PHYSICAL-CHEMICAL INVESTIGATION OF CHEMICAL INTERACTION AND GLASS FORMATION IN THE $TlAsSe_2$-InSe SYSTEM

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Abstract

Using physicochemical methods of analysis: differential thermal analysis (DTA), X-ray diffraction (XRD), microstructural analysis (MSA), as well as by measuring density and microhardness, chemical interactions and glass formation in the $TlAsSe_2$-InSe system were studied and a T-x phase diagram was constructed. It has been established that the phase diagram of the $TlAsSe_2$-InSe system is a quasi-binary section of the quasi-ternary Tl_2Se-As_2Se_3-InSe system and is eutectic. The composition of the eutectic formed between the $TlAsSe_2$ and InSe compounds in the system is 20 mol % InSe, temperature 170°C. In the system at room temperature, solid solutions based on $TlAsSe_2$ reach 5 mol % InSe, and solid solutions based on InSe amount to 2.5 mol % $TlAsSe_2$. The glass formation regions based on $TlAsSe_2$ extend up to 20 mol % InSe.

Keywords: glass formation, quasi-binary, eutectic, microhardness, phase diagram.

İntroduction

The $TlAsSe_2$ component included in the $TlAsSe_2$-InSe system is obtained from the As_2Se_3 and Tl_2Se compounds. These components that made up the system were materials with functional properties. Arsenic chalcogenides are widely used as photosensitive [1-5] and luminescent [6,7] materials in optical systems. In recent years, glassy chalcogenide fibers based on arsenic chalcogenides have found application as a compact nonlinear medium providing efficient Romanov amplification and lasing, pulse compression, optical regeneration, and wavelength conversion [8–10]. Thallium compounds with ternary chalcogenide phases obtained on their basis are photosensitive semiconductors in the visible region of the spectrum [11,12]. The InSe compound, its ternary compounds and solid solutions are semiconductor materials with photosensitive and thermoelectric properties [13,14]. Many systems consisting of arsenic hacogenides have been studied in the literature [15–20]. From this point of view, alloys of complex composition obtained by chemical interaction of $TlAsSe_2$ and InSe compounds can also be photosensitive materials.

The $TlAsSe_2$ compound melts congruently at 265°C, its microhardness is 920 MPa, Tg=100°C [21]. The InSe compound melts congruently at 660°C and crystallizes in the hexagonal syngony, lattice parameter: a = 0.405 nm, c = 1.693 nm, space gr. P63/mmc has a density of 5.56 g/cm^3 [22].

Experimental part

Alloys of the $TlAsSe_2$-InSe system were synthesized from the $TlAsSe_2$ and InSe components by comelting in quartz ampoules, evacuated to a pressure of 0.133 Pa in the temperature range 500-800°C. To bring the alloys to equilibrium, they were subjected to heat treatment at a temperature of 170°C for 350 hours. Then the alloys of the system were studied by DTA, X-ray diffraction analysis, MSA, density and microhardness measurements.

Differential thermal analysis was carried out using a TERMOSCAN-2 device. The heating rate of the alloys was 5 degrees/min. Chromel-alumel was used as a thermocouple.

X-ray phase analysis of the alloys was carried out on a D2 PHASER X-ray diffractometer. A CuKα electrode was used as an irradiator. Microhardness was measured using a PMT-3 metallographic microscope. Microstructure analysis was carried out using a MIM-8 microscope. When determining the densities of the system alloys, the pycnometric method was used and toluene was used as a filling solution.

Results and its discussion

In the $TlAsSe_2$-InSe system, alloys obtained in the range of 0-20 mol % InSe is glassy, and the remaining alloys are dark gray substances obtained in the form of crystals. During the differential thermal analysis of the alloys, it was established that two endothermic effects are observed in the thermograms of the samples. It has been established that in the thermograms of alloys in the concentration range of 0–20 mol % InSe has a softening temperature Tg = 100°C, characteristic of glasses. When studying the microstructure of alloys of the $TlAsSe_2$-InSe system, single- and two-phase regions were discovered. In Fig. 1 shows the microstructures of alloys of the $TlAsSe_2$-InSe system with a content of 5, 60 and 97.5 mol % InSe.

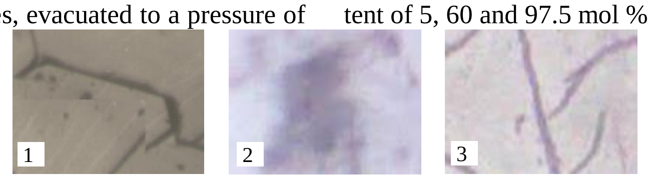

Figure 1. Microstructures of $TlAsSe_2$-InSe system alloys.
1-5 mol %, 2-60 mol %, 5-97.5 mol % InSe.

As can be seen from the microstructure, single-phase samples 5 and 97.5 mol % InSe are solid solution alloys based on $TlAsSe_2$ and InSe compounds, respectively. Sample 60 mol % InSe is a two-phase field alloy.

To clarify the results of microstructural and differential thermal analysis, X-ray phase analysis of alloys containing 5, 10, 20, 60 and 97.5 mol % InSe (Fig. 2).

