CHEMICAL SCIENCES

PHYSICAL-CHEMICAL STUDIES OF INTERACTION AND GLASS FORMATION IN THE As_2Te_3-Tl_2Se SYSTEM

Aliyev I.,
Doctor of Chem. Sci., Prof., Head of Lab.
Institute of Catalysis and Inorganic Chemistry named after M.F. Nagiyev, Ministry of Science and Education of the Azerbaijan Republic.
Mustafayev A.,
Candidate of Physical and Mathematical Sciences, Associate Professor
Azerbaijan State Pedagogical University
Ahmedova C.,
Doctor of Chem. Sci., Prof.,
Adiyaman University, Faculty of Arts and Sciences, Faculty of Chemistry, Turkey
Khalilova K.,
Researcher
Isgandarova G.
Researcher
Institute of Physics named after H. Abdullayev, Ministry of Science and Education of the Azerbaijan Republic
https://doi.org/10.5281/zenodo.15657602

Abstract

Physicochemical studies of interaction and glass formation in the As_2Te_3-Tl_2Se system were carried out using the following methods: differential thermal analysis (DTA), X-ray diffraction analysis (XRD), microstructural analysis (MSA), and by measuring microhardness and density, T-x was constructed phase diagram. The system is a partially quasi-binary diagonal section of the ternary reciprocal system Tl,As//Se,Te. When the component ratio is 1:1, a quaternary compound of the composition $Tl_2As_2SeTe_3$ is formed, which melts congruently at 270°C. It has been established that the $Tl_2As_2SeTe_3$ compound crystallizes in the tetragonal syngony with lattice parameters: a=11.47 Å; c=9.50 Å, z=6, $\rho_{pucn.}$ =7.98 g/cm^3, $\rho_{X\text{-}ray}$ =8.13 g/cm^3. In the system at room temperature, solid solutions based on As_2Te_3 reach 3.3 mol % Tl_2Se, and solid solutions based on Tl_2Se are practically not established. Under normal conditions, extensive areas of glass formation based on $Tl_2As_2SeTe_3$ were found in the concentration range of 35-70 mol % Tl_2Se.

Introduction

One of the important tasks facing the chemistry and physics of semiconductors is the study of the synthesis and properties of materials consisting of energy converters with photo- and thermoelectric properties for the efficient use of alternative energy sources. Obtaining phase diagrams of the corresponding systems in new semiconductor materials with complex properties is of great importance.

It is known that arsenic chalcogenides and alloys based on them, new complex phases, are materials with photoelectric [1-8], luminescent [9,10], properties widely used in color television, IR optics in memory centres [11-13] .

In recent years, chalcogenide fibres [14–19] based on As_2S_3 and As_2Se_3 have been used to transmit light in the mid-IR range and have found application as a compact nonlinear medium allowing Raman amplification [20] and lasing [21]. The As_2Te_3 compound does not form glass under normal conditions, but ternary and quaternary compounds obtained in systems consisting of thallium chalcogenides are glassy and form large areas. The As_2Te_3 compound and the complex phases obtained on its basis are materials with photoelectric properties [22,23]. Many systems involving arsenic and thallium chalconides have been studied in the literature [24-27].

The purpose of this work is to study the interaction and glass formation in the As_2Te_3-Tl_2Se system, as well as the search for new semiconductor phases.

The initial components of the system As_2Te_3 and Tl_2Se are characterized by the following data: The As_2Te_3 compound melts at 381°C and crystallizes in a monoclinic syngony with lattice parameters: a = 1.4339; b = 0.4006; c = 0.9873 nm, β = 95°, sp. gr. C2/m [28]. The Tl_2Se compound melts the open maximum at 390°C and crystallizes in a tetragonal syngony with lattice parameters: a = 0.854 nm, c = 0.271 nm, density ρ = 9.65 g/cm^3 [29].

