STRUCTURAL AND THERMODYNAMIC ASPECTS OF POLYMORPHOUS TRANSFORMATIONS IN Ag_2Te

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The polymorphous transformations in crystals Ag_2Te have been investigated by high-temperature roentgen-diffractometric method. It is shown, that Ag_2Te, consisting from monoclinic modification at room temperature transfers in FCC modification at 426K. The lattice parameters of both modifications have been calculated from temperature diffractograms. The thermodynamic aspects which eased the clearing of polymorphous transformation mechanism in Ag_2Te are analyzed with help of reference data.

1. On crystal structure of α- and β- modifications Ag_2Te

The one stoichiometric compound – Ag_2Te [1], which has polymorphous transformation has been established on constitution diagram of Ag-Te system.

The different data are existed considering to crystal structure of low-temperature modification and temperature of polymorphous transformations of low-temperature modification into high-temperature modification [2-4]. In paper [2] it is shown, that low-temperature modification Ag_2Te crystallizes in monoclinic structure with parameters: a=6.57Å, b=6.14Å, c=6.10Å, β=61°15′, which transfers in cubic modification at 422K. In paper [3] the orthorhombic structure with parameters: a=16.27Å, b=26.68Å, c=7.55Å is supposed for α-Ag_2Te, atom number in elementary cell Z=48, space symmetry group is D_{2h}^{25}-Immm. In paper [4] the orthorhombic structure with parameters: a=13.0Å, b=12.7Å, c=12.2Å, which transfers at in high-temperature β-Ag_2Te at 414K is also supposed for α-Ag_2Te.

Total crystal structure α-Ag_2Te has been decoded in papers [5,6]. In paper [5] it is shown, that monoclinic structure α-Ag_2Te presents the order of modification with lattice parameters: a=8.09Å, b=4.48Å, c=8.96Å, β=123°21′, Z=4, space symmetry group is C_{2h}^{5}-$P2_1/c$. All atoms orderly have general four-times positions: *4(e)±(xyz; ½-y; z+½)*. Atom positions and atomic spacings in α-Ag_2Te are given in table 1 and 2.

Table 1

Atom positions in Ag_2Te (in Å)

Atoms	Coordinates		
	x	*y*	*z*
Ag (I)	0,018	0,152	0,371
Ag(II)	0,332	0,837	0,995
Te	0,272	0,159	0,243

Table 2

Atomic spacings in Ag_2Te

Atom	Te	Te	Te	Te
Ag(I)	2.87	2.91	3.04	2.99
Ag(II)	3.04	3.01	2.05	2.90

In paper [6] it is shown, that α-Ag_2Te crystallizes in monoclinic structure with lattice parameters: a=8.13Å, b=4.48Å, c=8.09Å, β=112°55′, Z=4, space symmetry group is $P2_1/n$ and ρ_x=8.402 g/cm^3.

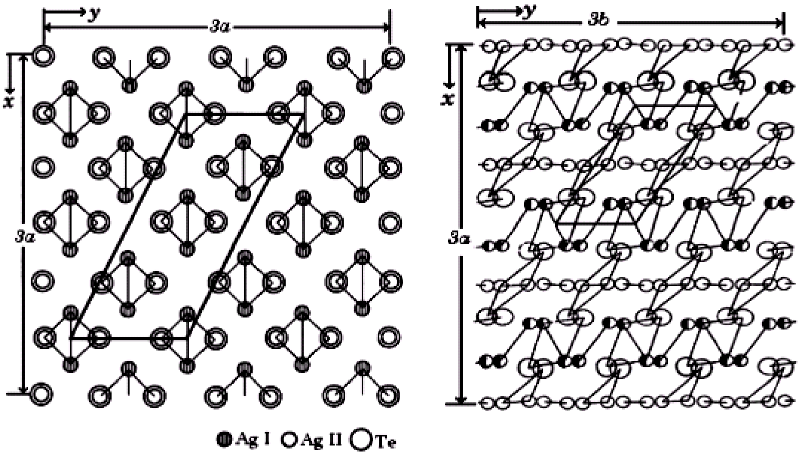

Fig.1. (a) - The structure projection of monoclinic modification on plane (001), the emphasized cell is given by bold lines.
(b) - The projection of second variant of structure.

