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Character of the interaction in the As_2Te_3-TlSe System and Electrophysical Propertes of the Phases Obtained

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Abstract

The character of the interaction in the As_2Te_3-TlSe system was studied by the methods of Differential Thermal Analysis (DTA), X-ray Diffraction (XRD), Microstructure analysis (MCA), and also by measuring the microhardness and determining the density of alloys, and state diagram was constructed. It is established that the As_2Te_3-TlSe state diagram is a quasibinary section of the triple mutual system As, Tl // Se, Te. Two new compounds, $TlAs_2Te_3Se$ and $Tl_3As_2Se_3Te_3$, are formed in the As_2Te_3-TlSe system. Both compounds are obtained in the vitreous state. Solid solutions based on As_2Te_3 at room temperature reach up to 3 mol.% TlSe, and based on TlSe-2 mol.% As_2Te_3. The electrical conductivity and thermoelectric power coefficient of the $(As_2Te_3)_{1-x}(TlSe)_x$ solid solutions have been measured as functions of temperature.

Keywords: Alloys, compound, congruently, thermoelectric

As_2Te_3-TlSe Sistemindeki Etkileşimin Karakteri ve Elde Edilen Fazların Elektrofiziksel Özellikleri

Öz

As_2Te_3-TlSe sistemindeki etkileşimin karakteri, Diferansiyel Termal Analiz (DTA), X-ışını Kırınım (XRD), Mikroyapı analizi (MCA) yöntemleri ile ve ayrıca mikrosertlik ölçülerek ve alaşımların yoğunluğu belirlenerek incelenmiştir ve durum diyagramı oluşturulmuştur. As_2Te_3-TlSe faz diyagramı As, Tl // Se, Te üçlü karşılıklı systemin kuvazi binar kesiti olduğu tespit edilmiştir. As_2Te_3-TlSe sisteminde iki yeni bileşik, $TlAs_2Te_3Se$ ve $Tl_3As_2Se_3Te_3$ oluşturulmuştur. Her iki bileşik de camsı halde elde edilir. Oda sıcaklığında As_2Te_3 bileşiğine dayalı katı çözelti alanı 3 mol. % TlSe ve TlSe bileşiğine dayalı katı çözelti alanı ise 2 mol. % As_2Te_3 olarak belirlenmiştir. $(As_2Te_3)_{1-x}(TlSe)_x$ katı çözeltilerinin elektrik iletkenliği ve termoelektrik gücü, sıcaklığın fonksiyonu olarak ölçülmüştür.

Anahtar Kelimeler: Alaşımlar, bileşik, kongruent, termoelektrik

INTRODUCTION

To elucidate the character of the chemical interaction of arsenic and thallium chalcogenides, as well as to search for new compounds, solid solutions, and areas of glassy alloys, the As_2Te_3-TlSe system was studied. The creation of physical and chemical bases for obtaining multicomponent phases with desired characteristics requires the study of phase diagrams in the corresponding systems.It is known that arsenic and thallium chalcogenides, as well as solid solutions based on them, are used as light-sensitive materials in the photoelectronic industry (Kandpal and Kushvakha, 2007; Littler et al., 2006; Rustamov et al., 1984; Aliev, 2007).There are many

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data in the literature on the interaction of arsenic and thallium chalcogenides in ternary and quaternary systems (Aliev et al., 1988; Farzaliev et al., 2006; Veliyev et al., 2007; Aliev, 1992). The initial components are characterized by the following data: As_2Te_3 melts congruently at 654 K and crystallizes in a monoclinic system with lattice parameters: *a* = 1.4339; *b* = 0.4006; *c* = 0.9873 nm, β = 95º, space group C2/m (Khvostorenko, 1972). The TlSe compound melts congruently at 603 K and has a B37 type structure with the following tetragonal lattice parameters: a = 0.803; c = 0.7014 nm (Lyakishev N.P., 2001).