Experimental part

To study the As_2Te_3-Tl_2Se system, alloys were synthesized from the As_2Te_3 and Tl_2Se components in evacuated quartz ampoules at a pressure of 0.133 Pa in the temperature range 500-700°C. Then the alloys were homogenized by annealing at 190°C for 540 hours. After homogenization of the alloys, the systems were studied using the methods of physicochemical analysis (DTA, X-ray diffraction, MSA), as well as density and microhardness measurements. Differential thermal analysis of the samples was carried out using a TERMOSCAN-2 device. Al2O3 was used as standard, heating rate was 5 deg/min.

X-ray phase analysis was performed on a D2 PHASER X-ray diffractometer. A CuKα cathode and a

Ni filter were used as irradiators. Microhardness was measured using a PMT-3 metallographic microscope. Microstructural analysis of the alloys was carried out using a MIM-8 microscope.

Results and its discussion

Alloys of the As_2Te_3-Tl_2Se system were synthesized from As_2Te_3 and Tl_2Se components in quartz ampoules evacuated to 0.133 Pa at a temperature of 700-800°C. The melts were cooled slowly at a rate of 150 deg/h. up to 400°C, then at a speed of (50-60) deg/h. Alloys containing 35-70 mol % Tl_2Se is obtained in glassy form. Alloys with a high content of As_2Te_3 are stable in water and air at room temperature; they dissolve in mineral acids HCl, HNO_3 and alkalis NaOH, KOH.

To homogenize the alloys, the As_2Te_3-Tl_2Se systems were annealed at 190, 250 and 300°C for 750 hours. After annealing, the alloys were studied using a set of methods of physicochemical analysis: DTA. XRF. MSA, microhardness and density measurements.

Some physicochemical properties of alloys of the As_2Te_3-Tl_2Se system were studied before and after annealing (Table 1.2). Thermal analysis showed that in the concentration range of 35-70 mol. % Tl_2Se on thermograms of cast alloys a softening temperature of 155-125°C is observed. DTA indicates that with the exception of alloys in the range of 20-80 mol % Tl_2Se all effects, in the thermograms of the obtained alloys, are endothermic and reversible. Glass-crystalline regions are observed in the concentration range of 20-35 mol % Tl_2Se and 70-80 mol % Tl_2Se.

The XRF results also confirm the DTA and MSA data. In the diffraction patterns of alloys of the As_2Te_3-Tl_2Se system in the range of 35-70 mol % $T1_2Se$ no intense diffraction maxima are observed (Fig. 1). After long-term annealing, softening temperatures disappear from the glass region in the heating curves of the alloys, and intense diffraction reflections appear in the diffraction pattern (Fig. 2). In Fig. 1 shows X-ray diffraction patterns of alloys from the region of glasses of the As_2Te_3-Tl_2Se system containing 30, 50, 60 and 70 mol % $T1_2Se$.