The projection of first variant of monoclinic modifications Ag_2Te on plane (001) is presented on fig. 1(a). In paper [7] the above mentioned structure is proved in thin-film sample α-Ag_2Te by electron-graphical method. Besides, in paper [8]it is said, that monoclinic α-modification transform high-temperature FCC modification through intermediate tetragonal modification with lattice parameters a=10.4Å and c=6.7Å.

In paper [9] it is defined, that high-temperature modification β-Ag_2Te crystallizes in face-centered cubic lattice with parameters, a=6.585Å and elementary cell consists Z=4, space symmetry group is T^2-F23 from powdergram, taken off at 443K. The structure similarity, supposed in paper [9] and structural model, supposed by authors [10] through 32 years, is revealed in situation of four Te atoms on face-centered cubic lattice points and in preferably in disordered location of Ag atoms. However, 4Ag(I)take up 4 tetrahedral blank spaces from 8ones, 2Ag(II) with probability in 50% of octahedral blank spaces take up and rest 2Ag (II) situate disorderedly on two situations: 16(e) xxx at x=2/3 and 1/3, in model, supposed in paper [9]. The projection of second variant of α-Ag_2Te structure on (001) plane is presented on fig.1(b).

Thus, Ag atoms in first variant of structure are distributed on five crystal-graphical positions of summation multiplicity response ratio, which is equal to 40. 6,5Ag (I) situate on 8 tetrahedral blank spaces and 1,5Ag (II) situate on 4 tetrahedral ones, statistically taking up 12 positions in model, presented in paper [10].

The contradictory data about temperature of structural transformations in Ag_2Te crystal are given in references; $T_{ch.}$=414-422K in paper [1,2-4], $T_{ch.}$=419K in paper [8], $T_{ch.}$=378K in paper [11] and $T_{ch.}$=421K in paper [12].

The given paper is dedicated to structural and thermodynamic aspects of polymorphous transformations in Ag_2Te monocrystal.

2. The synthesis and growth of Ag_2Te monocrystals

The argentums-99.999 and tellurium (T-B4) were used for Ag_2Te synthesis. The initial components were mechanically crushed till small particles, and ampoules with corresponding composition were put into stove, the temperature of which increased till tellurium melting-point (T_m=725K). At this temperature the ampoules were stand during two hours, for which the total reaction of argentums with tellurium took place. This prevents the ampoule explosion because of the increase of tellurium steam pressure at temperature increase. Further, the stove temperature was increased with velocity 50k/h till the temperature, which was higher, than Ag_2Te melting-point (T_m=1232K). The stove with velocity 50k/h was cooled till 350K after four-hour endurance at this temperature and ampoules during 200 hours were treated by the annealing for total composition homogenization at this temperature. Later, the component surpluses, and also separate creations in them were absent at ampoule inspection at room temperature. The samples in powder form were prepared for definition of phase compositions from ingot. The powder was filled into glass capillary with internal diameter 0.8mm and its extrusion from capillary with the wire of 0.7mm diameter and pressed samples in wire form were obtained. The powdergrams in RKD-57.3 camera on CuK_α radiation were taken from such samples. The calculation results of obtained powdergrams are given in table 3. The interplanar spacings, calculated from diffraction data, and also interplanar spacings with corresponding indexes hkl, calculated on computer on structure data Ag_2Te, are given in the table. The comparison of interplanar spacings ($d_{ex.}$) with data, calculated on computer ($d_{calc..}$) shows that powdergrams Ag_2Te are totally indexing with help of Ag_2Te lattice parameters.

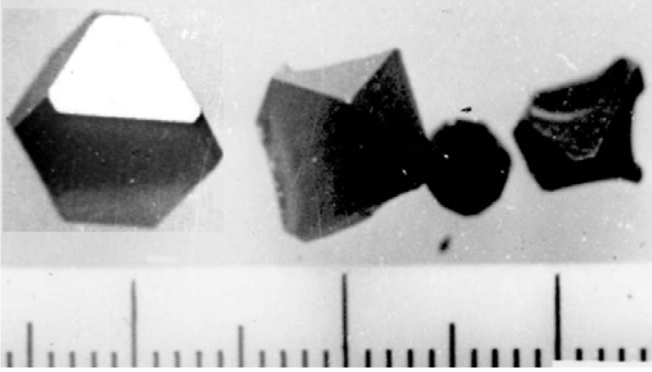

Fig.2. Ag_2Te monocrystals, grown up by method of gas-transport reaction.

