CHEMICAL SCIENCES

PHYSICO-CHEMICAL STUDY OF PHASE EQUILIBRIUM AND GLASS FORMATION IN THE As_2Se_3-$TlPr_2Se_4$ SYSTEM AND STUDY OF ELECTRICAL CONDUCTIVITY OF GLASSY ALLOYS

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Abstract

Using physicochemical methods of analysis (DTA, MSA, X-ray diffraction, as well as determination of microhardness and density), the phase equilibrium in the As_2Se_3-$TlPr_2Se_4$ system was studied and its T-x phase diagram was constructed. As a result, it was found that the As_2Se_3-$TlPr_2Se_4$ system is quasi-binary and belongs to the eutectic type. The eutectic formed between the As_2Se_3 and $TlPr_2Se_4$ compounds has a composition of 10 mol. % $TlPr_2Se_4$ and a temperature of 270ºC. It was found that the solubility of the system is 2 mol. % $TlPr_2Se$ based on the As_2Se_3 compound and 3.5 mol. % As_2Se_3 based on the $TlPr_2Se_4$ compound at room temperature. The glassy field of 15 mol. % $TlPr_2Se_4$ was determined based on As_2Se_3 upon slow cooling in the system. The temperature dependence of electrical conductivity of 5, 10 and 15 mol. % $TlPr_2Se_4$ glass alloys based on As_2Se_3 was studied.

Keywords: phase equilibrium, glass, eutectic, quasi-binary, microhardness.

Introduction

Arsenic compounds, As_2S_3 (As_2Se_3), are classical glassy semiconductors. Arsenic chalcogenides and their ternary and more complex phases are materials with photovoltaic [1-6], luminescent [7,8] properties and are widely used in IR optics [9,10], color television [11,12] and memory centers [13-15]. Recently, glassy semiconductor fibers based on chalcogenides As_2S_3 (As_2Se_3) [16-20] have been widely studied.

The $TlPr_2Se_4$ compound was obtained as a result of a chemical reaction between the TlSe and Pr_2Se_3 compounds. The TlSe compound and the phases obtained on its basis are materials with photovoltaic properties [3,21-24]. Ternary phases based on the compound Pr_2Se_3 are semiconductor materials with thermoelectric [25] and magnetic [26] properties. A large number of systems consisting of arsenic chalcogenides have been studied in the literature [27–32].

The aim of this work is to construct a T-x phase diagram by studying the phase equilibrium and glass formation in the As_2Se_3-$TlPr_2Se_4$ system, as well as to study the electrical conductivity properties of the obtained phases.

The data for the As_2Se_3 and $TlPr_2Se_4$ compounds are as follows: The As_2Se_3 compound melts congruently at 380ºC and crystallizes in the monoclinic syngony, the lattice parameters are: a = 12.053; b = 9.890; c = 4.277 Å, β = 90º28′, space group P21/n [33]. The microhardness and density of the As_2Se_3 compound in the glassy state are: ρ = 4.618 g/cm^3 and Hμ = 1280-1400 MPa, respectively [33]. The $TlPr_2Se_4$ compound melts at 1290ºC and crystallizes in the rhombic syngony, lattice parameters: a = 7.98; b = 9.88; c = 11.19 Å, density ρ = 7.42 g/cm^3, microhardness Hμ = 2150 MPa [34].

Experimental part

Alloys of the As_2Se_3-$TlPr_2Se_4$ system were synthesized from the components As_2Se_3 and $TlPr_2Se_4$ in a quartz ampoule with air evacuation to a pressure of 0.133 MPa. They were synthesized in the temperature range of 800-1200ºC. To achieve equilibrium, the alloys were heat treated at a temperature of 270°C for 500 hours.

Crystallized alloys were studied using the methods of physicochemical analysis DTA, X-ray phase analysis, MSA, as well as determination of microhardness and density.