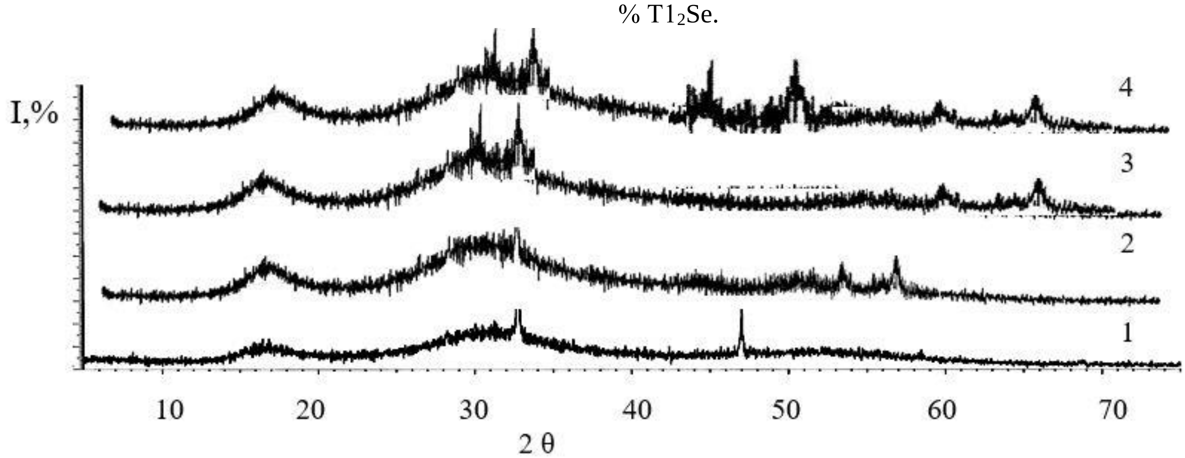

Fig.1. X-ray diffraction patterns of alloys from the glass region of the As_2Te_3-Tl_2Se system. 1-40 mol %, 2-50 mol %, 3-60 mol %, 4-70 mol. % Tl_2Se.

A microscopic study of alloys of the As_2Te_3-Tl_2Se system showed that alloys in the concentration range of 35-70 mol % Tl_2Se are glasses, and in the region of 15-35 mol % Tl_2Se and 70-80 mol. % Tl_2Se are glasses with crystalline inclusions. Finally, it was revealed that with slow cooling in the system, the glass formation region based on $Tl_2As_2SeTe_3$ extends from 35 to 70 mol % Tl_2Se. Some physicochemical properties of the alloys of the system before and after annealing are given in (Tables 1 and 2). As can be seen from Table 1, the softening temperature Tg of alloys from the glass region, in the concentration range of 20-70 mol % Tl_2Se, varies between 155-125°C. The microhardness of alloys from the glass region varies within the range (810-850) MPa (Table 1). After prolonged annealing in the concentration range of 35-70 mol % Tl_2Se in thermograms of glassy alloys, the temperature Tg disappears, and the temperatures associated with the liquidus and solidus remain unchanged (Table 2).

This means that after heat treatment, glassy alloys are completely crystallized. As can be seen from table. 1 and 2, the microhardness of alloys from the glass region is greater than from the crystalline state. On the other hand, the density of glassy alloys is lower compared to the density of crystalline alloys. The results obtained are in good agreement with the literature data on the properties of glasses.

Table 1.

Composition, DTA results, microhardness measurements and determinations density of alloys of the As_2Te_3-Tl_2Se system before annealing (S_1- $Tl_2As2SeTe_3$), (S_2- $Tl_2As_2Se_3Te$)

Composition, mol %		Thermal effects, ˚C	Density, g/cm^3	Microhardness, MPa				
As_2Te_3	Tl_2Se			α	S_1	S_2	Tl_2Te	Tl_2Se
				P=0,15 N				
100	0,0	381	6.23	1650	-	-	-	-
97	3,0	285.365	6.27	1690	-	-	-	-
95	5,0	245.350	6.40	1700	-	-	-	-
90	10	190.340	6.57	1700	-	-	-	-
80	20	155.190.285	6.91	1700	-	-	-	-
75	25	150.90.235	7.08	-	-	-	-	-
70	30	150.190	7.32	Eutec.	Eutec.	-	-	-
65	35	140.190;225	7.42	-	810	-	-	-
60	40	130.190.240	7.60	-	830	-	-	-
55	45	125.190.260	7.76	-	840	-	-	-
50	50	125.270	7.98	-	850	-	-	-
45	55	125.255,265	8,.10	-	850	-	-	-
40	60	125,225.255.260	8.28		850	-	-	-
35	65	125.225.245.290	8.45	-	Eutec.	Eutec.	Eutec.	
30	70	125.225.325	8.63	-	-	980	-	-
25	75	320.350	8.79	-	-	980	550	-
20	80	300.315.345	8.97	-	-	980	560	-
15	85	300.310.340	9,13	-	-	-	-	-
10	90	300.345	9.31	-	-	Eutec.	Eutec.	Eutec.
5.0	95	300.345.365	9.47	-	-	-	-	540
3,0	97	300.345.380	9.55	-	-	-	-	530
0,0	100	390	9.65	-	-	-	-	520