The diffusion variant of gas-transport method has been chosen for obtaining of Ag_2Te monocrystals; moreover the iodine is used in the capacity of carrier. The synthesized samples Ag_2Te were put into ampoules from high-quality quartz tubes by length 20 cm and internal diameter 1 cm after roentgenophase analysis. The ampoule with Ag_2Te composition (~5g) in granule form by diameter 4mm and iodine (7 mg/cm^3), applied in the capacity of conveyer, was evacuated till 1.3 MPa pressure. Further, the ampoule was put into horizontal two-region tube furnace with given temperature distribution. The ampoule was situated in the middle part of stove thus, that all initial material was on the one its end. The temperature measurement was carried out by platinum-platinum-rhodium thermocouple was carried out. The process of transfer and crystallization was lasted 10 days. The obtained volume monocrystals, as it is shown on fig.2, had average sizes 4×3×2 mm.

3. Structural aspects of polymorphic transformations in Ag_2Te

The monocrystals, grown up by method of gas-transport reaction were used for temperature-diffractometric investigations. 14 diffraction reflections, the calculation of which is given in table 4, were fixed at room temperature from crystal of arbitrary orientation with sizes 4×2×1 mm in angle interval $10^\circ \le 2\theta \le 100^\circ$.

The stove was put on and in every 20K the control notes were carried out after record of diffraction reflection at room temperature, not changing sample orientation. The temperature was supported constant during 40 minutes before each record. The changes of number and reflection intensities weren't observed in these conditions till 413K. The six new reflections, belonging to high-temperature face-centered crystal of FCC modification Ag_2Te (see table 4) is fixed.

Table 3

The calculation of powdergram Ag_2Te.
Rad. CuK_{α} (λ_{α}=1. 5418Å), filter – Ni, mode 35kV, 8 mA, exp. 24h.

