UNEC Journal of Engineering and Applied Sciences
Vol. 2, No. 2, 2022, pp. 45-50

Synthesis and investigation of physico-chemical properties alloys of the As_2S_3-Tl_2Te_3 system

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Abstract

The physico-chemical properties of alloys of the As_2S_3-Tl_2Te_3 system were studied by differential thermal (DTA), X-ray phase (XRD), microstructural (MSA) analysis, as well as density determination, microhardness measurement, and its phase diagram was constructed. As a result of the study, it was found that the phase diagram of the As_2S_3-Tl_2Te_3 system is quasi-binary and eutectic. A quaternary compound $Tl_2As_2S_3Te_3$ is formed in the system in a ratio of components 1:1. The compound is formed at 287°C. According to the results of X-ray phase analysis, it was found that the $Tl_2As_2S_3Te_3$ compound crystallizes in a tetragonal syngony with lattice parameters: a = 11.09; c = 9.60 Å, z=5 $\rho_{pucn.}$= 6.28 g/cm^3 , $\rho_{X\text{-}ray}$= 6.30 g/cm^3. In a system at room temperature based on As_2S_3, a solid solution of 1.0 mol. % Tl_2Te_3, and the region of the solid solution based on Tl_2Te_3 is practically not defined. In the As_2S_3-Tl_2Te_3 system, the glass formation region is 80 mol. % Tl_2Te_3 during normal cooling, and in the mode of quenching in liquid nitrogen up to -100 mol. % $T1_2Te_3$.

Keywords: system, solid solution, eutectic, microhardness, solidus.

Received: 3 march 2022 *Accepted: 2 may 2022* *Published: 26 may 2022*

1. Introduction

One of the most important problems facing chemists and physicists today is the organization of the synthesis and study of functional semiconductor materials that can meet the requirements of the constantly developing microelectronic and optical industries. Such materials include arsenic chalcogenides with optical properties. As_2S_3 and As_2Se_3 compounds and phases based on them are photosensitive [1–8], acousto-optical, and luminescent [9–11] materials and are used in the microelectronics industry. Chalcogenide fibers based on As_2S_3 and As_2Se_3 are used to transmit light in the mid-IR region, and have also found application as a compact nonlinear medium, allowing Raman amplification [12] and optical regeneration [13,14], wavelength conversion [15]. With the participation of thallium chalcogenides, many semiconductor materials have been obtained, both with electrical and thermoelectric properties [16–18].

In this work, the interaction between As_2S_3 and Tl_2Te_3 was studied, which is

undoubtedly important for elucidating the chemistry in the ternary mutual system As, Tl//S, Te, as well as the search for new phases with semiconductor properties.

2. Experiments

The initial components As_2S_3 and Tl_2Te_3 were synthesized from elemental arsenic grade B5, high purity sulfur, thallium Tl-000, and tellurium grade A-1; the latter was subjected to sevenfold zone purification. Alloys of the system were synthesized from As_2S_3 and Tl_2Te_3 master alloys in quartz ampoules evacuated to 0.133 Pa in a single-temperature furnace.

The study was carried out by DTA, XRD, MSA analysis, as well as by measuring microhardness by determining density.

The DTA of the alloys of the system was carried out on an NTR-73 instrument at a rate of 10 deg/min. XRF was performed on an X-ray device model D2 PHFSER with Cu Kα-radiation with a Ni-filter.

MSA of the alloys of the system was carried out on a MIM-8 microscope on pre-etched sections polished with GOI paste. The microhardness of the system alloys was measured on a PMT-3 microhardness tester. The density of the alloys of the system was determined by the pycnometric method; toluene was used as a filler.

3. Results and discussion

In order to elucidate the nature of the interaction between arsenic sulfide and thallium telluride, alloys were synthesized over a wide range of concentrations. The obtained samples are compact alloys with a high content of As_2S_3, brittle, dark brown; further increase in the content of Tl_2Te_3 alloys become black. The resulting alloys of the As_2S_3 and Tl_2Te_3 system are resistant to water and air, dissolve in mineral acids HNO_3, H_2SO_4 and alkalis NaOH, KOH. The synthesis mode was chosen on the basis of a preliminary recording of thermograms of alloy synthesis. The alloys were homogenized at temperatures of 190 and 200°C for 980 h.