When measuring microhardness, five rows of values were obtained (Tables 1 and 2). After annealing at 190°C for 540 hours (Table 2), microhardness for the gray phase (1650-1700) MPa (α-phase based on As_2Te_3), for the dark phase (730-760) MPa ($Tl_2As_2SeTe_3$), for light gray phase (980) MPa ($Tl_2As_2Se_3Te$), for the light phase (550-560) MPa (Tl_2Te) and for the dark gray phase (520-540) MPa (Tl_2Se).

Table 2.

Composition, DTA results, microhardness measurements and determinations densities of alloys of the As_2Te_3-Tl_2Se system after annealing (S_1- $Tl_2As_2SeTe_3$), (S_2- $Tl_2As_2Se_3Te$)

Composition, mol %		Thermal effects, ˚C	Density, g/cm^3	Microhardness, MPa				
As_2Te_3	Tl_2Se			α	S_1	S_2	Tl_2Te	Tl_2Se
				P=0,10 N				
100	0,0	381	6.23	1650	-	-	-	-
97	3,0	285.365	6.27	1690	-	-	-	-
95	5,0	245.350	6.40	1700	-	-	-	-
90	10	190.340	6.57	1700	-	-	-	-
80	20	190.285	6.91	1700	-	-	-	-
75	25	190.235	7.18	-	-	-	-	-
70	30	190	7.40	Eutec.	Eutec.	-	-	-
65	35	190.225	7.52	-	730	-	-	-
60	40	190.240	7.70	-	730	-	-	-
55	45	190.260	7.87	-	740	-	-	-
50	50	270	8.11	-	750	-	-	-
45	55	225.255.265	8.16	-	760	-	-	-
40	60	225.255.260	8.38		760	-	-	-
35	65	225.245.290	8.55	-	Eutec.	Eutec.	Eutec.	
30	70	225,325	8.68	-	-	980	-	-
25	75	320.350	8.79	-	-	980	550	-
20	80	300.315.345	8.97	-	-	980	560	-
15	85	300.310.340	9.13	-	-	-	-	-
10	90	300.345	9.31	-	-	Eutec.	Eutec.	Eutec.
5.0	95	300.345.365	9.47	-	-	-	-	540
3,0	97	300.345.380	9.55	-	-	-	-	530
0,0	100	390	9.65	-	-	-	-	520

The microhardness of the glassy compound $Tl_2As_2SeTe_3$ before and after annealing changes noticeably (Tables 1, 2). The state diagram of the As_2Te_3-Tl_2Se system is shown in Fig. 2. The nature of the chemical interaction in the As_2Te_3-Tl_2Se and As_2Te_3-Tl_2S systems is the same. Both systems are partially quasi-binary and represent diagonal sections of the ternary reciprocal systems As,Tl//Se,Te and As,T1//S,Te, respectively.

One chemical compound of the composition $Tl_2As_2SeTe_3$ is formed in the system, which melts congruently at 270ºC. The $Tl_2As_2SeTe_3$ compounds have a similar character and can be considered derivatives of $Tl_2As_2X_4$ = $TlAsX_2$. Here, isomorphic substitution of chalcogens occurs.