N	*sinθ*	*I/I₀*	$d_{exp.}$(Å)	On data [5]		On data [6]		Parameters of crystal lattice
				$d_{calc.}$(Å)	*hkl*	$d_{calc.}$(Å)	*Hkl*	
1.	$13^{\circ}13'$	40	3.371	3.3797	$\bar{2}02$	3.3795	200	
2.	$14^{\circ}08'$	20	3.157	3.1682	111	3.1678	112	
3.	$14^{\circ}58'$	30	2.986	2.9910	$\bar{2}11,\bar{1}12$	2.9910	$\bar{2}11$	
4.	$15^{\circ}34'$	70	2.873	2.8726	210	2.8724	012	
5.	$15^{\circ}37'$	80	2.864	2.8646	012	2.8644	$\bar{2}12$	
6.	$16^{\circ}54'$	20	2.652	2.6914	$\bar{2}12,\bar{1}03$	2.6980	210	
7.	$18^{\circ}20'$	30	2.450	2.4464	211	2.4459	113	
8.	$19^{\circ}26'$	100	2.317	2.3158	$\bar{3}11$	2.3154	112	
9.	$20^{\circ}06'$	90	2.243	2.2438	$\bar{3}12$	2.2436	211, 020	
10.	$20^{\circ}40'$	40	2.184	2.1805	310	2.1800	013	
11.	$21^{\circ}04'$	70	2.144	2.1452	021	2.1452	$\bar{1}21$	
12.	$22^{\circ}31'$	40	2.021	2.0174	$\bar{4}02, \bar{2}04$	2.0170	202	
13.	$23^{\circ}35'$	20	1.927	1.9238	311	1.9233	$\bar{1}14$	
14.	$24^{\circ}48'$	10	1.838	1.8339	$\bar{1}14,411$	1.8392	212	
15.	$25^{\circ}24'$	10	1.797	1.7774	$221,\bar{1}22$	1.7772	$\bar{1}23$	Monoclinic [5] *a*=8.09Å *b*=4.48Å *c*=9.83Å $\beta=133^{\circ}46'$ *Z*=4 sp. gr. C_{2h}^{5} -$P2_1/c$
16.	$25^{\circ}50'$	50	1.769	1.7754	122	1.7757	$\bar{2}23$	
17.	$27^{\circ}24'$	50	1.675	1.6671	$\bar{4}04, 223$	1.6669	023	
18.	$28^{\circ}54'$	10	1.595	1.5930	501,222	1.5885	320	
19.	$29^{\circ}36'$	30	1.561	1.5637	411	1.5632	$\bar{1}15$	
20.	$30^{\circ}50'$	10	1.504	1.5009	511	1.5006	114	
21.	$31^{\circ}12'$	10	1.488	1.4887	315	1.4887	$\bar{5}12$	
22.	$32^{\circ}34'$	10	1.432	1.4323	024	1.4322	424	
23.	$33^{\circ}48'$	100	1.386	1.3855	214	1.3861	232	
24.	$35^{\circ}18'$	40	1.334	1.3350	124	1.3348	$\bar{4}25$	
25.	$36^{\circ}20'$	70	1.301	1.3044	$115, \bar{5}21$	1.3043	$\bar{5}16$	
26.	$36^{\circ}48'$	10	1.287	1.2830	316	1.2879	313	
27.	$37^{\circ}24'$	40	1.269	1.2638	611	1.2635	115, 033	
28.	$38^{\circ}13'$	50	1.244	1.2448	333	1.2447	330, 025	
29.	$40^{\circ}30'$	40	1.187	1.1860	215	1.1757	511	Monoclinic [6] *a*=8.09Å *b*=4.48Å *c*=8.96Å $\beta=123^{\circ}20'$ *Z*=4 sp. gr. C_{2h}^{5} -$P2_1/c$
30.	$41^{\circ}18'$	10	1.168	1.1681	521	1.1678	$\bar{1}26$	
31.	$43^{\circ}24'$	10	1.122	1.1219	624	1.1218	422	
32.	$43^{\circ}54'$	10	1.112	1.1128	431	1.1126	135	
33.	$44^{\circ}30'$	40	1.100	1.0998	532	1.0997	233	
34.	$45^{\circ}49'$	10	1.075	1.0749	513	1.0730	042	
35.	$47^{\circ}25'$	10	1.047	1.0457	241	1.0457	$\bar{1}43$	
36.	$50^{\circ}30'$	40	0.999	0.9992	532	0.9992	333	
37.	$52^{\circ}42'$	20	0.969	0.9692	334	0.9651	341	
38.	$54^{\circ}29'$	10	0.959	0.9592	226	0.9575	036, 444	
39.	$55^{\circ}12'$	30	0.939	0.9336	444	0.9385	621	
40.	$56^{\circ}10'$	10	0.928	0.9290	144	0.9288	$325,\bar{4}25$	
41.	$56^{\circ}55'$	10	0.920	0.9162	541	0.9196	424	
42.	$57^{\circ}48'$	10	0.911	0.9134	$34\bar{5}$	0.9131	235	
43.	$59^{\circ}28'$	10	0.895	0.8953	045	0.8953	545	
44.	$60^{\circ}14'$	10	0.888	0.8878	406	0.8882	$150, \bar{2}46$	
45.	$62^{\circ}39'$	10	0.868	0.8671	632	0.8706	622	
46.	$63^{\circ}58'$	10	0.858	0.8590	346	0.8501	$64\bar{3}$	
47.	$64^{\circ}14'$	10	0.856	0.8564	152	0.8564	$\bar{2}53$	
48.	$65^{\circ}59'$	30	0.844	0.8475	644	0.8484	613	
49.	$67^{\circ}24'$	10	0.835	0.8336	640	0.8358	434	

Table 4

The calculation of powdergram Ag_2Te.
Rad. CuK_α (λ_α=1. 5418Å), filter – Ni, mode 35kV, 8 mA