Differential-thermal analysis of the alloys was carried out on an NTR-73 pyrometer using a chromel-aluminum thermocouple with a heating rate of 9°C/min. X-ray phase analysis was carried out on an X-ray diffractometer D2 PHASER. Microstructural analysis was carried out on a metallographic microscope MIM-8. Microhardness was measured using a PMT-3 device. The density of the alloys of the system was determined by pucnometric weighing, toluene was used as the working fluid. Physical measurements were carried out using the compensation method [35].

Results and discussion

Alloys of the As_2Se_3-$TlPr_2Se_4$ system in the range of 0-20 mol. % $TlPr_2Se_4$ are glassy and represent shiny black substances. The remaining alloys are gray-black substances. Alloys rich in the As_2Se_3 compound are resistant to water, air and organic solvents. They dissolve well in hot acid HNO_3 and alkalis (NaOH, KOH). Alloys rich in the $TlPr_2Se_4$ compound dissolve well in strong acids (HNO_3, H_2SO_4).

Alloys of the As_2Se_3-$TlPr_2Se_4$ system were studied in glass and crystalline form using physicochemical methods of analysis. Thermal analysis of alloys 0-30 mol. % $TlPr_2Se_4$ before heat treatment showed that the softening temperature Tg is observed on the thermograms of the alloys. Alloys in the range of 0–15 mol.% $TlPr_2Se_4$ are glassy, and alloys in the range of 15–30 mol.% $TlPr_2Se_4$ are glassy-crystalline. The remaining alloys are in the crystalline state.

After crystallization of the alloys of the system for 700 hours at 190°C, the softening temperature disappears from their thermograms, and instead, temperature effects corresponding to the solidus and liquidus are observed. The temperature effects observed in the thermograms of glassy alloys are irreversible.

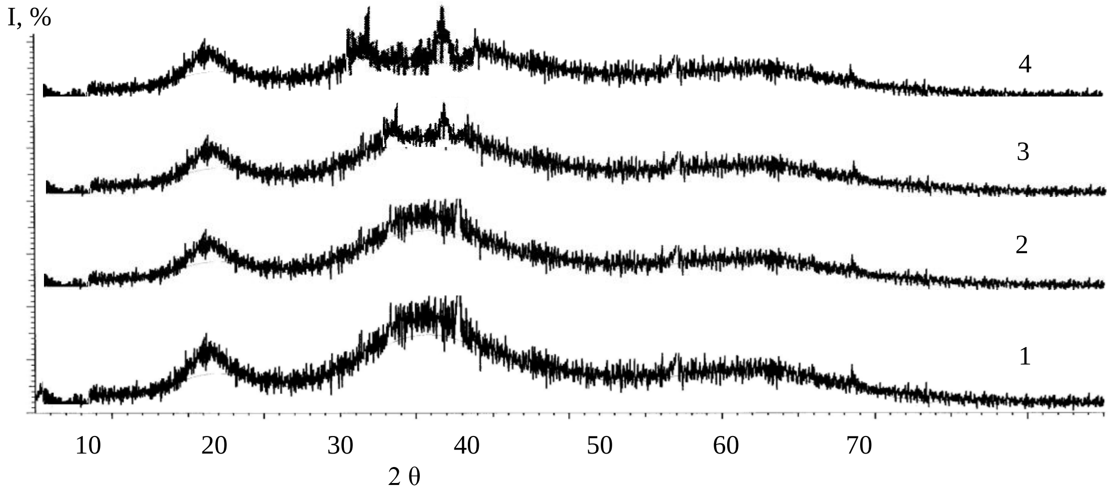
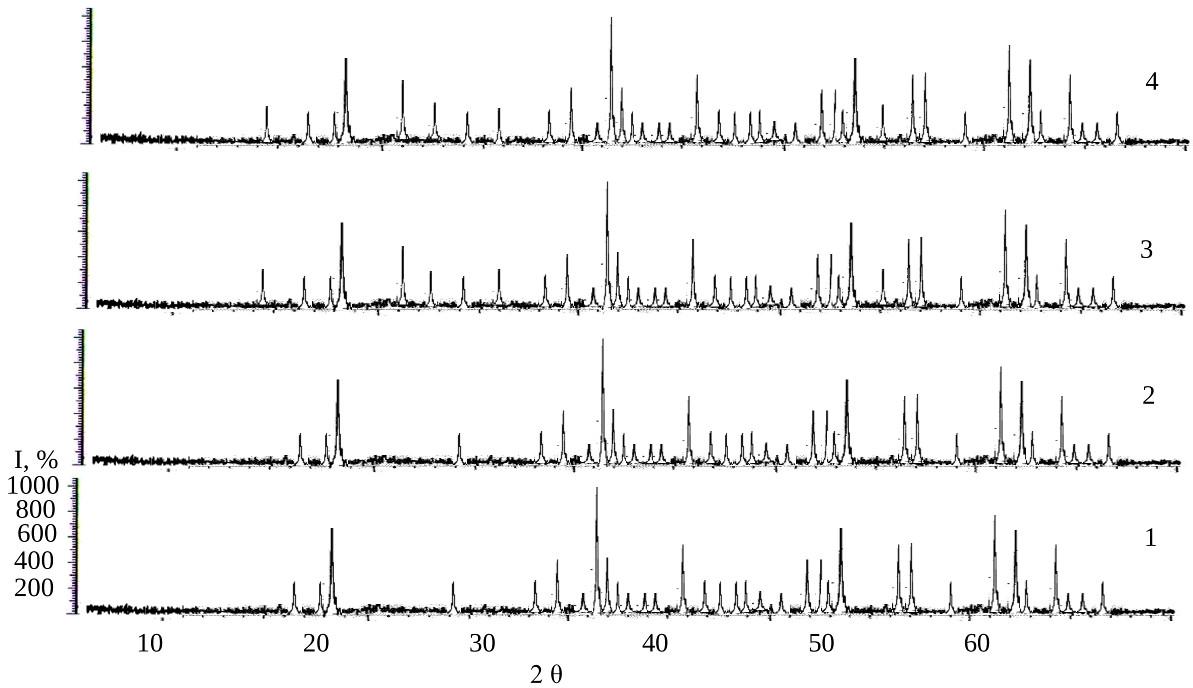