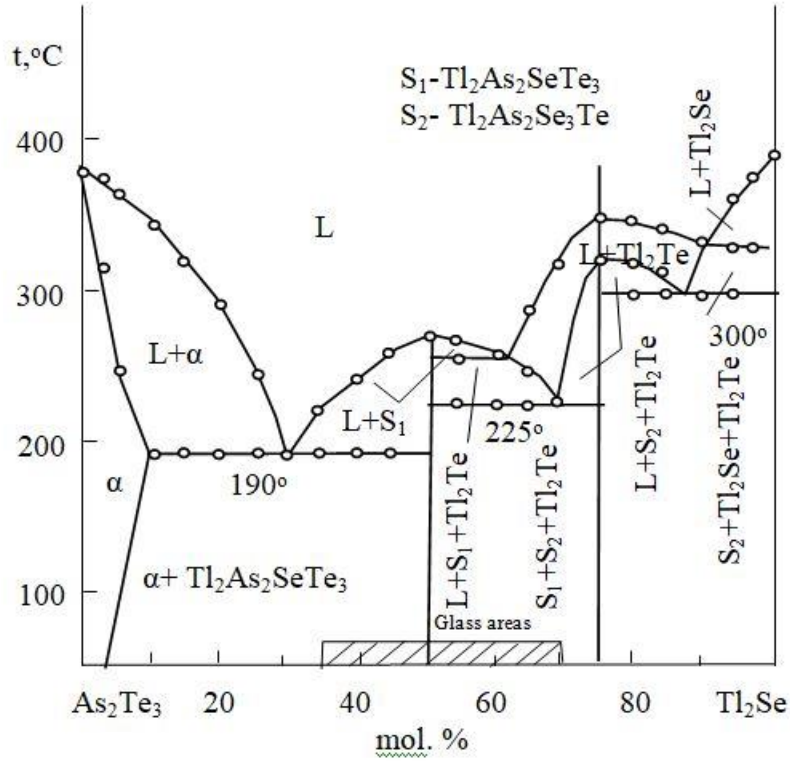

Fig.2. Phase diagram of the As_2Te_3-Tl_2Se system.