N	$\sin\theta$	I/I_0	$d_{exp.}$(Å)	hkl	$T_{exp.}$, K	Parameters of crystal lattice
1	2	3	4	5	6	7
1.	13°11′	40	3.3745	200	299	Monoclinic a=8.0718Å b=4.4588Å c=8.9876Å β=123°20′ Z=4 sp. gr. C_{2h}^{5} -$P2_1/c$ V=270.4520 Å^3 ρ=8.4275 g/cm^3
2.	14°08′	20	3.1568	$\bar{1}12$		
3.	14°58′	30	2.9857	$\bar{2}11$		
4.	15°34′	70	2.8759	012		
5.	18°20′	80	2.4504	$\bar{1}13$		
6.	19°26′	100	2.3171	$\bar{1}12$		
7.	20°06′	90	2.2429	211, 021		
8.	20°40′	40	2.1838	013		
9.	21°04′	70	2.1443	$\bar{1}21$		
10.	22°25′	40	2.0212	202		
11.	23°35′	20	1.9272	$\bar{1}14$		
12.	25°50′	50	1.7693	$\bar{2}23$		
13.	30°50′	10	1.5042	114		
14.	36°21′	70	1.3006	$\bar{5}16$,124		
1.	13°09′	40	3.3886	200	350	Monoclinic a=8.1055Å b=4.4659Å c=9.0065Å β=123°20′ Z=4 sp. gr. C_{2h}^{5} -$P2_1/c$ V=272.5857 Å^3 ρ=8.3616 g/cm^3
2.	14°06′	20	3.1646	$\bar{1}12$		
3.	14°56′	30	2.9915	$\bar{2}11$		
4.	15°32′	70	2.8786	012		
5.	18°17′	80	2.4574	$\bar{1}13$		
6.	19°24′	100	2.3206	$\bar{1}12$		
7.	20°04′	90	2.2462	211, 021		
8.	20°38′	40	2.1882	013		
9.	21°02′	70	2.1480	$\bar{1}21$		
10.	22°23′	40	2.0244	202		
11.	23°33′	20	1.9297	$\bar{1}14$		
12.	25°48′	50	1.7714	$\bar{2}23$		
13.	30°48′	10	1.5057	114		
14.	36°19′	70	1.3018	$\bar{5}16$,124		
1.	13°07′	40	3.3960	200	400	Monoclinic a=8.1232Å b=4.4753Å c=9.0275Å β=123°20′ Z=4 sp. gr. C_{2h}^{5} -$P2_1/c$ V=274.3943 Å^3 ρ=8.3065 g/cm^3
2.	14°03′	20	3.1763	$\bar{1}12$		
3.	14°53′	30	3.0019	$\bar{2}11$		
4.	15°30′	70	2.8851	012		
5.	18°15′	80	2.4622	$\bar{1}13$		
6.	19°21′	100	2.3269	$\bar{1}12$		
7.	20°02′	90	2.2508	211, 021		
8.	20°35′	40	2.1932	013		
9.	21°00′	70	2.1509	$\bar{1}21$		
10.	22°20′	40	2.0287	202		
11.	23°30′	20	1.9335	$\bar{1}14$		
12.	25°45′	50	1.7742	$\bar{2}23$		
13.	30°45′	10	1.5077	114		
14.	36°16′	70	1.3033	$\bar{5}16$,124		
1	2	3	4	5	6	7
1.	13°06′	40	3.4005	200	418	Monoclinic a=8.1340Å b=4.4757Å c=9.0440Å Z=4 sp. gr. C_{2h}^{5} -$P2_1/c$ V=275.2359 Å^3 ρ=8.2796 g/cm^3
2.	14°02′	20	3.1790	$\bar{1}12$		
3.	14°51′	30	3.0090	$\bar{2}11$		
4.	15°29′	70	2.8883	012		
5.	18°13′	80	2.4661	$\bar{1}13$		
6.	19°20′	100	2.3290	$\bar{1}12$		
7.	20°00′	90	2.2541	211, 021		
8.	20°33′	40	2.1963	013		
9.	21°59′	70	2.1528	$\bar{1}21$		
10.	22°18′	40	2.0314	202		
11.	23°29′	20	1.9350	$\bar{1}14$		
12.	25°43′	50	1.7763	$\bar{2}23$		
13.	30°44′	10	1.5086	114		

14.	36°15′	70	1.3037	$\bar{5}16,124$		
1.	11°42′	60	3.8013	111	450	FCC a=6.5839Å, sp. gr. T^2-F23 V=285.3972$Å^3$, ρ=7.9862 g/cm^3 Z=4
2.	19°21′	100	2.3269	220		
3.	22°51′	80	1.9852	311		
4.	27°55′	50	1.6465	400		
5.	30°42′	30	1.5101	331		
6.	31°34′	20	1.4726	420		
1.	11°41′	60	3.8069	111	500	FCC a=6.5922Å, sp. gr. T^2-F23 V=286.4779$Å^3$, ρ=7.9561 g/cm^3 Z=4
2.	19°19′	100	2.3307	220		
3.	22°49′	80	1.9879	311		
4.	27°53′	50	1.6486	400		
5.	30°40′	30	1.5116	331		
6.	31°32′	20	1.4740	420		
1.	11°40′	60	3.8126	111	550	FCC a=6.6023 Å, sp. gr. T^2-F23 V=287.7967$Å^3$, ρ=7.9196 г/$см^3$ Z=4
2.	19°17′	100	2.3346	220		
3.	22°46′	80	1.9920	311		
4.	27°51′	50	1.6504	400		
5.	30°37′	30	1.5137	331		
6.	31°29′	20	1.4760	420		