MATERIAL AND METHODS

The initial components of the system were synthesized from high-purity elements in evacuated quartz ampoules evacuated to 0.133 Pa in the temperature range 670–870 K. B5 grade arsenic, Tl-000 thallium, and B4 grade selenium and tellurium were used as initial elemental substances. The ternary alloys of the system were synthesized from As_2Te_3 and TlSe master alloys in the temperature range 770–1070 K. Samples of the As_2Te_3–TlSe system were annealed at 470, 500, and 510 K for 700 h.

The interaction in the As_2Te_3-TlSe system was studied by differential thermal (DTA), X-ray phase (XRD), microstructural (MSA) analyses, as well as by measuring microhardness and determining density.

The DTA of the alloys was carried out on a TERMOSCAN-2 device with calibrated chromel-alumel thermocouples, and Al_2O_3 was used as a reference. The heating rate was 10 deg/min. X-ray phase analysis was performed on a D-2 PHASER instrument using Cuα radiation with a Ni filter. The microstructure of alloys of the As_2Te_3-TlSe system was studied using a MIM-8 metallographic microscope on pre-etched sections polished with GOI paste. The microstructure was revealed with an etchant composition of 10 ml conc. NaOH: 5 ml C_2H_5OH = 1:1, etching time 20 s. The microhardness of the system alloys was studied on an RMT-3 installation at loads of 0.10 and 0.20 N. The density of the system alloys was determined by the pycnometric method, toluene was used as the working fluid. Their electrical conductivity and thermoelectric coefficient were measured by the standard compensation method (Gorbachev and Okhotin, 1972; Kolomiets, 1962; Okhotin et al., 1969) on parallelepiped-shaped samples. The measurement error was 2.7–3.0%.

RESULTS AND DISCUSSION

All obtained samples are compact. Alloys with a high content of As_2Te_3 have a metallic luster, the rest of the alloys are black. At room temperature, all samples of the As_2Te_3-TlSe system are resistant to water, air and organic solvents. Strong mineral acids decompose them. Equilibrium alloys were investigated by physical-chemical analysis methods before and after annealing.

DTA alloys before annealing showed that from the region of 0-40 mol.% TlSe all fixed effects on the heating and cooling curves except for alloys from the region of 40-90 mol.% TlSe are reversible. On the thermograms of the alloys of these regions, there are two ranges of softening temperatures Tg-411 K and Tg-433 K.

X-ray diffraction study of alloys from the region of 40-90 mol.% TlSe confirms the data of DTA. No strong diffraction peaks are observed in the diffraction patterns of cast alloys (Figure 1a). The results obtained provide grounds for the formation of a glass formation region in the system. To crystallize glassy alloys based on $TlAs_2Te_3Se$ and $Tl_3As_2Se_3Te_3$, they were annealed at 440 and 470 K for 800 h, respectively. After annealing, thermograms of alloys from the region of 40–90 mol. % TlSe, the softening points disappear and, accordingly, diffraction maxima appear on the diffraction patterns (Figure 1b). This indicates that glassy alloys become crystalline after prolonged annealing.

To confirm the region of glass formation, the microstructure, microhardness, and density of the samples were studied before and after annealing. Microstructure in the concentration range of 40-90 mol. % TlSe shows that there are no crystalline inclusions in this range. Alloys containing 0-2, 50, 75 and 98-100 mol.% TlSe are single-phase, the remaining alloys are two-phases. It is established that in the system with slow cooling the