DTA analysis of alloys of the As_2S_3-Tl_2Te_3 system showed that two and three endothermic heating effects are obtained on the thermograms of the samples. A large number of thermal effects in the system indicates that a complex interaction has taken place.

In the As_2S_3-Tl_2Te_3 system, extensive regions of glass formation are obtained. To determine the boundary of the glass formation region, DTA, XRD, MCA, density determination, and microhardness measurements were performed.

DTA of the alloys before annealing showed that the thermograms of the studied samples have two values of softening temperatures, which on the thermograms correspond to Tg As_2S_3 and Tg of the new $Tl_2As_2S_3Te_3$ phase and are equal to 170 and 135ºC. With an increase in the content of Tl_2Te_3, the softening temperature decreases from 170 to 135°C. Tg =135ºC corresponds to the softening temperature of $Tl_2As_2S_3Te_3$ (Table 1). In order to crystallize glassy alloys, rich in As_2S_3 were annealed at 190°C, and for $Tl_2As_2S_3Te_3$ at 150°C for 800 hours. It was found that glassy alloys could not be crystallized in this mode.

An attempt was made to achieve crystallization from the concentration range of 0-80 mol. % Tl_2Te_3, having subjected them to annealing in the form of a powder for 1250 h. A microstructural study of alloys of the As_2S_3-Tl_2Te_3 system showed that they are glassy, and alloys within 80-100 mol. % Tl_2Te_3 are phases with crystalline inclusions. Therefore, the alloys in this region consist of glass crystals. On each phase found in the As_2S_3-Tl_2Te_3 system, the microhardness was measured before and after annealing.

As can be seen from Table 1 and 2, the microhardness of glasses based on As_2S_3 before annealing is (1350-1380) MPa, and after annealing - (660-690) MPa. For the new $Tl_2As_2S_3Te_3$ phase, the microhardness is (1130-1160) MPa, and after annealing (900-960) MPa. For the Tl_2Te_3 compound, the microhardness varies within (680-700) MPa.

Composition, mol %		Thermal effects, ˚C	Density, 10^3 kg/m^3	Microhardness, MPa		
As_2S_3	Tl_2Te_3			α	$Tl_2As_2S_3Te_3$	Tl_2Te_3
				P=0.15 N	P=0.10 N	
100	0.0	170.310	3.20	1350	-	-
99	1.0	170.305	3.23	1350	-	-
97	3.0	170.255.300	3.29	1370	-	-
95	5.0	170.210.290	3.42	1380	-	-
90	10	170.210.280	3.75	1380	-	-
80	20	165.210.240	4.30	1380	-	-
75	25	160.210	4.62	-	-	
70	30	155.210.235	4.90	-	-	-
60	40	150.210.165	5.50	-	1160	-
55	45	140.210.280	5.78	-	1140	-
50	50	135.287	6.12	-	1130	-
45	55	135.195.220.285	6.38	-	1130	-
40	60	135.195.220.270	6.65	-	1140	-
35	65	135.195.220.255	6.92	-	1140	-
30	70	135.195.220.235	7.25	-	-	-
23	77	135.195.240	7.62	-	-	-
20	80	135.195.210.250	7.82	-	-	-
15	85	135.195.220.265	8.10	-	-	700
10	90	195.227.280	8.42	-	-	700
5.0	95	195.239.290	8.70	-	-	700
3.0	97	195.235.292	8.80	-	-	700
1.0	99	190.238.295	8.90	-	-	690
0.0	100	238.300	8.90	-	-	680

Table 1. Composition, DTA results, microhardness measurements and density determination of alloys of the As_2S_3-Tl_2Te_3 system before annealing (glassy)