The Ag_2Te diffractometer counter for definition of equilibrium temperature between α- and β-modifications was established on intensity maximum of diffraction reflection (2θ=31°08′) from plane with indexes (012), which after total $\alpha\rightarrow\beta$ transformation disappears. Beginning with 418K, the crystals of low-temperature α-Ag_2Te were heated with velocity 2 k/h and very slow decay of reflection intensity from plane (012) was began at temperature 426K. This is the sign of $\alpha\rightarrow\beta$ transformation beginning. Thus, such temperature point, at which the intensity decay is stopped and both modifications exist long time indefinably, is found. This method revealed, that equilibrium temperature between α- and β-modifications of Ag_2Te is equal to 426±1K.

It is need to note, that crystal returns in previous orientation at multiple $\alpha\rightleftharpoons\beta$ transformation, i.e. the structure memory exist. Naturally the question: "Where the information about orientation memory of α-crystal in β- and vice versa of β-crystal in α- at mutual $\alpha\rightleftharpoons\beta$ transformation is saved?", rises. Logically the one variant is possible: the potential germ of α-crystal after transition in β-crystal, saved in defect place and vice versa, can be "storage" element.

The volume of elementary cell increases on ΔV=10.11 $Å^3$ at transformation of monoclinic modification Ag_2Te in face-centered crystal modification and density decreases on $\Delta\rho$=0.293 g/cm^3 correspondingly and this is the main reason of transformation of monocrystal into polycrystal.

The parameters of monoclinic lattice were calculated from diffraction record of reflection angles, given in table 4 from Ag_2Te crystal at 299, 350, 400, 418K, and lattice parameters of face-centered cubic modification were calculated from diffraction record at 450, 500 and 550K (see fig. 3).

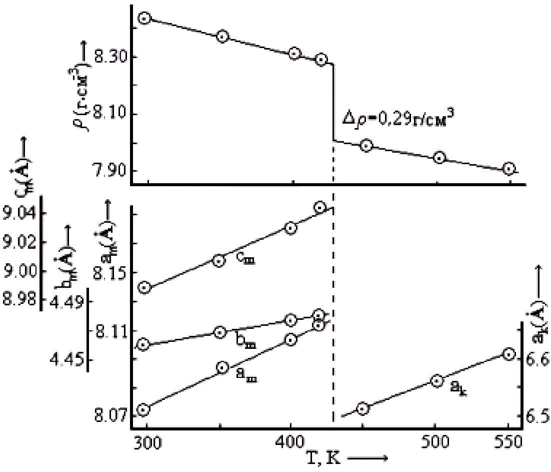

Fig.3. The temperature dependence of parameters of elementary cell and micro-density of α- and β-modifications Ag_2Te.

As it is seen from fig.3 the lattice parameters a, b, c of monoclinic modification and parameter a of face-centered cubic one in dependence on temperature increase linearly. The thermal expansion coefficients of monoclinic modification, which are presented in table 5 have been calculated from temperature dependence of lattice parameters.

Table 5

Thermal expansion coefficients of monoclinic modification Ag_2Te.

Temperature, K	$\alpha_{(100)}10^{-6}K^{-1}$	$\alpha_{(100)}10^{-6}K^{-1}$	$\alpha_{(100)}10^{-6}K^{-1}$	$\bar{\alpha}=\frac{\alpha_{(100)}+\alpha_{(010)}+\alpha_{(001)}}{3}\times10^{-6}*K^{-1}$
299-350	81.86	31.22	41.23	51.44
350-400	43.67	42.10	46.63	44.13
400-418	73.86	73.86	101.54	60.12

The strong anisotropy of thermal expansion is the one of polymorphism reasons in Ag_2Te. The average value of linear expansion coefficient of high-temperature face-centered cubic modification is α=27.93×10^{-6}K^{-1}. The positive jumps of atom volume are carried out at formation of high-temperature face-centered cubic modification.

4. Thermodynamic aspects of polymorphic transformations in Ag_2Te

It is known, that the initial chemical composition doesn't change at polymorphic transformation. The change takes place in crystal structure of modifications, i.e. at polymorphic transformation the matrix crystal structure destructions, where the destruction begins, there the crystal germ of new modification forms.