Fig. 1. Diffraction patterns of alloys of the As_2Se_3-$TlPr_2Se_4$ system from the glassy region.



1- As_2Se_3, 2-5 mol %, 3-10 mol %, 4-15 mol % $TlP_{r2}Se_4$.

Fig. 2. Diffraction patterns of crystalline alloys of the As_2Se_3-$TlPr_2Se_4$ system.
1- As_2Se_3, 2-5 mol %, 3-10 mol %, 4-15 mol % $TlPr_2Se_4$.

Microstructural analysis (MSA) of glassy alloys of the As_2Se_3-$TlPr_2Se_4$ system shows that the phases that make up the glassy alloys are opaque and look like a single phase, which makes it difficult to detect the phase boundary and solid solution. After crystallization of the samples, the phase boundaries inside them become clear. To confirm the results of differential-thermal and microstructural analysis, X-ray phase analysis of samples from different regions of the system was carried out in both the glassy and crystalline states.

As a result of the X-ray phase analysis, it was established that no diffraction maxima were found on the diffractograms of glassy samples (Fig. 1). After a long thermal treatment, diffraction maxima are observed on the diffractograms of the samples (Fig. 2). This indicates that the vitreous alloys of the system are completely crystallized after heat treatment.

If we consider the crystalline and glassy state of the system As_2Se_3-$TlPr_2Se_4$ with As_2Se_3, 5, 10 and 15 mol. % $TlPr_2Se_4$, then you can see that noticeable changes in the diffractograms of samples As_2Se_3 and 5 mol. % $TlPr_2Se_4$ is not observed. However, on the diffractograms of samples 10 and 15 mol. % $TlPr_2Se_4$ additional small diffraction lines are observed.

Thus, the results of DTA and microstructural analysis were confirmed by the X-ray phase analysis method.