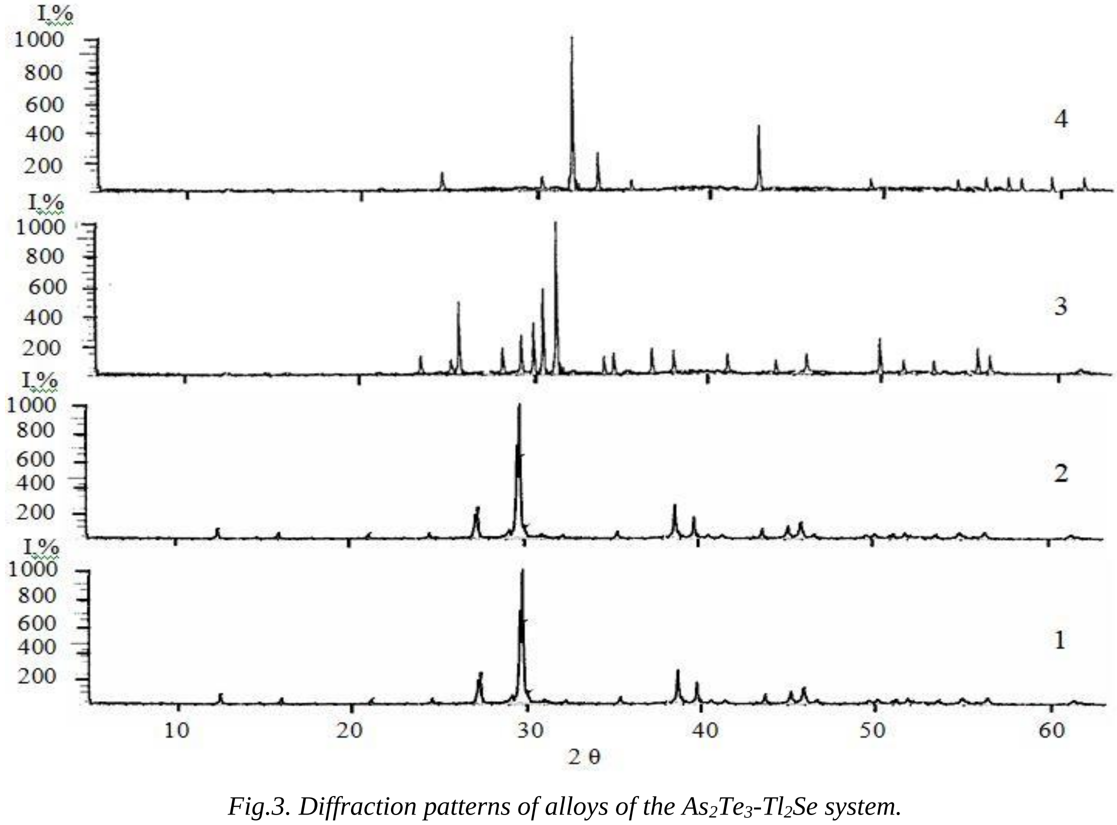

Fig.3. Diffraction patterns of alloys of the As_2Te_3-Tl_2Se system.
1-As_2Te_2, 2-3 mol %, 3-50 mol % ($Tl_2As_2SeTe_3$), 4-100 mol % Tl_2Se.

The existence of the $Tl_2As_2SeTe_3$ compound was confirmed by methods of physicochemical analysis (DTA, XRF, MSA, determination of microhardness and density). The XRD results of alloys of the As_2Te_3-Tl_2Se system are shown in Fig. 3. As can be seen from Fig. 3, the X-ray diffraction pattern of the 1:1 alloy ($Tl_2As_2SeTe_3$) contains diffraction lines that differ from the lines of the original components both in intensity and in the value of interplanar distances (Fig. This indicates the presence of a new phase in the As_2Te_3-Tl_2Se system, formed by the reaction: As_2Te_3-Tl_2Se = $Tl_2As_2SeTe_3$

Interplanar distances and line intensities in the X-ray diffraction patterns of the remaining alloys, excluding the regions of solid solutions, indicate the presence of a mixture of other phases in them. Identification of the powder pattern shows that $Tl_2As_2SeTe_3$ crystallizes in the tetragonal syngony with lattice parameters: a=11.47 Å; c=9.50 Å, z=6, density $\rho_{puc/}$=7.98 g/cm^3, $\rho_{X\text{-}ray}$=8.13 g/cm^3. Table 3 shows the crystallographic data of the compound $Tl_2As_2SeTe_3$.

Table 3.

Crystallographic data of the compound $Tl_2As_2SeTe_3$

№	I, %	d_{exp}, Å	d_{cal}, Å	h	k	l
1	17	3,7319	3,7920	2	2	1
2	12	3,3903	3,3903	3	1	1
3	57	3,2318	3,1814	3	2	0
4	21	3,1605	3,1670	0	0	3
5	29	3,0780	3,0846	2	2	2
6	96	2,9785	2,9785	3	0	2
7	61	2,9308	2,9501	1	1	3
8	100	2,8665	2,8687	4	0	0
9	14	2,6397	2,6943	3	2	2
10	19	2,5996	2,6011	3	3	1
11	21	2,4295	2,4390	3	0	3
12	17	2,3678	2,3756	0	0	4
13	14	2,1963	2,2947	2	0	4
14	9	2,0498	2,0498	2	2	4
15	14	1,9672	1,9672	5	3	0
16	24	1,8241	1,8176	5	3	2
17	9	1,7841	1,7817	6	2	1
18	9	1,7187	1,7206	2	2	5
19	19	1,6556	1,6502	5	0	4
20	16	1,6393	1,6386	7	0	0

Conclusion

Thus, a state diagram of the As_2Te_3-Tl_2Se system has been constructed. The system is characterized by the formation of one chemical compound $Tl_2As_2SeTe_3$. The $Tl_2As_2SeTe_3$ compound crystallizes in the tetragonal syngony with lattice parameters: a=11.47 Å; c=9.50 Å, z=6, $\rho_{pucn.}$ =7.98 g/cm^3, $\rho_{X\text{-}ray}$ =8.13 g/cm$_3$. It has been established that in the As_2Te_3-Tl_2Se system based on As_2Te_3, solid solutions reach 3.3 mol % Tl_2Se. It was revealed that with slow cooling, the boundary of the glass formation region extends from 35 to 70 mol % Tl_2Se. A study of the chemical interaction of thallium chalcogenides with arsenic chalcogenides showed that the alloys exhibit a greater tendency to glass formation. The resulting alloys are compact, with a high content of As_2Te_3, the color of the alloys has a metallic luster, the remaining alloys are dark brown.

