THE STRUCTURAL AND THERMODYNAMIC ASPECTS OF POLYMORPHIC TRANSFORMAIONS IN Ag_2Se

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The monocrystals Ag_2Se have been synthesized and grown by sublimation method. The polymorphic transformations in Ag_2Se have been investigated by high-temperature X-ray-diffractometer method and it is established, that low-temperature orthorhombic modification at 406K transforms into high-temperature OCC modification. The transformation is reversible and takes place by the type monocrystal – monocrystal. The existing thermodynamic data were widely used at result discussion.

1. The crystal structure Ag_2Se

From the state diagram, given in [1,2], it is seen, that the argentum with selenium form the one compound Ag_2Se, containing the 26,79 weight% Se.

The reference data about crystal structure of low-temperature modification α–Ag_2Se are contradictory. In [3] it is given only the table of interplanar spacings, calculated from powdergram of low-temperature α-Ag_2Se. In [4], studying the thin films of Ag_2Se, obtained in vacuum by method of electron diffraction, it is shown that low-temperature modification is crystallized in tetragonal syngony with lattice parameters a=7,06Å and c=4,98Å. In [5,6] the sample investigation, obtained on crystal surface KCl and NaCl with evaporation in vacuum of Se and Ag was carried out by electron-diffraction method at room temperature. It is seen, that FCC modification is obtained from the film, obtained at 573K at room temperature, and orthorhombic modification with lattice parameters a=7,06Å, b=7,76Å and c=4,34Å is obtained from FCC modification below 473K. In [7] it is seen, that low-temperature modification has pseudocubic structure with lattice parameters a=4,978Å. The same author gives the rhombic modification with lattice parameters a=7,046Å, b=14,32Å and c=7,82Å, which transforms into pseudocubic one after a time. In [8] it is informed, that the monoclinic and triclinic modifications with lattice parameters a=7,0Å, b=7,8Å and c=4,3Å, α =920, β=91,50, γ=920 are detected as result of some heating and cycles in some region of Ag_2Se film. In [9] Ag_2Se investigation was also carried out in thin-film state and it is shown, that at low temperatures there are tetragonal, orthorhombic and triclinic modification of Ag_2Se in the one and the same film.

From above mentioned it has became clear, that different investigators give the contradictory syngonies for low-temperature modification of Ag_2Se: cubic [6], tetragonal [4,10], orthorhombic [7,11-18], monoclinic [8,19] and triclinic [9,10,20]. Note that in the given papers the conditions of sample derivations just as investigation methods were different. This especially related to investigations of thin-film states. The different types of structure are related to unit low-temperature modification of Ag_2Se by this reason.

In many papers [21-23], where metal block samples were used, the temperature of polymorphic transformation in Ag_2Se was in the temperature interval 406-413K.

The crystal structure of low-temperature modification was considered in more detail in [14,18]. In [14] the orthorhombic structure with lattice parameters a=7,05Å, b=7,85Å and c=4,33Å is established by electron-diffraction method for low-temperature modification of Ag_2Se. The elementary cell contains Z=4Ag_2Se, space symmetry group is D^2_2-$P222_1$.

In [18] the orthorhombic structure with lattice parameters a=4,333Å, b=7,062Å and c=7,764Å for low-temperature modification of Ag_2Se is also supposed. The elementary cell contains Z=4Ag_2Se, space symmetry group is $D^4_2 - P2_12_12_1$.

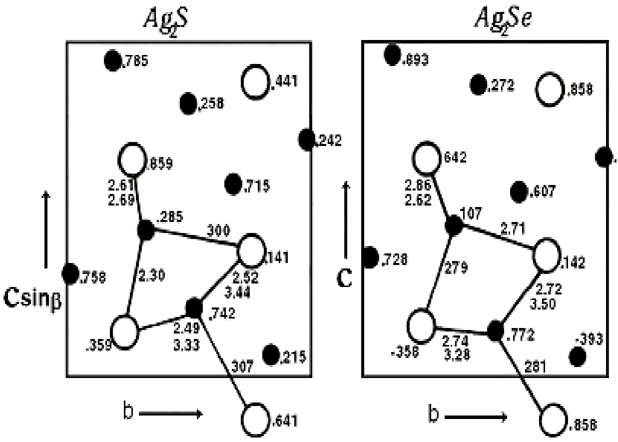

Fig.1. The structure projection of monoclinic α-Ag_2S and orthorhombic α-Ag_2Se on the [011] direction.