Each modification is stable at definite thermodynamic conditions (temperature, pressure). Under this conditions of stability any crystal with stable chemical composition has minimum of Gibbs free energy G: $G=H-TS$, where H is enthalpy, S is crystal entropy. The polymorphic transformations are always accompanied by heat effects. That's why $\Delta S=Q/T$ (Q is heat, obtained by crystal at reversible transformation).

As it is seen in [1], the argentums with tellurium creates the one stoichiometric compound Ag_2Te, which melts at T_m=1232 K. The data, obtained by different authors for heat of formation ΔH^0_{298} Kcal/mol, Gibbs free energy ΔG Kcal/mol, formation entropy ΔS^0_{298} Kcal/mol and standard entropy S^0_{298} Kcal/mol are given in table 6.

Table 6

Compound	$-\Delta H^0_{298}$	ΔG^0_{298}	ΔS^0_{298}	S^0_{298}	Investigation temperature	Authors
Ag_2Te	11.4	12.6	2.8	35.0	320-420	Abbasov A.S. at all[13]
	8.4	9.0	5.0	36.3	-	H. Reinhold [14]
	7.0	8.3	-	35.512	265	Walsh P., Art E. [15]
	-	-	3.26	-	-	Gerasimov Y.I. at all[16]
	7.7	-	-	-	-	Laffite C., Claire [17]
	8.01	-	-	-	-	Vecher A.A., Merkovskii L.A. [18]
	7.0	8.3	-	-	-	Kubachewski O., Ewanc [19]
	8.65	10	-	-	-	Kiukkola K., Wagner C. [20]
	8.3	-	-	36.3	-	Mills K.C. [21]
	8.6	-	-	-	-	Pool M. [22]
	-	-	-	38.1	-	Gultyayev P.V., Petrov A.I. [23]

The results of thermodynamic papers, dedicated to formation of low-temperature monoclinic modification Ag_2Te are summed up in table 6. The C_p heat capacity at constant pressure, H(T)-H(298) enthalpy, the S(T)-S(298) entropy and Gibb's free energy [G(T)-H(298)]/T in temperature interval 298-800K, covering the temperatures of polymorphic transformations in Ag_2Te are given in paper [24]. The graph of temperature dependence C_p, where C_p strongly increases in monoclinic structure and at temperature transformations $\alpha\rightarrow\beta$ 426K strongly decrease ΔC_p=2.34cal/(K·mol)is presented on fig. (4b). The heat capacity value C_p continues to decrease till temperature 550K and till temperature 800K stays constant after transformation temperature. The strong increase of C_p is connected with redistribution of Ag cations in monoclinic structure Ag_2Te till transformation temperature of monoclinic modification in face-centered cubic one .

The heat capacity C_v is calculated from data C_p in temperature interval 298-800K, using Nernst empirical formula $C_p=C_v+0.0214C_p^2\frac{T}{T_{пл}}$ and it is presented graphically on fig.4(a), and entropy S(T)-S(298) is presented on the fig.4(c). As it is seen from the fig.4(c), the crystal entropy endures jumps at transformation temperature, i.e. at 426K ΔS=3.74cal/(K·mol)..

The thermal expansion coefficients, which are graphically presented on the fig.5, have been calculated, using isochoric and isobaric heat capacities from formula Magnus-Lindeman $C_p=C_v+\alpha T^{3/2}$.

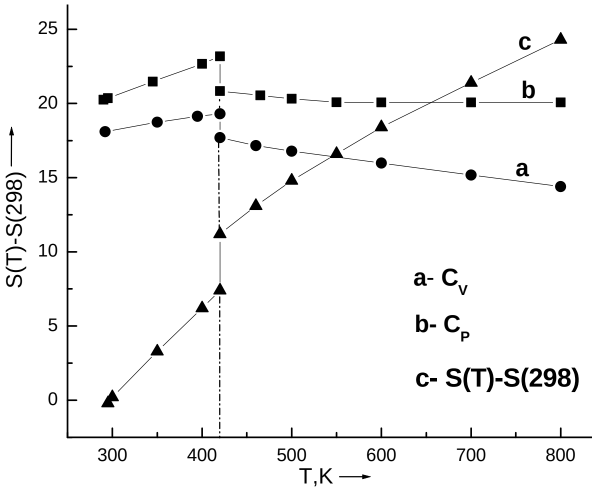

Fig.4. The temperature dependence of specific heat capacity $C_v(T)$ (a), $C_p(T)$ (b) and entropy S(T)-S(298) (c) in Ag_2Te.