References:

1. Thomsen C., Strait J., Vardeny Z., et al. Picosecond optical-generation and detection of phonon waves in A-As^2Te^3 // AIP Conference proceedings. 1984. Issue: 120 Pages: 102-109.
2. Globus TR., Gaskill DK., Groshens T. Optical characterization of As^2Te^3 films for optical interconnects // Materials research society symposium proceedings. 1998. V. 486. P. 391-396.
3. Uemura O., Sugawara Y., Kameda Y., Nishimiya Y., Electronic-properties of the liquid in As^2Te^3 system // Journal of Non-crystalline solids. 1993 V. 156. P. 744-747. DOI: 10.1016/0022-3093(93)90060-B
4. Zhang YH, Ma YM, Geng AH et al. Pressure-induced electron phase transitions of alpha-As^2Te^3 // Journal of alloys and compounds. 2016. V. 685. P. 551-558. DOI: 10.1016/j.jallcom.2016.05.309
5. Kolobov A. V. J. Tominaga J. Chalcogenide glasses as prospective materials for optical memories and optical data storage // Journal of Materials Science: Materials in Electronics. 2003. P. 677-680.
6. Zakery A. Elliott S. Optical properties and applications of chalcogenide glasses: a review // Journal of Non-Crystalline Solids. –2003. № 1-3 (330). C. 1-12.
7. Kirilenko V.V., Dembovsky S.A., Polyakov Yu.A. Optical properties of glasses in the As_2S_3–TlS and As_2Se_3–TlSe systems // Proceedings of the USSR Academy of Sciences. Inorganic materials, 1975. T.11. No. 11. C.1923-1928.
8. Aliyev I.I., Babanly M.B., Farzaliev A.A. Optical and photoelectric properties of thin films of glasses $(As_2Se_3)_{1-x}(TlSe)_x$ (x=0.05-0.10) // XI International Conference on Physics and Technology of Thin Films. Ivanovo-Frankivsk, Ukraine, May 7-12, 2007. P. 86.

9. Babaev A.A., Muradov R., Sultanov S.B., Askhabov A.M. Influence of production conditions on the optical and photoluminescent properties of glassy As_2S_3 // Inorg. materials. 2008. T.44. No. 11. pp. 1187-1201.

10. Kurganova A., Snopatin G.E., Suchkov A.I. X-ray fluorescence determination of the macroscopic composition of As-S, As-Se and As-S-Se glasses // Inorg. materials. 2009. T.45. No. 12. P. 1408-1413.

11. Seema Kandpal, Kushwaha R. P. S.. Photoacoustic spectroscopy of thin films of As_2S_3, As_2Se_3 and $GeSe_2$ // Indian Academy of Sciences. PRAM ANA journal of physics. 2007. V. 69. No. 3. P. 481-484.

12. Diez A., Birks T.A., Reeves W.H., Mangan B.J., and Russell P.St. J., Excitation of cladding modes in photonic crystal fibers by flexural acoustic waves // Optics Lett. 2000. V.25. P. 1499-1501.

13. 13. Kochemirovsky V.A., Kurochkin A.V., Manshina A.A., Sokolov I.A. Physicochemical and optical methods for studying glassy alloys. - St. Petersburg: VVM, 2012. - 48 p.

14. Slusher R.E., Lenz G., Hodelin J., Sanghera J., Shaw L.B., Aggarwal I.D. Large Raman gain and nonlinear phase shifts in high-purity As_2Se_3 Chalcogenide fibers // J. Opt. Soc. Am. 2004. V. 21. P. 1146-1155.