In orthorhombic lattice Ag(I) is in tetrahedral Se atom surroundings, and Ag(II) is in triangular one. Further at working of experimental data we will use the space symmetry group $P222_1$. The choice of especially this structural model, but not $P2_12_12_1$ doesn't connect with falsity of the last one. In spite of the fact, that low-temperature modification of Ag_2Se crystallizes in orthorhombic syngony there is big similarity with monoclinic structure of Ag_2Se. The atom distribution in both structures is shown on the fig.1.

The structural investigation of high-temperature modification β-Ag_2Se [24] proves the similarity with structure β-Ag_2Se, i.e. Se^{2-} form OCC lattice, and Ag atoms distribute in big number of empty spaces of this lattice, mainly in larger from them. The lattice parameter slightly increases in the comparison with β-Ag_2S in β-Ag_2Se, i.e. Δa=(4.98-4.88)Å=0,10Å. This difference is equal to difference of ion radii of Se (1.93) and S (1.82).

On data [24] the parameter of elementary cell β-Ag_2Se is equal to α=4.983Å, elementary cell contains Z=2Ag_2Se, space symmetry group is O^5_h – Fm3m.

2. The synthesis and growing of monocrystals Ag_2Se

In [25] it is shown, that Ag_2Se compound can be prepared by the fusion of elements in evacuated quartz ampoules at temperature higher than 1323K keeping the melt during 15-20 hours. By author opinion, the transmission method of selenium steams in nitrogen or argon current under the surface of heated wood-wool of argentums up to 673K. The process is carried out during 6-8 hours till the appearance of selenium mirror behind boat with argentums. After finish of selenium absorption the obtained selenide is kept in vacuum during several hours for distillation of excess selenium. It isn't recommended to increase the temperature at that as essential dissociation of argentums selenide is taken place already at temperatures higher than 673K. The vacuum distillation can be changed by remelting in evacuated quartz ampoules, if there isn't much free selenium in selenide. The band recrystallization method can be also used for obtaining of very pure samples of Ag_2Se [10].

In the given paper samples of Ag_2Se were synthesized from components. The initial elements had purity: Ag-99.999%, selenium has the mark "B5". The double-walled ampoules from high-quality quartz were used as reactor. The internal diameter of ampoule is 1.5 cm and length is 10 cm. The ampoules were filled by initial components of Ag_2Se in necessary quantities, were evacuated till pressure 1.3 MPa, and further were soldered up. The quantities of initial components, necessary for synthesis are: Ag is 66.6666 at%, Se is 33.3333 at%. The ampoule with Ag_2Se was in temperature-stable band of furnace, further furnace temperature was increased till selenium melting point 493K and ampoule was kept at this temperature during two hours, for which the total reaction of selenium-argentums carries out. This prevents the ampoule explosion because of the increase of selenium steams at temperature increase. After that the furnace temperature was increased with velocity 50K/hour higher, than melting point 1170K of Ag_2Se. After 4-hour keep at this temperature the furnace with velocity 50K/hour was cooled till 350K and the annealing for total homogenization of composition was carried out at this temperature during 200 hours. After that the component excesses, and also separate formations were absent at ampoule inspection.

3. The roentgen-phase analysis

The roentgen-phase analysis was carried out for establishment of the fact that obtained ingot is one-phase. The powder, which was filled in glass capillary with internal diameter ~0,8 mm and extrusion of it from capillary by wire of diameter 0,7 mm was prepared from synthesized composition, the pressed samples in the form of wire were obtained. The powdergrams in camera RKD-57.3 on CuK_α radiation were taken from such samples. The calculation results of powdergrams are given in the table 1. The interplanar spacings, calculated from diffraction data, and also interplanar spacings with corresponding indexes *hkl*, calculated on computer on lattice parameters are given in this table.