Based on the results of complex physicochemical analysis methods, the T-x phase diagram of the As_2Se_3-$TlPr_2Se_4$ system was constructed (Fig. 3). The As_2Se_3-$TlPr_2Se_4$ system is quasi-binary and eutectic. The eutectic formed in the system has a composition of 10 mol. % $TlPr_2Se_4$ and a temperature of 270°C. In the system at room temperature, solid solutions based on the As_2Se_3 compound reach up to 2 mol. % $TlPr_2Se_4$, and based on $TlPr_2Se_4$ - up to 3.5 mol. % As_2Se_3. The glass formation region based on As_2Se_3 during slow cooling extends to 15 mol. % $TlPr_2Se_4$ in the As_2Se_3-$TlPr_2Se_4$ system.

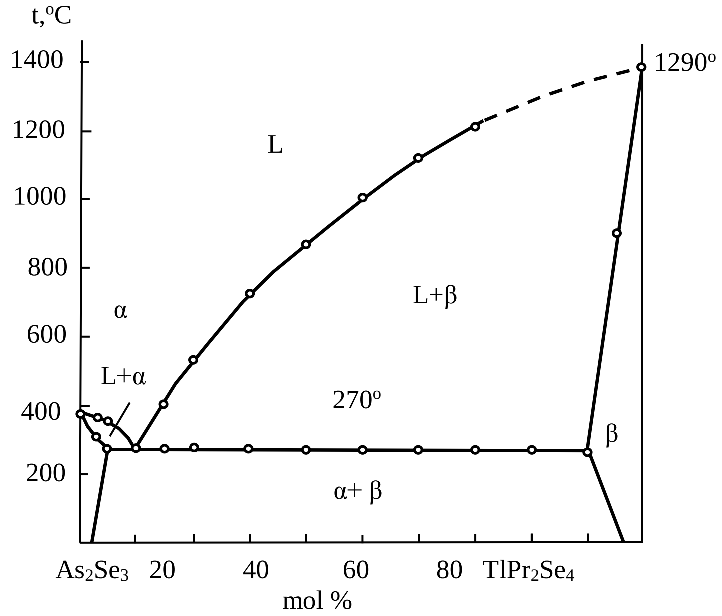


Fig. 3. T-x phase diagram of the As_2Se_3-$TlPr_2Se_4$ system.

The microhardness and density of the As_2Se_3-$TlPr_2Se_4$ system alloys were also studied in the glassy and crystalline states and are given in Tables 1 and 2. Thermal effects, density and microhardness of the alloys in the glassy state are given in Table 1.

When measuring the microhardness of the alloys, two different microhardness values were obtained. One of them corresponds to the microhardness of the α-solid solution obtained on the basis of the As_2Se_3 compound, and the other - to the β-solid solution obtained on the basis of $TlPr_2Se_4$.

Table 1.

Composition, results of DTA, density and microhardness measurements of alloys of the As_2Se_3 - $TlPr_2Se_4$ system (in glassy form)

Composition, mol %		Thermal effects, °C	Density, q/cm^3	Microhardness, MPa	
As_2Se_3	$TlPr_2Se_4$			α	β
				P=0.15 N	
100	0,0	180.380	4,62	1380	–
97	3,0	180,260,375	4,65	1390	
95	5,0	180,270.360	4,72	1390	–
90	10	185,270	4,90	1400	–
85	15	185,270,400	5,04	1400	
80	20	190,270,530	5,17	1400	–
70	30	190,270,730	5,45	1400	–
60	40	270,825	5,74	-	2180
50	50	270,1010	6,02	-	2180
40	60	270,1125	6,30	–	2180
30	70	270,1220	6,58	–	2180
20	80	270	6,86	–	2180
10	90	270	7,30	–	2180
5.0	95	910	7,45	–	2170
0.0	100	1290	7,42	–	2150

Table 2.