15. Diez A., Birks T.A., Reeves W.H., Mangan B.J., and Russell P.St. J., Excitation of cladding modes in photonic crystal fibers by flexural acoustic waves // Optics Lett. 2000. V.25. P. 1499-1501.

16. Churbanov M.F., Shiryaev V.S., Skripachev I.V., Snopatin G.E., Pimenov V.G., Smetanin S.V., Shaposhnikov R.M., Fadin I.E.,Pyrkov Yu.N., and Plotnichenko V.G. Высокочистые как $As_2S_{1,5}$ Se $_{1,5}$ стекла оптических волокон // Неорган. материлы. 2002. T.39. №2. P. 193-197.

17. Moon J.A. and Schaafsma D.T., “Chalcogenide Fibers: An Overviewof Selected Applications”, Fiber and Integrated Optics, 2000. V.19. P. 201- 210.

18. Jackson S.D., Anzueto-Sánchez G.; Chalcogenide glass Raman fiber laser // Appl. Phys. Lett., 2006. V.88. P. 221106.

19. Fu L.B., Fuerbach A., Littler I.C.M., Eggleton B.J., Efficient optical pulse compression using Chalcogenide single-mode fibers // Appl. Phys. Lett. 2006. V.88. P. 081116.

20. Ta’eed V.G., Fu L.B., Rochette M., Littler I.C.M., Moss D.J., Eggleton B.J. XPM wavelength conversion in highly nonlinear singlemode As_2Se_3 Fiber,” Proceedings of the Conference on Lasers and Electro-Optics, Long Beach, CMW4 (2006).

21. Fu L.B., Rochette M., Ta'eed V., Moss D., Eggleton B.J. Investigation of self-phase modulation based optical regeneration in single mode As_2Se_3 Chalcogenide glass fiber // Opt. Express. 2005. V.13. P. 7637-7641.

22. Aliyev I.I., Ahmedova C.A. Character of the Interaction in the As_2Te_3-TISe System and Electrophysical Propertes of the Phases Obtained Int.// J. Pure Appl. Sci. 2022. V. 8. № 2. P. 302-311. Turkey.

23. Aliyev I.G., Ismailov F.I., Veliev J.A., Aliev I.I. Synthesis and physicochemical research in the As_2Te_3-$TlAs_2Se_2Te_2$ system // International conferences Advances in synthesis and complex formation Moscow, April 18-22, 2011. P. 122-124.

24. Aliyev I.I., Yusibov Y.A., Gurbanov G.B., Mehdiyeva S.A. Phase equilibrium in the As_2Te_3-In_2S_3 system // Ganja State University News. 2017. No. 1. P. 36-40.

25. Aliyev I.I. , Akhmedova C.A., Shafagatova G.G. Phase equilibria in the As_2Te_3-In_2Te_3 system // International Journal of Applied and Fundamental Studies (Moscow "Academy of Natural Sciences"). 2018. No. 12. Part 1. C. 31-35.

26. Aliyev I.I., Ismailova S.Sh., Shakhbazov M.G. Investigation of interactions in the As_2Te_3-$CuCr_2Te_4$ system // Eurasian Union of Scientists 2019. No. 6(63). Part 1. C.46-49.

27. Aliyev I.I., Ismailova S.Sh., Babanly K.N., Mehtieva S.T. Physico-chemical and radiographic research of alloys of the As_2Te_3-Cr_2Te_3 system // Journal inorganic chemistry. 2022. T. 67. No. 4. C. 497-501.

28. Khvorestenko A.C. Arsenic chalcogenides. Обзор из серии Physical and chemical properties of a solid body. - M., 1972. 93 p.

29. State diagram of double metallic systems. Reference: В 3 т.: Т. 3. Kn. 2/ Под. общ. red. Н.П. Лякишева. -М.: Машиностроение, 2000.-448 с.