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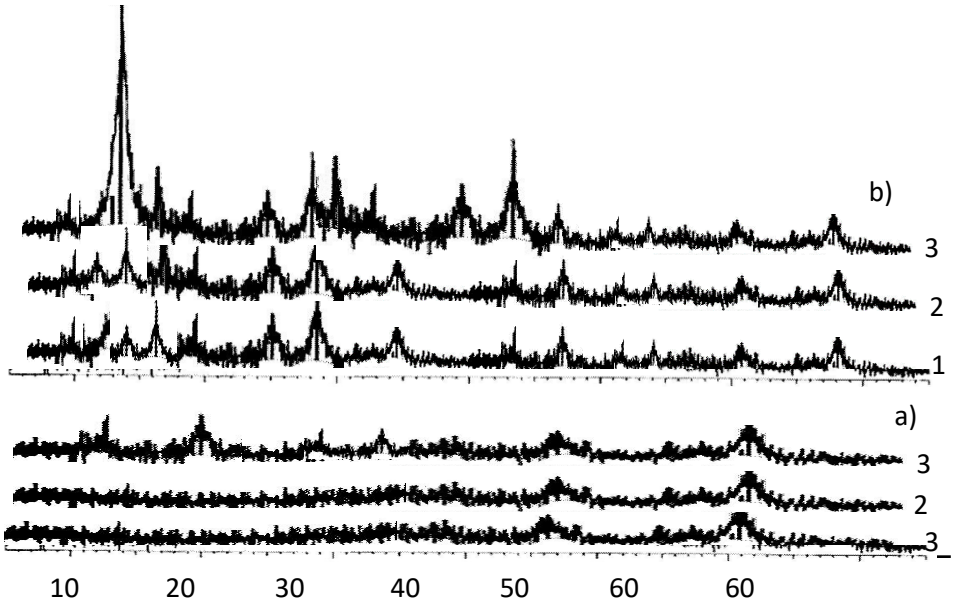

Figure 1. Diffractograms of glassy alloys of the As_2Te_3-TlSe system. 1-60, 2-70, 3-80 mol. % TlSe before annealing (a), after annealing (b).

boundary of the glass formation region extends from 40 to 90 mol.% T1Se, and in the quenching regime in liquid nitrogen, from 40 to 100 mol% T1Se.

As a result of the physicochemical analysis, a diagram of the state diagram of the As_2Te_3-TlSe system was constructed (Figure 2). Two new chemical compounds of the $TlAs_2Te_3Se$ and $Tl_3As_2Se_3Te_3$ were found in the system. The $TlAs_2Te_3Se$ compound melts incongruently at 513 K, and $Tl_3As_2Se_3Te_3$ melts congruently at 558 K. Both compounds are obtained in the vitreous state. The results of X-ray diffraction alloys containing 50, 75 mol.% TlSe, confirm the existence of the compounds $TlAs_2Te_3Se$ and $Tl_3As_2Se_3Te_3$ (Figure 3).

On the diffractograms of alloys of 50 and 75 mol % TlSe (Figure 3), the diffraction maxima obtained are different in intensity and interplanar distances from the original components.

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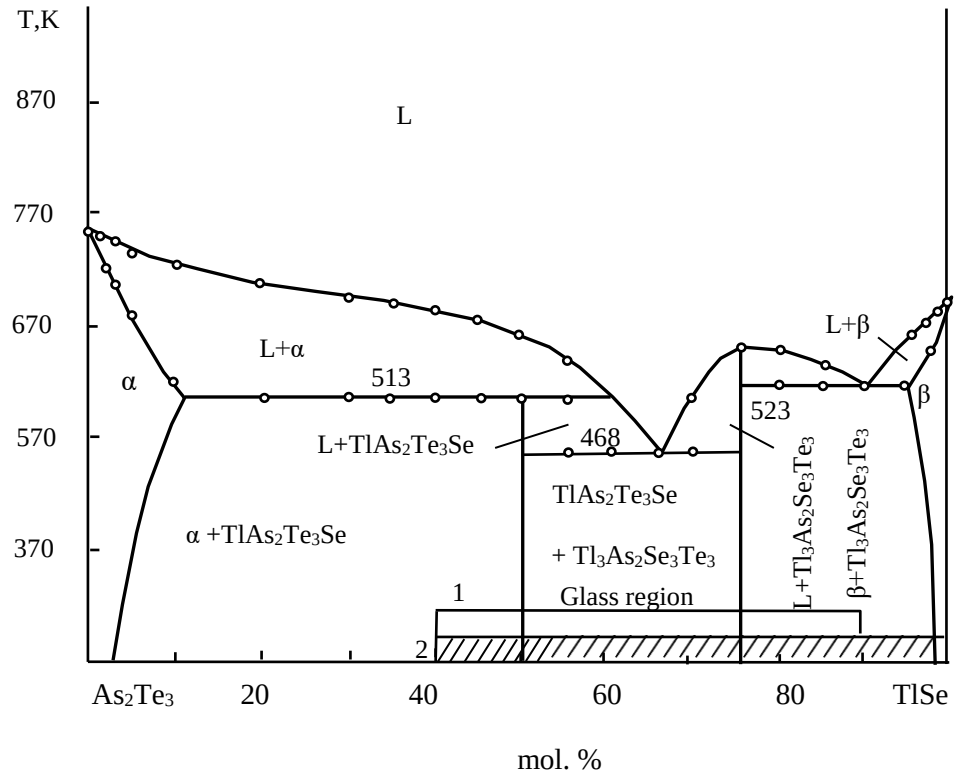