Composition, results of DTA, density and microhardness measurements of alloys of the As_2Se_3 - $TlPr_2Se_4$ system (in crystal form)

Composition, mol %		Thermal effects, °C	Density, q/cm^3	Microhardness, MPa	
As_2Se_3	$TlPr_2Se_4$			α	β
				P=0.10 N	P=0.20 N
100	0,0	380	5,10	860	–
97	3,0	260,375	5,18	900	
95	5,0	320.360	5,25	900	–
90	10	270	5,33	Eutec.	Eutec.
85	15	270,400	5,44	–	–
80	20	270,530	5,56	–	–
70	30	270,730	5,80	–	2180
60	40	270,825	6,03	–	2180
50	50	270,1010	6,26	–	2180
40	60	270,1125	6,49	–	2180
30	70	270,1220	6,72	–	2180
20	80	270	6,96	–	2180
10	90	270	7,19	–	2180
5.0	95	910	7.48	–	2170
0.0	100	1290	7,42	–	2150

The microhardness of the glass of the α-solid solution obtained on the basis of As_2Se_3 varies in the range of (1380-1400) MPa. The microhardness of the β-solid solution based on $TlPr_2Se_4$ is (2150 - 2180) MPa. After crystallization of the samples, the microhardness of the α-solid solution alloys obtained on the basis of As_2Se_3 was (860-900) MPa. Since the β-solid solution alloys based on $TlPr_2Se_4$ are in the crystalline state, the microhardness of the alloys remained unchanged (2150 - 2180) MPa. The temperature dependence of the electrical conductivity of glasses of the As_2Se_3-$TlPr_2Se_4$, As_2Se_3, 5, 10 and 15 mol. % $TlPr_2Se_4$ system was studied (Fig. 4). Samples of the specified composition were cooled equally slowly.

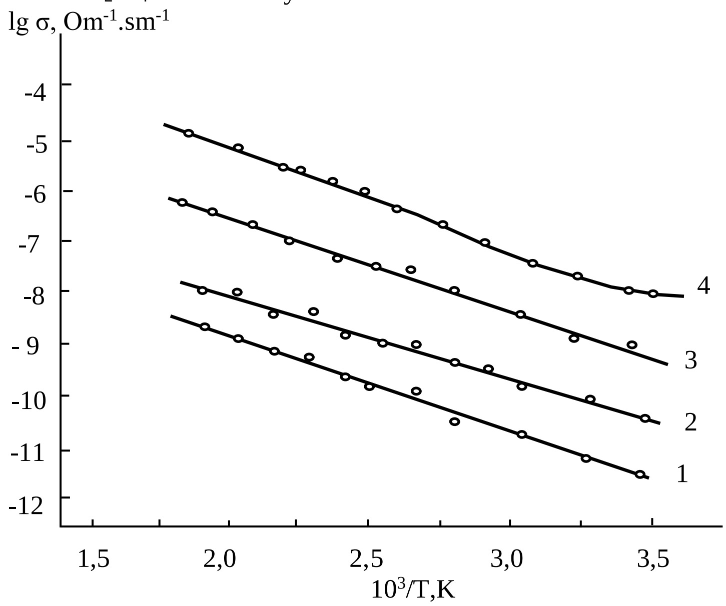


Fig. 4. Diffraction patterns of crystalline alloys of the As_2Se_3-$TlPr_2Se_4$ system.
1- As_2Se_3, 2-5 mol. %, 3-10 mol. %, 4-15 mol. % $TlPr_2Se_4$.

As can be seen from the temperature dependence graph of electrical conductivity, the electrical conductivity of As_2Se_3 samples, 5, 10 and 15 mol % $TlPr_2Se_4$ increases linearly depending on temperature and composition. Electrical conductivity is achieved by means of an electronic mechanism.

Conclusion

To study the phase equilibrium in the As_2Se_3-$TlPr_2Se_4$ system, alloys were synthesized in a wide range of concentrations and then subjected to heat treatment at a temperature of 270°C for 700 hours. Then the alloys were studied using the methods of physicochemical analysis (DTA, MSA, X-ray diffraction, as well as determination of microhardness and density) and the T-x phase diagram of the As_2Se_3-$TlPr_2Se_4$ system was constructed. It was found that the As_2Se_3-$TlPr_2Se_4$ system is quasi-binary and belongs to the eutectic type. The eutectic formed between the As_2Se_3 and $TlPr_2Se_4$ compounds has a composition of 10 mol. % $TlPr_2Se_4$

and a temperature of 270ºC. It was found that the solubility of the system is 2 mol. % based on the As_2Se_3 compound and 3.5 mol. % based on the $TlPr_2Se_4$ compound at room temperature. The glassy field of 15 mol. % $TlPr_2Se_4$ was determined based on As_2Se_3 during slow cooling in the system. The dependence of the electrical conductivity of the As_2Se_3-$TlPr_2Se_4$ system and glass alloys containing As_2Se_3, 5, 10 and 15 mol. % $TlPr_2Se_4$ on temperature and composition was studied. The indicated glassy alloys are high-resistance semiconductors.