Composition, mol %		Thermal effects, ˚C	Density, 10^3 kg/m^3	Microhardness, MPa		
As_2S_3	Tl_2Te_3			α	$Tl_2As_2S_3Te_3$	Tl_2Te_3
				P=0.15 N	P=0.10 N	
100	0.0	310	3.46	660	-	-
99	1.0	305	3.50	680	-	-
97	3.0	255.300	3.60	690	-	-
95	5.0	210.290	3.72	690	-	-
90	10	210.280	4.02	690	-	-
80	20	210.240	4.53	690	-	-
75	25	210	4.80	-	Eutect.	Eutect.
70	30	210.235	5.10	-	-	-
60	40	210.165	5.75	-	970	-
55	45	210.280	5.92	-	960	-
50	50	287	6.28	-	950	-
45	55	195.220.285	6.46	-	950	-
40	60	195.220.270	6.75	-	900	-
35	65	195.220.255	7.05	-	900	-
30	70	195.220.235	7.30	-	-	-
23	77	195.240	7.70	-	-	-
20	80	195.210.250	7.70	-	-	-
15	85	195.220.265	8.12	-	-	700
10	90	195.227.280	8.41	-	-	700
5.0	95	195.239.290	8.70	-	-	700
3.0	97	195.235.292	8.80	-	-	700
1.0	99	190.238.295	8.90	-	-	690
0.0	100	238.300	8.90	-	-	680

Tabel 2. Composition, DTA results, microhardness measurements and density determination of alloys of the As_2S_3-Tl_2Te_3 system before annealing (crystalline)

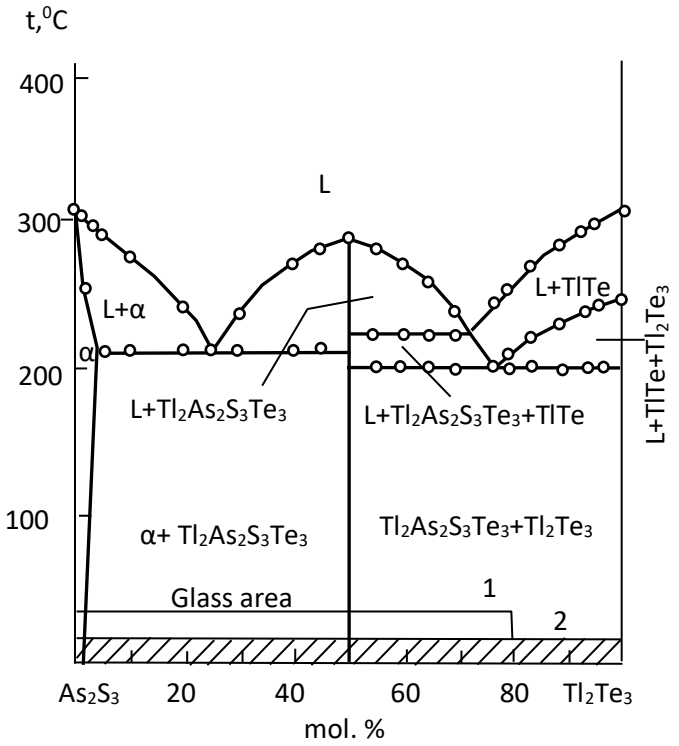

Figure 1. State diagram of the As_2S_3-Tl_2Te_3 system
(glass formation area obtained in slow cooling mode 1 and in liquid nitrogen quenching mode 2)