Figure 2. The phase diagram of the As_2Te_3-TlSe system (the glassformation region obtained in the slow cooling mode (1), in the quenching regime in liquid nitrogen (2).

The X-ray diffraction showed that the $TlAs_2Te_3Se$ compound crystallizes in tetragonal system with lattice parameters: a = 1.085; c = 0.932 nm, Z = 6, the density is $\rho_{puc.} = 7.20 \cdot 10^3$ kg/m^3, and $\rho_{X\text{-}eay.} = 7.34 \cdot 10^3$ kg/m^3.

The $Tl_3As_2Se_3Te_3$ compound crystallizes in a hexagonal system with lattice parameters: a = 1.172; c = 0.976 nm, Z = 4, the density is $\rho_{puc.} = 7.62 \cdot 10^3$ kg/m^3 and $\rho_{X\text{-}ray.} = 7.82 \cdot 10^3$ kg/m^3 (see Table 1).

In the As_2Te_3-TlSe system, limited homogeneity regions on the Ae_2Te_3 basis were found up to 3 mol.% TlSe, and based on TlSe -2 mol.%As_2Te_3.

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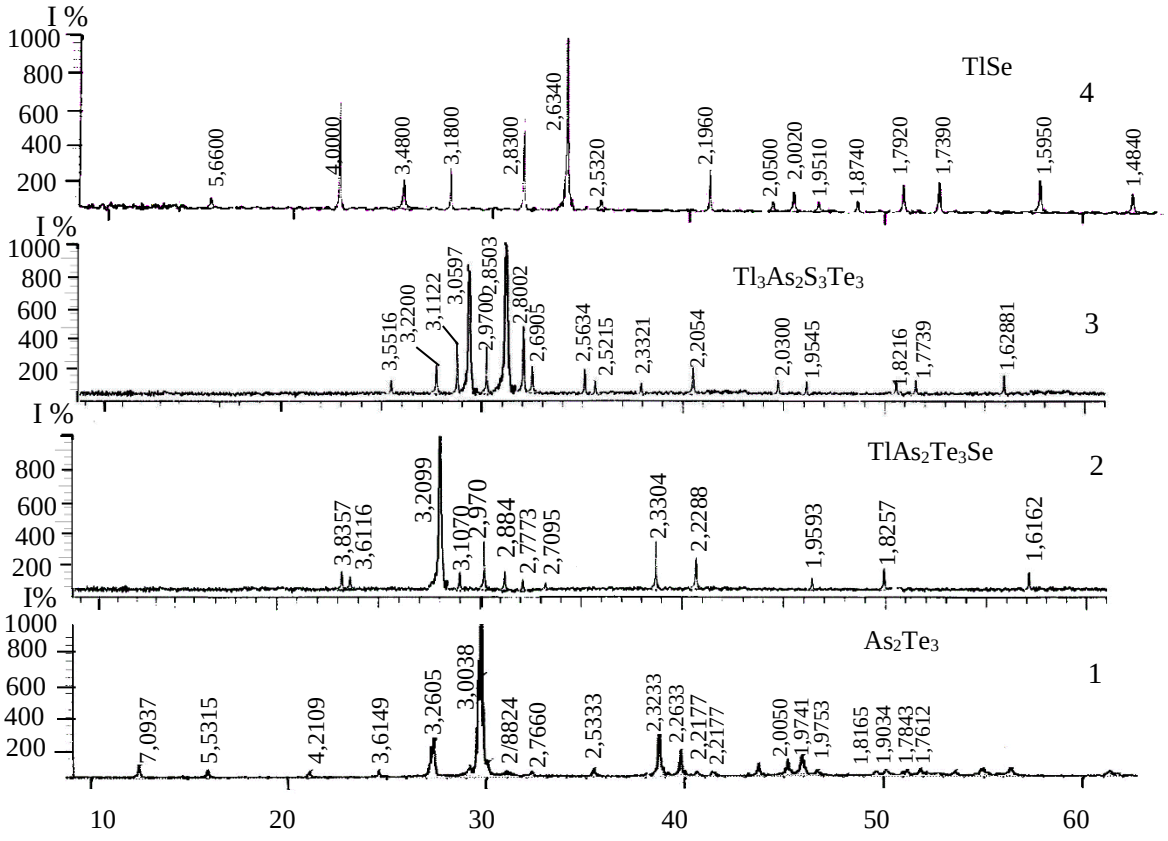