References:

1. 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.
2. 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.
3. Алиев И.И., Бабанлы М.Б., Фарзалиев А.А. Оптические и фотоэлектрические свойства тонких пленок стекол $(As_2Se_3)_{1-x}(TlSe)_x$ (x=0,05-0,10) // XI Международная конференция по физике и технологии тонких пленок. Иваново-Франковск, Украина, 7-12 мая, 2007. С. 86.
4. Dinesh Chandra SATI1, Rajendra KUMAR, Ram Mohan MEHRA Influence of Thickness Oil Optical Properties of a: As_2Se_3 Thin Films // Turk J. Phys. 2006. V.30. P. 519- 527.
5. Burdiyan I.I., Feshchenco I.S. Photocurrent and Optical Transmission Spectra of Sn-and Pb-Doped $(As_2S_3)_{0,3}(As_2Se_3)_{0,7}$ Glass Films, Inorgan. Materials. 2005. T.41. № 9. P. 1013-1016.
6. HinevaT., PetkovaT., Popov C., PektovP., Reithmaier J. P., Funrmann-Lieker T.,Axente E., Sima F., Mihailescu C. N., Socol G., MihailescuI. N. Optical study of thin $(As_2Se_3)_{1-x}(AgI)_x$ films // Journal of optoelektronics and Advanced Materials. 2007. V.9. No. 2. February. P. 326-329.
7. Бабаев А. А., Мурадов Р., Султанов С. Б., АсхабовА.М. Влияние условий получения на оптические и фотолюминесцентные свойства стеклообразных As_2S_3 // Неорган. материалы. 2008. Т.44. №11. С. 1187-1201.
8. Курганова А., Snopatin G.E., Сучков А. И. Рентгено-флуоресцентный Определение макроскопической состава As-S, As-Se и As-S-Seочки // Неорган. материалы. 2009. Т.45. № 12. С. 1408-1413.
9. Wozniak R.L. Infrared transmitting optical element. -U.S. Pat.3.033.701. May 8. 1962.
10. Kapany N.S.,Simms R.J.Recent development in ififrared fiber optics.-"Infrared Phys."1965. N. 5. N 2. P. 69-80.
11. Коломиец Б.Т., Любин В.М. Некоторые особенности фотоэффекта в аморфных слоях трехселенистого мышьяка. - "Докл. АН СССР". 1959. Т. 129. С. 789-793.
12. Любин В.М., Коломиец Б.Т. Электрические и фотоэлектрические свойства слоев селенида мышьяка. -'Физ. тв. тела"/ 1962. Т. 4. N 2. С. 401-106.
13. Ovshinsky S.R. Symmetrical current controlling device.- U.S.Pat.3. 271. 591. Sept. 6. 1966.
14. Mackenzie J.D.Glass as material for the nww active components. -"Electronics" .1966. V.39. 19. P.129-136.
15. Perry G.A.,Riseman J.New dimensions in IC's through films of glass.-"Electronics". 1966. V.39. N 20. P. 108-110.
16. Pudo D., Mägi E.C., and Eggleton B.J. Long-period gratings in Chalcogenide fibers. Opt. Express 2006. V. 14. P. 3763-3766.
17. Lee S.S., Kim H.S., Hwang I.K. and Yun S.H. Highly-efficient broadband acoustic transducer for all-fiber acousto-optic devices. Electron. Lett. 2003. V. 39. P. 1309-1310.
18. 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. 1499-150.
19. Hari P., Cheneya C., Luepkea G., Singha S., Tolka N., Sanghera J.S., Aggarwal D.. Wavelength selective materials modification of bulk As_2S_3 and As_2Se_3 by free electron laser irradiation // Journal of Non-Crystalline Solids. 2000. V. 270. P. 265-268.
20. L.B. Fu, M. Rochette, V. Ta'eed, D. Moss, and B.J. Eggleton, "Investigation of self-phase modulation based optical regeneration in single mode As_2Se_3 Chalcogenide glass fiber," Opt. Express 2005. V. 13. P. 7637-7640.
21. Кириленко В.В., Дембовский С.А., Поляков Ю.А. Оптические свойства стекол в системах As_2S_3–TlS и As_2Se_3–TlSe // Известия АН СССР. Неорган. материалы. 1975. Т.11. № 11. С. 1923-1928.
22. Ahmedova C. Investigations of chemical interaction and glass formation in the system As_2S_3-$TlGaTe_2$ //Sciences of Europe (Praha, Czech Republic) # 127, (2023) P. 8-12.
23. Ahmedova C. Synthesis and investigation of glass formation and properties of obtained phases in the As_2S_3-$TlInSe_2$ system. Norwegian Journal of development of the International Science No 87/2022. P. 12-17. https://doi.org/10.5281/zenodo.6778279
24. Selahattin Ozdemir, Mahmut Bucurgat. Photoelectical properties of $TlGaSe_2$ Single Crystals // Solid State Sciences 2014. V.33. P. 26-30. DOI:10.1016/j.solidstatesciences.2014.04.006
25. Никифоров В. Н., Морозкин А. В., Ирхин В. Ю. Термоэлектрические свойства редкоземельных сплавов // Физика металлов и материаловедение 2013. Т. 114. № 8. С.711-720.
26. Кудреватых Н. В., Волегов А. С. Магнетизм редкоземельных металлов и их интерметаллических соединений -Екатеринбург Издательство Уральского университета 2015. 196 с.
27. Велиев Дж.А, Алиев И.И., МамедоваА.З. Фазовое равновесие в системе As_2S_3-TlSe // Журн. неорган. химии. 2007. Т. 52. № 2. С. 312-315.
28. Фарзалиев А.А., Алиев И.И., Алиев О.М., Алиев И.Г. Фазообразование в системе As_2Se_3-TlSe // Химические Проблемы. 2006. № 2. С. 284-287.
29. Алиев И.И., Ильясов Т.М. СистемаAs_2Se_3-Tl_2S // Известия АН СССР, Неорган.материалы, 1987. Т. 24. № 5.С. 867-868.