From table 1 it is seen that experimental interplanar spacings $d_{exp.}$ well coordinate with interplanar spacings $d_{calc.}$, calculated with the help of computer on parameters of elementary cell, given in papers [14,18]. As all experimentally fixed diffraction lines are well indicated by both structural models, i.e. $P222_1$ and $P2_12_12_1$, then further we will use structural model $P222_1$.

4. The growth of monocrystals of Ag_2Se

The monocrystals of Ag_2Se are grown by gas-transport reaction or sublimation method. The monocrystals of Ag_2Se, grown by sublimation method, were big enough and well faceted (see fig.2). The powder of synthesized sample was filled in quartz ampoule and ampoules, evacuated till pressure 10^{-3}Pa, were put in central part of horizontal furnace. The crystallization temperature was below the melting point, and process duration was 70 hours.

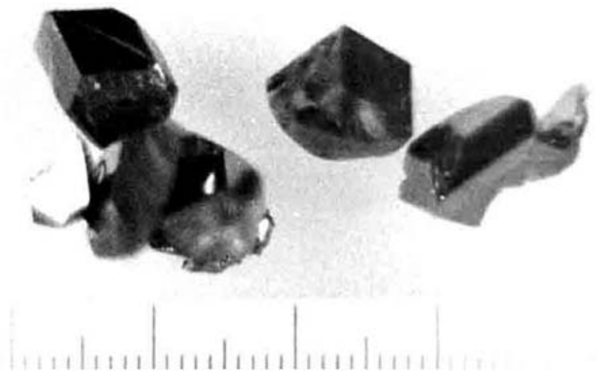

Fig. 2. The monocrystals of low-temperature modification α-Ag_2Se with facets of high-temperature OCC modification.

Note that temperature, at which crystal growth takes place at growing of monocrystals by sublimation method or gas-transport reaction, is higher than temperature of polymorphic transformation. That's why usually crystals of high-temperature OCC modification, i.e. β-Ag_2Se grow. Only at cooling below equilibrium temperature the monocrystals of high-temperature modification transform into low-temperature α-Ag_2Se. The monocrystals of Ag_2Se, which are illustrated on the fig.2, are low-temperature modifications, accepted of external habit of OCC modification.

5. The polymorphic transformations in Ag_2Se

The monocrystals α-Ag_2Se by dimension 5x3x1mm were set up on holder of plane samples of diffractometer. The seven clear diffraction reflections, the calculations of which are given in the table 2 were written at room temperature in interval of angles $10^0 \leq 2\theta \leq 90^0$. After record of diffraction reflections at room temperature the furnace was taken on and the record at 323K, 373K and 393K was carried out. Note that the change in line numbers and intensities at these temperatures doesn't take place. Continuing sample heating till 433K, in previous interval of angles of reflection the only three diffraction reflections on planes (200), (211) and (220) of high-temperature OCC modification was fixed (table 2). The repeated record was carried out at room temperature after sample cooling. It was established, that orientation of α- and β-crystal at tenfold cycle of transformations hadn't changed, i.e. α-crystal "remembers" its initial orientation, and β-crystal "remembers" its one. Naturally, the question arises, where information on orientation memory of α-crystal in β and vice versa, β-crystal in α at mutual transformation $\alpha\rightleftharpoons\beta$ is saved. Logically the one variant is possible: the potential germ of α-crystal after the transition in β-crystal and vice versa, saving on defect place can be “remembering” element.

The gauge for finding of equilibrium temperature between α- and β-modifications in Ag_2Se was set up on intensity maximum of the one of more intensive and structurally-sensitive diffraction reflections ($2\theta=36^0 44'$) from plane (130) of low-temperature α-Ag_2Se, which disappears after total transformation $\alpha\rightarrow\beta$. Beginning from 393K the crystal was heated with velocity 2K/hour. Observing the beginning of intensity slump (at heating) or reversible reconstruction (at cooling), it was established, that equilibrium temperature between α- and β-modifications is equal to Ttr=406±1K. The parameter of elementary cell of high-temperature modification of Ag_2Se is calculated from diffraction record of angles of refractions from planes (200), (211) and (220) at temperatures 433K, 473K and 523K. The calculation of lattice parameters and microdensity of α- and β-modifications in the dependence on temperature, which are graphically illustrated on the fig.3 are given in table 2.

