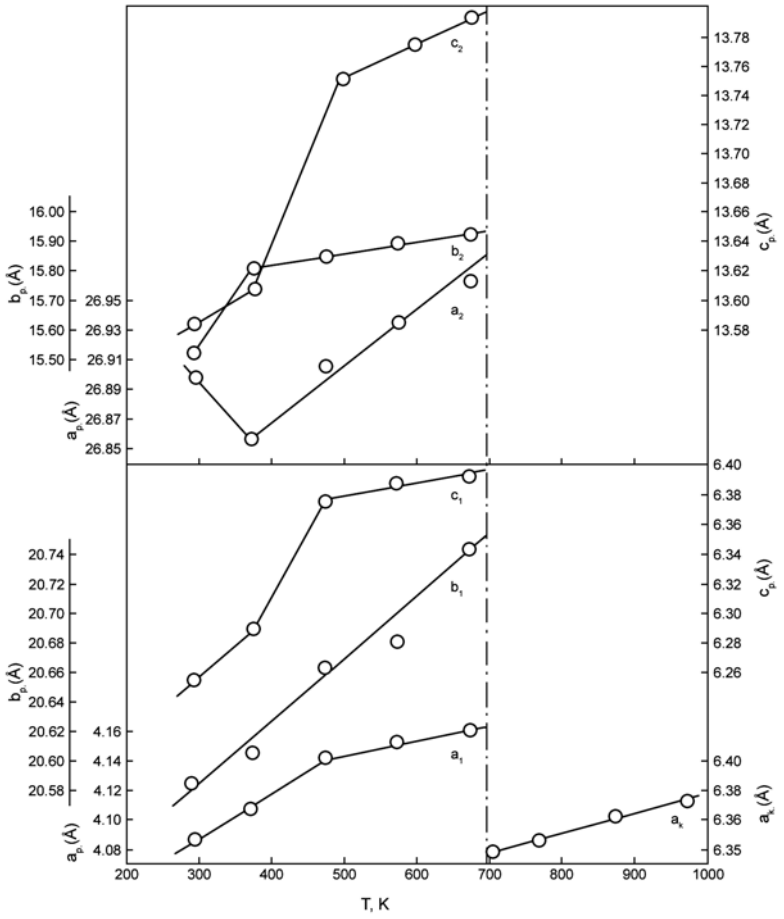

Fig. 1. Temperature dependence of lattice parameters in $CuAgS_{0.5}Se_{0.5}$

Fig 1 shows temperature dependence of lattice parameters. As we see, lattice parameters a_1, b_1, c_1 of monocline $Cu_{1.96}S$ deviate from linearity at 373 K, parameters b_1 and c_1 quickly increase and a_1 decreases and linearly grows after 373 K. Lattice parameters a_2 and c_2 of modifications identical to orthorhombic CuAgSe structure, deviate from linearity at 473 K. In spite of such changing in lattice parameters of both phases with temperature, there is not much difference in number and intensity of diffraction peaks.

Table 2 contains coefficients of thermal expansion calculated using temperature dependence of lattice parameters. As we can see, the thermal expansion for modification identical

to $Cu_{1.96}S$ along [010] significantly differ from that along [100] and [001] ($\alpha_{[100]} < \alpha_{[010]} > \alpha_{[001]}$). It's significant that in low temperature monocline modification, S atom layers form hexagonal close packages and Cu atoms are distributed among them in 3 different ways. In this structure 51 of Cu atoms distributed in distorted triangles, 9 – in tetrahedral spaces and one is in double coordination. Some of Ag atoms might replace Cu atoms.

Table 2

Thermal expansion coefficients for $CuAgS_{0.5}Se_{0.5}$

Modification	Temperature K	$\alpha_{[100]}10^{-6}K^{-1}$	$\alpha_{[010]}10^{-6}K^{-1}$	$\alpha_{[001]}10^{-6}K^{-1}$	$\overline{\alpha} = \frac{\sum \alpha_i}{3} \cdot 10^{-6} K^{-1}$
Orthorhomb. $Cu_{1.96}S$	293-373	-19.05	238.48	21.16	80.20
	293-473	1.65	120.67	68.70	63.67
	293-573	5.18	87.01	49.95	47.38
	293-673	6.46	68.86	40.29	38.54
Orthorhomb. CuAgSe	293-373	64.24	79.75	197.21	113.73
	293-473	76.14	35.44	87.65	66.41
	293-573	57.69	28.18	61.47	49.11
	293-673	47.66	28.71	46.97	41.11
FCC $CuAgS_{0.5}Se_{0.5}$	773-873	0.11			0.11
	773-973	0.13			0.13

In CuAgSe lattice, Ag atoms situated in planes perpendicular to c axis. Near each of them, there are 4 Ag atoms at 2.96 Å and 6 Se atoms at 2.67 Å (4 Se), 3.59 Å **(**1 Se), 3.64 Å **(**1 Se). Se atoms form elongated tetrahedrons in which Cu atoms situated. Distance between Se atoms is Se-Se=3.30 Å**,** between Cu and Se is from 2.06 Å to 2.50 Å and the least one is Cu-Ag=2.98 Å.

Thermal expansion coefficient of phase crystallized as CuAgSe structure has anisotropy along basic crystallographic directions ($\alpha_{[100]} \approx \alpha_{[010]} > \alpha_{[001]}$). Strong anisotropy of thermal expansion of both phases is one of the main reasons of thermal instability of low temperature phase. We should note, that monocline $Cu_{1.96}S$ at 377 K turns to FCC phase with *a*=5.707 Å and CuAgSe at 504 K turns to FCC phase (*a*=5.082 Å) as well. In our case that doesn't happen, i.e. both phases ($Cu_{1.96}S$ and CuAgSe) turn to FCC phase (*a*=6.356 Å) at 695 K at the same time.

At room temperature $CuAgS_{0.5}Se_{0.5}$ crystals consist of 2 phases and while heated, as seen from thermal expansion anisotropy, deform each other. The nucleus of high temperature FCC phase is formed in the interface of these two phases and grows at the expense of both phases. When cooled, FCC phase splits in two and crystal turns to initial state. Phase transitions are reversible and take place by single-poly crystal model.

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$CuAgS_{0.5}Se_{0.5}$ KRİSTALINDA POLİMORF KEÇİD

$CuAgS_{0.5}Se_{0.5}$ tərkibi sintez edilmiş və monokristalı alınmışdır. Yüksək temperatur difraktometrik metodu ilə polimorf keçid tədqiq edilmiş və göstərilmişdir ki, otaq temperaturunda kristal iki fazalıdır. Fazalardan biri $Cu_{1.96}S$ strukturasını, digəri isə AgCuSe-nin strukturasını qəbul edir. Hər iki faza 695 K-də səthinə mərkəzləşmiş kubik fazaya keçir.

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ПОЛИМОРФНЫЕ ПРЕВРАЩЕНИЯ В $CuAgS_{0.5}Se_{0.5}$

Синтезированы и выращены монокристаллы $CuAgS_{0.5}Se_{0.5}$. Высокотемпературным рентгенографическим методом исследовались полиморфные превращения. Показано, что при комнатной температуре кристаллы - двухфазные, одна из фаз принимает структуру $Cu_{1.96}S$, а другая - CuAgSe. Обе фазы при 695 К превращаются в единую ГЦК модификацию с параметром a=6.356 Å.

Received: 09.02.05