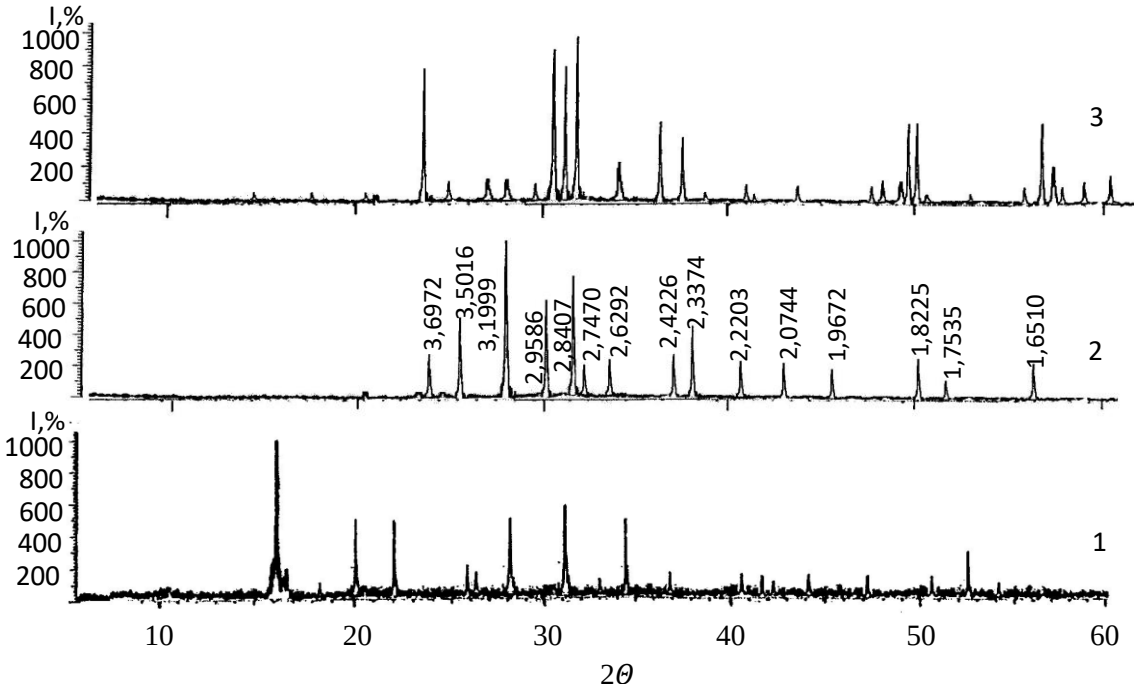

Figure 2. Diffractograms of alloys of the As_2S_3-Tl_2Te_3 system.
1-As_2S_3, 2-$Tl_2As_2S_3Te_3$, 3-Tl_2Te_3.

diffraction patterns differs from those for the initial components. This indicates that a new $Tl_2As_2S_3Te_3$ phase exists in the system. According to the results of X-ray phase analysis, it was found that the $Tl_2As_2S_3Te_3$ compound crystallizes in a tetragonal sygony with lattice parameters: a=11.09; c=9.60 Å, z=5, $\rho_{pucn/}$=6.28 g/cm^3, $\rho_{X\text{-}ray}$=6.30 g/cm^3. The results of X-ray diffraction analysis of the $Tl_2As_2S_3Te_3$ compound are given in Table 3.

№	I %	$d_{exp.}$, Å	$d_{calc.}$, Å	h	k	l
1	30	3,6972	3,6961	3	0	0
2	52	3,5016	3,5071	3	1	0
3	100	3,1999	3,2009	0	0	3
4	64	2,9586	2,9630	1	1	3
5	80	2,8407	2,8409	3	1	2
6	20	2,7470	2,7724	4	0	0
7	24	2,6292	2,6144	3	3	0
8	30	2,4226	2,4200	3	0	3
9	47	2,3374	2,3466	4	1	2
10	24	2,2203	2,2178	5	0	0
11	24	2,0744	2,0593	5	2	0
12	20	1,9672	1,9566	4	2	3
13	28	1,8223	1,8233	6	1	0
14	16	1,7535	1,7536	6	2	0
15	24	1,6510	1,6532	6	3	0

Table 3. Crystallographic data of the $Tl_2As_2S_3Te_3$ compound

In the As_2S_3-Tl_2Te_3 system based on As_2S_3, solid solutions reach 1.0 mol. %, and almost no solid solutions were found based on Tl_2Te_3. The liquidus of the As_2S_3-Tl_2Te_3 system consists of four branches of primary crystallization: α-solid solutions based on As_2S_3, $Tl_2As_2S_3Te_3$, TlTe and Tl_2Te_3. α-phase and $Tl_2As_2S_3Te_3$ form a eutectic of composition 25 mol. % Tl_2Te_3 and a temperature of 210 °C. In the concentration range of 50-100 mol. % Tl_2Te_3 there is a process of eutectic equilibrium and peritectic transformation.

Within concentrations of 0-50 mol. % Tl_2Te_3 below the malt line, α-phases and two-phase alloys α+ $Tl_2As_2S_3Te_3$ crystallize. The Tl_2Te_3 compound decomposes at temperatures above 238°C according to the following reaction: $Tl_2Te_3 \leftrightarrow L + TlTe$. Therefore, in the concentration range of 50-100 mol % Tl_2Te_3 he three-phase fields (L + TlTe + $Tl_2As_2S_3Te_3$) and (L + TlTe + Tl_2Te_3) are located above the solidus line. At a temperature of 195°C, peritectic processes L + TlTe ↔Tl_2Te_3 occur in this region. In the concentration range of 50–100 mol % Tl_2Te_3, two-phase alloys (TlTe + $Tl_2As_2S_3Te_3$) crystallize below the solidus line.