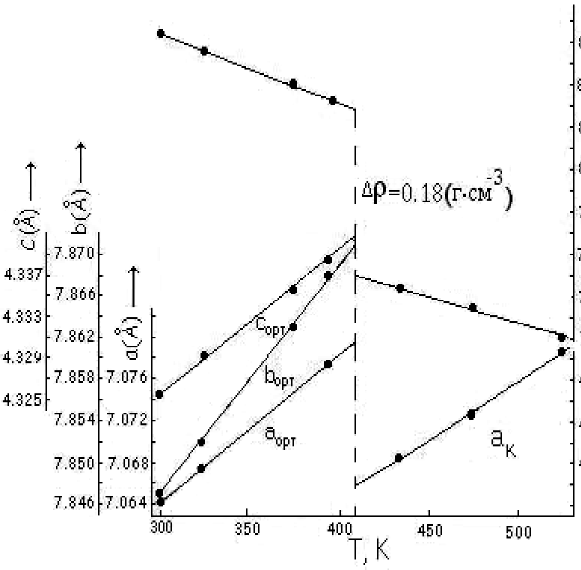

Fig.3. The temperature dependence of lattice parameters and of α- and β-modifications density of Ag_2Se.

As it is seen from fig.3 at $\alpha\rightarrow\beta$ transformation the microdensity changes by jump, i.e. $\Delta\rho=\rho_\alpha-\rho_\beta=0.18\ g\times cm^{-3}$. This density difference of α- and β-modifications increases the elastic voltages on the boundary of two modifications. At α↔β transformation the sample monocrystallinity remains and even becomes better for 4-times transformation. The monocrystallinity strongly worsens at further increase of transformation multiplicity because of the stress accumulations and defects. The thermal expansion of low-temperature orthorhombic and high-temperature OCC modifications of Ag_2Se is calculated from temperature dependence of lattice parameters. The values of coefficients of thermal expansion are given in the table 3.

As it seen from the table, the coefficient of thermal expansion of orthorhombic modification Ag_2Se slowly increases at temperature increase in direction [100] and [010], and decreases in direction [001]. The anisotropic expansion of orthorhombic modification in the dependence on temperature is the one of the transformation reasons of this modification in OCC modification.

6. The connection of thermodynamic polymorphic modifications

It is known, that the polymorphic modification of substance, which has the free Gibbs minimum energy is the most stable at given thermodynamic conditions (temperature and pressure). If their free energies are equal, then these modifications are in equilibrium state with each other:

$$G_1(T,P)=G_2(T,P).$$

One can ignore the energy change because of the volume change and the equality of Helmholtz free energies becomes the equilibrium condition:

$$F_1(T)=F_2(T),\ E_1 - TS_1=E_2 - TS_2,\ \Delta E - T\Delta S=0,$$

where E is internal energy, S is crystal entropy. The polymorphic modification with lesser internal energy is stable at absolute zero of temperature. The modification with more high entropy can become more stable at increase of modification temperature. This will take place at transformation temperature T_{tr}, when $\Delta E=(E_2 - E_1)_{tr}=T_{tr}(S_2 - S_1)=T_{trtr}$. From here it is followed, that values ΔS and ΔE are positive ones for the all transformations, which take place at T increase. By other words, the polymorphic transformations at temperature increase should be accompanied by heat absorption in the correspondence with Le-Shatelye principle. This means, that structural reconstruction carries out by such way, that new-formed structure assumes atom heat oscillations with bigger energy at lesser bond voltages. This takes place at the increase of crystal volume and often is accompanied by decrease of coordination number.