30. Алиев И.И., Алиев О.М., Рустамов Г.П., Ильясов Т.М. Химическое взаимодействие и стеклаобразование в системе As_2Se_3 –Tl_2Te// Журн. неорган. химии. 1988. Т. 33. № 9. С. 2376-2378.

31. Aliyev I.I., Rzaev R.M., Gashimov Kh..M., Ahmedova C.A, Zeynalova G.Z., Abbasova V.A Investigation of glass formation and physico0chemical properties obtained phases in the As_2Te_3-TlS system // Azerbaijan chemical journal. 2025. № 1. P. 119-126.

32. АлиевИ.И., Алиев О.М., Багиров Ш.А., Алиев Ф.Г. Химическое взаимодействие и стеклообразование в системе As_2S_3 - TlTe // Изв.АН СССР, Неорган. материалы. 1991. Т.27. № 11. С. 2271-2273.

33. Хворестенко А.С. Халькогениды мышьяка. Обзор из серии Физические и химические свойства твердого тела. - М., 1972. 93 с.

34. Велиев С., Чобан А.. Фазовая диаграмма состояния системы TISe-Pr_2Se_3 // Журн. неорган. химии. 2014. Т. 59. № 1. С. 81-84.

35. Охотин А.С., Пушкарский Н.С., Боровикова Р.П., Смирнов Р.А. Методы исследования термоэлектрических свойств полупроводников. М.: Атомиздат, 1969. 175 с.