Figure 3. Diffractograms of glassy alloys of the As_2Te_3-TlSe system. 1- As_2Te_3, 2- $TlAs_2Te_3Se$, 3- $Tl_3As_2S_3Te_3$, 4- TlSe.

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Table 1. X-ray diffraction data for the compounds $TlAs_2Te_3Se$ and $Tl_3As_2Te_3Se_3$.

$TlAs_2Te_3Se$				$Tl_3As_2Te_3Se_3$			
I	$d_{eksp.}$, Å	$d_{cal.}$, Å	hkl	I	$d_{eksp.}$, Å	$d_{cal.}$, Å	hkl
16	3.8357	3.8348	220	12	3.5516	3.5714	211
13	3.6116	3.6155	300	20	3.2200	3.2530	003
100	3.2099	3.2191	311	44	3.1122	3.0979	103
13	3.1070	3.1068	003	86	3.0597	3.0165	212
37	2.9700	3.0082	320	36	2.9700	2.9298	220
16	2.8845	2.8571	302	100	2.8503	2.8444	113
13	2.7773	2.7629	312	56	2.8002	2.8149	310
6	2.7095	2.7116	400	16	2.6905	2.7047	311
37	2.3304	2.3313	004	16	2.5634	2.5375	400
26	2.2288	2.2294	114	12	2.5215	2.5118	222
13	1.9593	1.9592	304	10	2.3321	2.3237	321
18	1.8257	1.8242	531	16	2.2054	2.2115	410
16	1.6162	1.6169	630	12	2.0300	2.0298	500
				12	1.9545	1.9518	330
				12	1.8216	1.8230	510
				12	1.7739	1.7851	242
				14	1.6288	1.6265	006

According to the measurements of the microhardness of alloys of the As_2Te_3-TlSe system, four series of values were found. The values (1650-1720) MPa correspond to the microhardness of α-solid solutions based on As_2Te_3 (Tables 2, 3). The values (670-900) MPa are the microhardness of glassy $TlAs_2Te_3Se$ and glasses based on it, the values (990-1000) MPa correspond to the microhardness of Tl3As2Se3Te3 and glasses based on it, and the values (700-740) MPa correspond to the microhardness of β-solid solutions based on TlSe (Table 2). After annealing, the microhardness to the region of the glasses varies in the range (570-620) MPa and (800-850) MPa, respectively. (Table. 3).

The liquidus of the As_2Te_3-TlSe system consists of four branches of primary crystallization: α-phase (solid solutions based on As_2Te_3), $TlAs_2Te_3Se$, $Tl_3As_2Se_3Te_3$ and β-phase (solid solutions based on TlSe).