Phase transformation of I type takes place: a) at strongly defined temperature T_{tr}, b) with transformation change of first derivatives of free energy, enthalpy, entropy, volume (heat capacity). The transformations on Le-Shatelye principle should be accompanied by increase of enthalpy or system internal energy, i.e. $H_\beta - H = \Delta H$, $C_{p(\beta)} - C_{p(\alpha)}=\Delta C_p$ and $S_\beta - S_\alpha=\Delta S$.

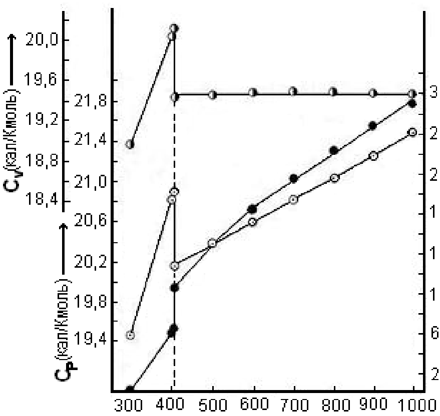

Fig.4. The temperature dependence of heat capacity of C_p and C_v entropies in temperature interval, capturing the polymorphic transformation α=β in Ag_2Se. ⊙ is C_p, ◑ is C_v and ● is entropy.

The heat capacity at constant pressure C_p, enthalpy $H(T) - H(298K)$, entropy $S(T) - S(298K)$ and free Gibbs energy $G(T) - G(298K)/T$ in temperature interval 298K-1000K, which captures the temperatures of polymorphic transformations in Ag_2Se are given in [28]. Using Nernst empiric formula $C_p = C_p + 0.0214 C_p^2 \frac{T}{T_{melt}}$ from data C_p in temperature interval 298-1000K, we calculate heat capacity C_v and (C_p, C_v) cal/mol·K and ΔS cal/mol·K, which endure the jumps at transformation temperature, are graphically given on the fig.4. The enthalpy jump is equal to $H(T)–H(298K)$=1681 cal.mol^{-1} at temperature of polymorphic transformation, and entropy jump is equal to $S_\beta - S_\alpha$= =4.14 cal.mol^{-1}K^{-1}. It is known, that polymorphic transformations take place, if $\Delta G=0$ and then $\Delta H_T - T_{tr}\Delta S_T=0$. The transformation temperature at these conditions are equal to $T_{tr} = \frac{\Delta H_T}{\Delta S_T} = \frac{1681}{4/14}$ = 406K. In [29-32] authors obtained the enthalpy and entropy values of polymorphic transformations in Ag_2Se, which are equal to $\Delta H^{tr.}_{406K} = 1.68 ccal \cdot mol^{-1}$ and $\Delta S^{tr}_{406K} = 4.14 cal \cdot mol^{-1} K^{-1}$ by different methods.

The structural and thermodynamic data prove that polymorphic transformations in Ag_2Se are related to phase transformations of first type. The transformation of orthorhombic modification in OCC modification is accompanied by jump change of internal energy, entropy and phase volume (density). This is well shown on the fig.3,4.

Table 1.

The calculation of Ag_2Se powdergram.
Rad. CuK$_\alpha$ (λ_α = 1.5418 Å), filter is Ni. The mode: 35 kV, 8 mA, exposition 24h.