From structural above mentioned and thermodynamic aspect it is clear, that reason and mechanism of polymorphic transformation in Ag_2Te.

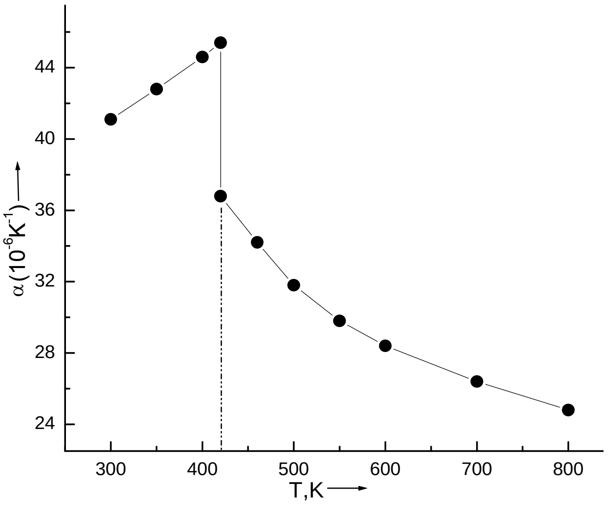

Fig.5. The dependence of thermal expansion coefficient α on temperature for Ag_2Te.

The similarity of structure models of high-temperature β-Ag_2Te, supposed in papers [9, 10], reveals in location of four Te atoms on of face-centered cubic lattice points and, preferably, it reveals in disordered location of Ag atoms. According to paper [10], in face-centered cubic lattice 6.5Ag(I) situate on 8 tetrahedral blank spaces and 1.5Ag(II) situate on 4 octahedral blank spaces, statistically taking 12 positions correspondingly. Authors of paper [24], analyzing in detail the crystal-chemical data of high-temperature β-Ag_2Te, preferred the structural model, supposed in paper [9]. According model [9] 4Ag(I) take up 4 from 8 tetrahedral blank spaces, 2Ag(II) take up octahedral blank spaces with probability 50%, and rest 2Ag(III) situate disorderly on two positions 16(*e*) (*xxx*) at x=2/3 and 1/3.

Thus, Ag^+ cations in β-Ag_2Te structure are distributed on 5 crystal-graphical positions by summation multiplicity ratio, which is equal to 40. This disordered FCC modification Ag_2Te, as it was mentioned above, transforms at 426K in monoclinic one, where all atoms take ordered general four-multiple positions.

In conclusion let's note, that Laue photographs, taken from α and β modifications at multiple transformation $\alpha \rightleftharpoons \beta$ in Ag_2Te showed, that transformations are carried out by type monocrystal-monocrystal.

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Ag_2Te MONOKRİSTALINDA POLİMORF ÇEVRİLMƏLƏRİN STRUKTUR VƏ TERMODİNAMİK ASPEKTLƏRİ

Yüksək temperaturlu rentgen-difraktometrik metodla Ag_2Te monokristalında polimorf çevrilmələr tədqiq edilmişdir. Göstərilmişdir ki, otaq temperaturunda monoklin modifikasiyadan ibarət olan Ag_2Te, 426K temperaturda SMK modifikasiyasına keçir. Temperatur difraktoqramlarından hər iki modifikasiyanın qəfəs parametrləri hesablanmışdır. Ədəbiyyat məlumatları əsasında termodinamik aspektlərin təhlil edilməsi, Ag_2Te-dakı polimorf çevrilmələrin mexanizmini izah etməyə imkan vermişdir.

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СТРУКТУРНЫЕ И ТЕРМОДИНАМИЧЕСКИЕ АСПЕКТЫ ПОЛИМОРФНЫХ ПРЕВРАЩЕНИЙ В Ag_2Te

Высокотемпературным рентгендифрактометрическим методом исследованы полиморфные превращения в монокристаллах Ag_2Te. Показано, что при комнатной температуре Ag_2Te, состоящий из моноклинной модификации, при 426К превращается в ГЦК модификацию. Из температурных дифрактограмм рассчитаны параметры решетки обеих модификаций. Используя литературные данные, подробно проанализированы термодинамические аспекты, которые облегчили выяснение механизма полиморфных превращений в Ag_2Te.

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