4. Conclusion

Thus, the phase diagram of the As_2S_3-Tl_2Te_3 system was constructed. It has been established that the As_2S_3-Tl_2Te_3 system is partially quasi-binary. A congruently melting compound at 287 °C of composition $Tl_2As_2S_3Te_3$ is formed in the system. The resulting compound is glassy and participates in the system as a glass former. Therefore, an extensive region of glass formation is formed in the As_2S_3-Tl_2Te_3 system. According to the results of X-ray phase analysis, it was found that the $Tl_2As_2S_3Te_3$ compound crystallizes in a tetragonal syngony with lattice parameters: a = 11.09; c = 9.60 Å, z = 4, $\rho_{pucn/}$ 6.28 g/cm^3, $\rho_{X\text{-}ray.}$ = 6.30 g/cm^3. The system based on As_2S_3 has a limited solubility range up to I mol % Tl_2Te_3. It has been established that in the system upon slow cooling, the region of glass formation extends up to 80 mol % Tl_2Te_3, and quenching in liquid nitrogen is about 100 mol % Tl_2Te_3.

References

1. Dinesh Chandra SATI1, Rajendra KUMAR, Ram Mohan MEHRA, Turk J Phys. **30** (2006) 519.
2. M. Lovu, S. Shutov, S. Rebeja, E. Colomeyco, M. Popescu, Journal of Optoelectronics and Advanced Materials **2**(1) (2000) 53.
3. J.Li Jun, D.A. Drabold, Phys. Rev. **64** (2001) 104206.

4. V.V. Kirilenko, S.A. Dembovsky, Yu.A. Polyakov, Inorganic Materials 11(11) (1975) 1923.
5. I.I. Aliev, M.B. Babanly, A.A Farzaliev, XI International conference on physics and technology of thin films, Ivanovo-Frankivsk, Ukraine (2007) 86.
6. T. Hineva, T. Petkova, C. Popov, P. Pektov, J.P. Reithmaier, T. Funrmann-Lieker, E. Axente, F. Sima, C.N. Mihailescu, G. Socol, I.N. Mihailescu, Journal of Optoelectronics and Advanced Materials **9**(2) (2007) 326.
7. Seema Kandpal, R.P.S. Kushwaha, Pramana journal of physics **69**(3) (2007) 481.
8. A.M. Andriesh, V.I. Verlan, Journal of Optoelectronics and Advanced Materials **3**(2) (2001) 455.
9. A.A. Babaev, R. Muradov, S.B. Sultanov, A.M. Askhabov, Inorgan. materials **11**(44) (2008) 1187.
10. Bhawana Dabas and R.K. Sinha, ICOP 2009-International Conference on Optics and Photonics Chandigarh, India (2009) 123.
11. I.C.M. Littler, L.B. Fu, E.C. Magi, D. Pudo, B.J. Eggleton, Optics Express **14(**18) (2006) 8088.
12. R.E. Slusher, G. Lenz, J. Hodelin, J. Sanghera, L.B. Shaw, I.D. Aggarwal, Journal of Optoelectronics and Advanced Materials **21** (2004) 1146.
13. S.D. Jackson, G. Anzueto-Sánchez, Appl. Phys. Lett. **88** (2006) 221106.
14. L.B. Fu, A. Fuerbach, I.C.M. Littler, B.J. Eggleton, Appl. Phys. Lett. **88** (2006) 081116.
15. L.B. Fu, M. Rochette, V. Ta'eed, D. Moss, B.J. Eggleton, Opt. Express **13** (2005) 7637.
16. J.A. Veliev, I.I. Aliev, A.Z. Mamedova, J. inorganic chemistry **52**(2) (2007) 312.
17. A.A. Farzaliev, I.I. Aliev, O.M. Aliev, I.G. Aliev, Chemical Problems **2** (2006) 284.
18. M.I. Zargarova, A.N. Mamedov, J.S. Azhdarova, J.A. Akhmedova (Veliyev), Ch.I. Abilov, Inorganic substances synthesized and investigated in Azerbaijan. Baku. Ed. Elm. (2004) 462 p.