№	$d_{exp.}$ (Å)	I/I_0	On data [14]		On data [18]		Parameters of crystal lattice
			$d_{calc.}(X)$	*hkl*	$d_{calc.}(X)$	*hkl*	
1	3.786	10	3.7915	011	3.7836	101	Orthorhombic [14] a=7,05 Å, b=7,85 Å c=4,33 Å, Z=4Ag_2Se, sp.gr. D_2^2 -P222$_1$ Orthorhombic [18] a=4,333 Å b=7,062 Å c=7,764 Å Z=4Ag_2Se sp.gr. D_2^4 -P2$_1$2$_1$2$_1$
2	3.338	10	3,3392	111	3.3351	111	
3	2.734	10	2.7337	201	2.7372	120	
4	2.679	100	2.6883	121	2.6158	112	
5	2.622	4	2.6226	220	2.6121	022	
6	2.580	10	2.5816	211	2.5815	121	
7	2.453	20	2.4531	130	2.4300	013	
8	2.238	60	2.2395	031	2.2370	122	
9	2.110	20	2.1011	230	2.1194	113	
10	2.085	60	2.0871	012	2.0874	023	
11	2.070	20	2.0695	102	2.0712	210	
12	2.001	40	2.0012	112	2.0012	211	
13	1.956	10	1.9625	040	1.9410	004	
14	1.890	20	1.8903	231	1.8918	202	
15	1.825	10	1.8278	321	1.8255	132	
16	1.720	10	1.7197	410	1.7216	041	
17	1.670	20	1.6696	222	1.6676	222	
18	1.609	10	1.6078	420	1.6071	042	
19	1.569	10	1.5700	050, 312	1.5615	231	
20	1.504	10	1.5063	340	1.5032	223	
21	1.474	20	1.4755	322	1.4746	232	
22	1.440	10	1.4447	151	1.4457	204	
23	1.413	20	1.4100	500	1.4150	310	
24	1.392	10	1.3916	113	1.3921	311	
25	1.354	10	1.3545	023	1.3573	233, 125	
26	1.324	10	1.3216	511	1.3232	151, 321	
27	1.311	10	1.3113	440, 060	1.3060	044	
28	1.282	20	1.2864	160	1.2907	242	
29	1.240	10	1.2413	530	1.2416	313, 053	
30	1.211	10	1.2115	432	1.2099	243	
31	1.192	10	1.1932	531, 233	1,1920	153, 225	
32	1.172	10	1.1723	450, 512	1.1735	332, 126	
33	1.143	10	1.1431	360	1.1434	314, 054	
34	1.122	10	1.1223	611	1.1239	161,244	
35	1.097	10	1.0894	621, 243	1,0974	216, 136	
36	1.075	10	1.0741	423	1,0745	107	
37	1.059	10	1.0602	114	1.0597	226	
38	1.043	10	1.0435	024	1.0434	402	
39	1.012	10	1.0122	542	1.0121	325	
40	1.001	10	1.0004	513, 034	1.0004	422, 071	
41	0.972	10	0.9706	443	0.9748	171, 344	

Table 2.

The calculation of Ag_2Se diffractogram.
Rad.CuK_α (λ_α=1.5418 Å), filter is Ni. The mode: 35kV, 8mA.

$T_{exp.}$, K	θ	I/I_0	$d_{exp.}$, (Å)	$d_{calc.}$, (Å)	hkl	Lattice Parameters
299	$17^0 06'$	40	2.6212	2.6212	220	Orthorhombic a=7,0645 Å b=7,8470 Å, c=4,3254Å Z=4, sp.gr. D_2^2 -P222$_1$ V=239.7791Å^3 ρ=8.1614 g/cm^3
	$18^0 22'$	20	2.4465	2.4531	130	
	$21^0 42'$	60	2.0852	2.0871	012	
	$24^0 03'$	20	1.8918	1.8906	140	
	$26^0 35'$	10	1.7227	1.7197	410	
	$29^0 25'$	10	1.5694	1.5700	050	
	$33^0 04'$	20	1.4129	1.4100	500	
323	$17^0 04'$	40	2.6266	2.6270	220	a=7,0645 Å b=7,852 Å c=4,3295Å Z=4, sp.gr. D_2^2 -P222$_1$ V=240.2613Å^3 ρ=8.145 g/cm^3
	$18^0 20'$	20	2.4512	2.4544	130	
	$21^0 41'$	60	2.0869	2.0874	012	
	$24^0 01'$	20	1.8941	1.8915	140	
	$26^0 33'$	10	1.7246	1.7239	410	
	$29^0 24'$	10	1.5704	1.5704	050	
	$33^0 03'$	20	1.4135	14135	500	
373	$17^0 02'$	40	2.6320	2.6298	220	A=7,0740 Å b=7,8630 Å c=4,3355Å Z=4, sp.gr. D_2^2 -P222$_1$ V=241.1529Å^3 ρ=8.115 g/cm^3
	$18^0 19'$	20	2.4528	2.4574	130	
	$21^0 39'$	60	2.0897	2.0897	012	
	$24^0 00'$	20	1.8955	1.8939	140	
	$26^0 31'$	10	1.7265	1.7254	410	
	$29^0 21'$	10	1.5726	1.5726	050	
	$33^0 01'$	20	1.4148	1.4148	500	
393	$17^0 00'$	40	2.6365	2.6307	220	a=7,0775 Å b=7,8680 Å c=4,3386Å V=241.5983Å^3 ρ=8.100 g/cm^3
	$18^0 17'$	20	2.4574	2.4589	130	
	$21^0 38'$	60	2.0909	2.0911	012	
	$23^0 59'$	20	1.8964	1.8949	140	
	$26^0 30'$	10	1.7277	1.7262	410	
	$29^0 20'$	10	1.5736	1.5736	050	
	$33^0 00'$	20	1.4155	1.4155	500	
433	$18^0 02'$	100	2.4900	2.4905	200	OCC, a=4,9809Å Z=2, sp.gr.Fm3m V=123.573Å^3, ρ=7.918g/cm^3
	$22^0 17'$	60	2.0330	2.0334	211	
	$25^0 57'$	80	1.7617	1.7610	220	
473	$18^0 01'$	100	2.4924	2.4923	200	A=4,9846Å Z=2 V=123.8486Å^3,ρ=7.901g/cm^3
	$22^0 15'$	60	2.0356	2.0349	211	
	$25^0 55'$	80	1.7629	1.7623	220	
523	$18^0 00'$	100	2.4948	2.4953	200	A=4,9906Å Z=2 V=124.2963Å^3,ρ=7.872g/cm^3
	$22^0 14'$	60	2.0373	2.0374	211	
	$25^0 54'$	80	1.7649	1.7645	220	