In the concentration range of 0-60 mol. % TlSe, primary crystals of the α-phase crystallize. The primary crystallization of $TlAs_2Te_3Se$, $Tl_3As_2Se_3Te_3$ ends with a double eutectic of composition 66 mol. % TlSe, melting point 468 K. The $Tl_3As_2Se_3Te_3$ compound and the β-phase form a eutectic at 523 K, the composition is 90 mol. % TlSe. Below the solidus line, two-phase alloys (α + $TlAs_2Te_3Se$) and ($Tl_3As_2Se_3Te_3$ + β) crystallize.

Some physical and chemical properties of alloys of the As_2Te_3-TlSe system before and after annealing, that is. the glassy and crystalline state is presented in the tables 2, 3.

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Table 2. Composition, DTA results, microhardness measurements and density determination of alloys of the As_2Te_3-TlSe system before annealing (glassy)

Composition, mol %		Thermal effects, K	Density, 10^3 kg/m^3	Microhardness, MPa			
As_2Te_3	TlSe			α	$TlAs_2SeTe_3$	$Tl_3As_2Se_3Te_3$	TlSe
				P=0,20 H			P=0,10 H
100	0.0	654	6,25	1650	-	-	-
99	1,0	653	6.27	1690	-	-	-
98	2,0	623.648	6.29	1720	-	-	-
97	3.0		6.31	1720	-	-	-
95	5.0	583.633	6.35	1710	-	-	-
90	10	523.628	6,40	1720	900	-	-
80	20	513.345	6.52	1720	900	-	-
70	30	513.603	6.61	1720	890	-	-
65	35	408.513.598	6.72	1720	890	-	-
60	40	408.513.593	6.81	-	870	-	-
55	45	411.513.578	6.92	-	880		
50	50	411.5132.57	7.12	-	870	-	-
45	55	413.463.513.	7.18	-	870	-	-
40	60	408.468.513	7.25	-	870	-	-
34	66	428.468	7.31	-	-	1000	-
30	70	433.468.518	7.43	-	-	1000	-
25	75	433.558	7.52	-	-	990	-
20	80	433.523.553	7.60	-	-	990	-
15	85	433.523.548	7.75	-	-	-	-
10	90	433.523	7.86	-	-	-	-
5.0	95	533.573	7.95	-	-	-	740
3.0	97	533.583	8.05	-	-	-	740
1,0	99	598	8.15	-	-	-	720
0.0	100	603	8.20	-	-	-	700

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Table 3. Composition, DTA results, measurements of microhardness and determination of the density of alloys of the As_2Te_3-TlSe system after annealing (crystalline)

Composition, mol %		Thermal effects, K	Density, 10^3 kg/m^3	Microhardness, MPa			
As_2Te_3	TlSe			α	$TlAs_2SeTe_3$	$Tl_3As_2Se_3Te_3$	TlSe
				P=0,10 H			P=0,10 H
100	0.0	654	6.25	1650	-	-	-
99	1,0	653	6.28	1690	-	-	-
98	2,0	623.648	6.32	1720	-	-	-
97	3.0	613.638	6.39	1720	-	-	-
95	5,0	583.633	6.40	1710	-	-	-
90	10	523.628	6.50	1720	-	-	-
80	20	513.345	6.61	1720	620	-	-
70	30	513.603	6.70	1720	620	-	-
65	35	513.598	6.82	1720	620	-	-
60	40	513.593	6.96	-	610	-	-
55	45	513.578	7.10	-	590		
50	50	513.573	7.20	-	570	-	-
45	55	468.513.548	7.25	-	570	-	-
40	60	468,513	7,31	-	570	-	-
34	66	468	7.39	-	Eutect.	Eutect.	-
30	70	468.518	7.50	-	-	850	-
25	75	558	7.62	-	-	850	-
20	80	523.553	7.70	-	-	830	-
15	85	523.548	7,77	-	-	800	-
10	90	523	7.88	-	-	Eutect.	Eutect.
5,0	95	533.573	7.96	-	-	-	740
з.о	97	553.583	8.10	-	-	-	740
1,0	99	598	8.18	-	-	-	720
0.0	100	603	8.20	-	-	-	700

The temperature dependences of electrical conductivity and thermopower coefficient for three single-phase alloys based on As2Te3 have been studied. The temperature dependence of the electrical conductivity of solid solutions (As2Te3)1-X (TlSe)x (x = 0.01, 0.02, 0.03) is shown in Figure 4. The behavior of the electrical conductivity curves of solid solutions (As2Te3)1- x (TlSe) x is identical to solid solutions. As can be seen from Figure 4, electrical conductivity increases over the entire temperature range, which is typical for semiconductors. Curves for dependence f ~ 103/T can be divided into two temperature ranges: 98-470 K and 470-570 K, the first value of electrical conductivity corresponds to the region of impurity conductivity, and the second value corresponds to intrinsic conductivity (Figure 4).

In Figure 5 shows the temperature dependence of the thermoelectric power coefficient of solid solutions (As2Te3)1-X (TlSe)x (x = 0.01, 0.02, 0.03). With an increase in temperature, the thermotltctric power coefficient of all three alloys first increases, passes through a maximum, and then decreases, which, apparently, is associated with the transition from the impurity region to the region of intrinsic conduction (Figure 5). All solid solution alloys have p-type conductivity.

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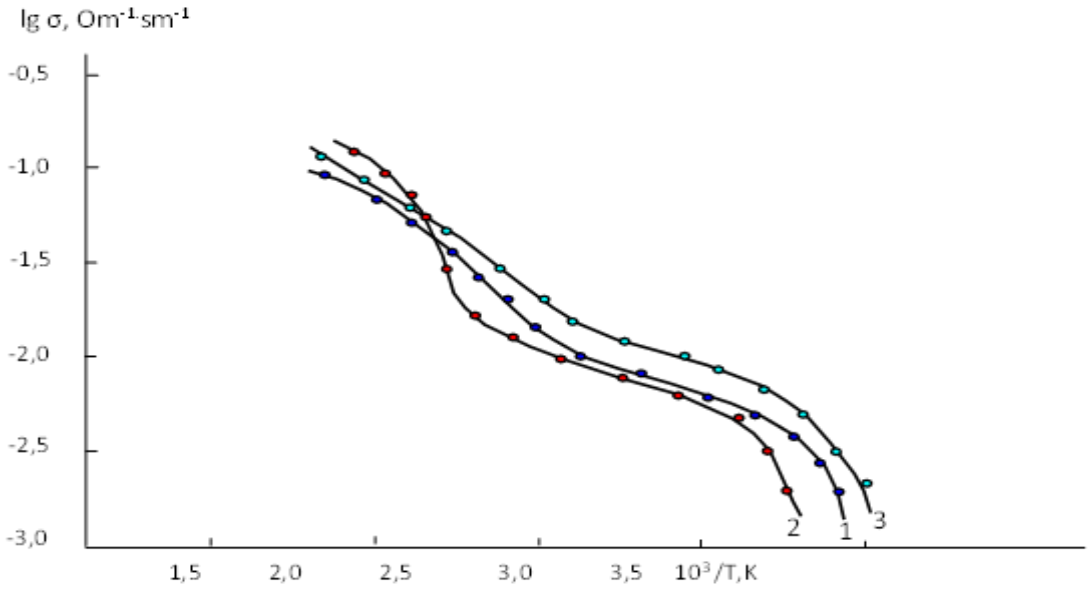

Figure 4. Temperature dependence of the electrical conductivity of solid solutions $(As_2Te_3)_{1-x}(TlSe)_x$. 1-1 mol. %, 2-2 mol. %, 3-3 mol. % TlSe.