Table 3.

The heat expansion of orthorhombic and OCC modification of Ag_2Se.

Temperature, K	$\alpha_{[100]}10^{-6}K^{-1}$	$\alpha_{[100]}10^{-6}K^{-1}$	$\alpha_{[100]}10^{-6}K^{-1}$	$\overline{\alpha} = \frac{\alpha_{[100]} + \alpha_{[010]} + \alpha_{[001]}}{3} \times 10^{-6} \times K^{-1}$
299-323	17.69	26.55	39.50	27.91
299-373	18.17	27.55	31.55	25.76
299-393	19.58	28.47	32.47	26.84
433-473	26.57			26.57
433-523	21.64			21.64

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Ag_2Se MONOKRİSTALLARININ POLİMORF ÇEVRİLMƏLƏRİNİN QURULUŞ VƏ TERMODİNAMİK ASPEKTLƏRİ

Ag_2Se monokristalı sintez edilmiş və sublimasiya üsulu ilə monokristalı yetişdirilmişdir. Yüksək temperaturlu rentgendifraktometrik üsul ilə Ag_2Se monokristalının polimorf çevrilmələri tədqiq edilmiş və göstərilmişdur ki, Ag_2Se monokristalının aşağı temperaturlu ortorombik modifikasiyası 406 K-də yüksək temperaturlu həcməmərkəzləşmiş kubik fazaya çevrilir. Çevrilmə prosesi dönər xarakterə malik olmaqla monokristal-monokristal tip çevrilməyə aiddir. Tədqiqat nəticələrinin müzakirəsi Ag_2Se monokristalına aid termodinamik məlumatlar əsasında aparılmışdır.

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СТРУКТУРНЫЕ И ТЕРМОДИНАМИЧЕСКИЕ АСПЕКТЫ ПОЛИМОРФНЫХ ПРЕВРАЩЕНИЙ В Ag_2Se

Синтезированы и методом сублимации выращены монокристаллы Ag_2Se. Высокотемпературным рентгендифрактометрическим методом исследованы полиморфные превращения в Ag_2Se и показано, что низкотемпературная орторомбическая модификация при 406К превращается в высокотемпературную ОЦК модификацию. Превращение обратимое и происходит по типу монокристалл-монокристалл. При обсуждении результатов широко использовались существующие термодинамические данные.

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