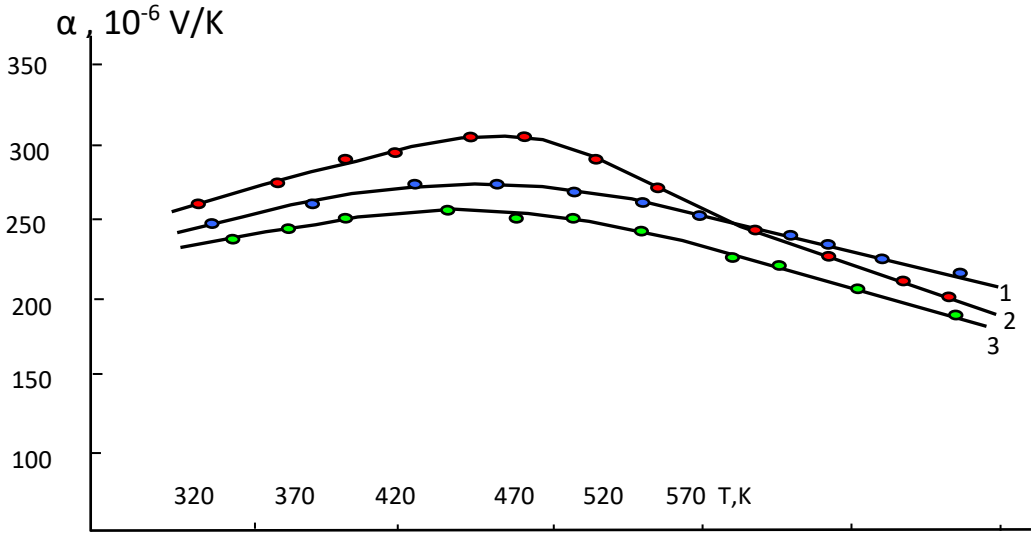

Figure 5. Temperature dependence of the thermo-emf coefficient of solid solutions $(As_2Te_3)_{1-x}(TlSe)_x$. 1-1 mol. %, 2-2 mol. %, 3-3 mol. % TlSe.

The As_2Te_3-TlSe system has been studied by DTA, XPA, MSA, as well as microhardness measurements and alloy density determinations, and its state diagram has been constructed. It has been established that the state diagram of the As_2Te_3-TlSe system is a quasi-binary section of the quaternary system As, Tl // Se, In the As_2Te_3-TlSe system, two new compounds $TlAs_2Te_3Se$ and $Tl_3As_2Se_3Te_3$ are formed. The $TlAs_2Te_3Se$ compound melts congruently at 513 K and crystallizes in the tetragonal

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syngony with unit cell parameters: a = 1.085; c = 0.932 nm, Z = 6, density $\rho_{puc.}$ = $7.20 \cdot 10^3$ kg/m^3, and $\rho_{X\text{-}ray}$ = $7.34 \cdot 10^3$ kg/m^3. The $Tl_3As_2Se_3Te_3$ compound crystallizes in a hexagonal syngony with lattice parameters: a = 1.172; c = 0.976 nm, Z = 4, the density is $\rho_{puc.}$ = $7.62 \cdot 10^3$ kg/m^3 and $\rho_{X\text{-}ray}$ = $7.82 \cdot 10^3$ kg/m^3. Solid solutions based on As_2Te_3 at room temperature reach up to 3 mol. % TlSe, and based on TlSe -2 mol.% As_2Te_3. The electrical conductivity and thermoelectric power coefficient of the $(As_2Te_3)_{1-x}(TlSe)_x$ solid solutions have been measured as functions of temperature.

The behavior of the electrical conductivity curves of solid solutions $(As_2Te_3)_{1-x}(TlSe)_x$ is identical to solid solutions. Electrical conductivity increases over the entire temperature range, which is typical for semiconductors.

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CONFLICT OF INTEREST

The Authors report no conflict of interest relevant to this article

RESEARCH AND PUBLICATION ETHICS STATEMENT

The authors declare that this study complies with research and publication ethics.

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