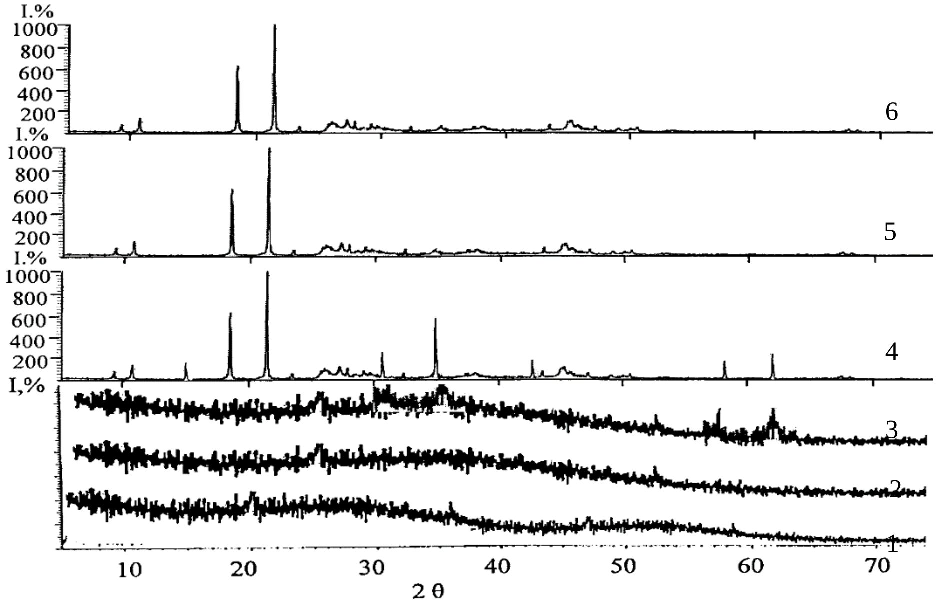

Fig. 2. X-ray diffraction patterns of alloys of the $TlAsSe_2$-InSe system. 1-$TlAsSe_2$, 2-5, 3-10, 4-20, 5-93 mol %, 6-100 mol % InSe.

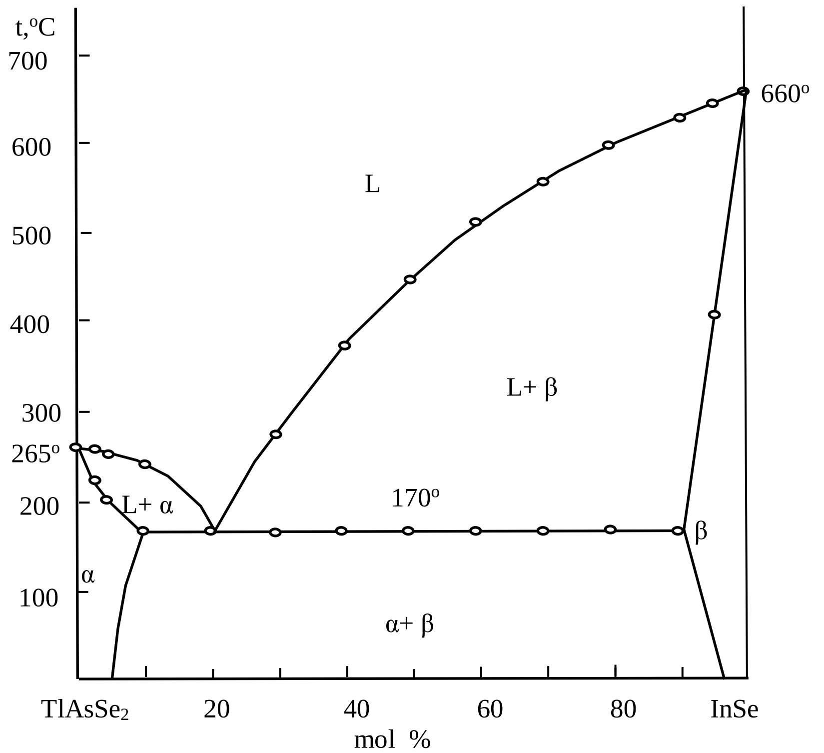

Fig. 3. T-x phase diagram of the $TlAsSe_2$-InSe system.

It was found that samples containing 5, 10, 20 mol % InSe are glassy. Existing diffraction lines in the diffraction pattern of the 60 mol % InSe alloy is a mixture of diffraction lines of $TlAsSe_2$ and InSe compounds, that is, it is a two-phase alloy. Diffraction lines of a sample containing 97.5 mol % InSe are identical to the diffraction lines of the InSe compound, that is, they are solid solutions based on InSe. The T-x phase diagram of the $TlAsSe_2$-InSe system was constructed based on the results of physicochemical analysis methods (Fig. 3). The $TlAsSe_2$-InSe system is quasi-binary and eutectic. The composition of the eutectic formed between the $TlAsSe_2$ and InSe compounds is 20 mol % InSe, temperature 170°C. In a system at room temperature, the region of solid solution based on the $TlAsSe_2$ compound is 5 mol % InSe, and the base InSe is up to 2.5 mol % $TlAsSe_2$. In the $TlAsSe_2$-InSe system, upon slow cooling based on $TlAsSe_2$, the glass transition regions expand to 20 mol % InSe.

liquidus of the $TlAsSe_2$-InSe system consists of the primary crystallization curves of an α-solid solution based on the $TlAsSe_2$ compound and a β-solid solution based on InSe. Two-phase alloys consisting of (α+β) crystallize below the solidus line in the system.

When measuring the microhardness of alloys of the $TlAsSe_2$-InSe system, two different values were obtained. The microhardness of α-solid solutions obtained based on the $TlAsSe_2$ compound varies within the range (920-1050) MPa. The microhardness of β-solid solutions based on the InSe compound varies within the range (600-680) MPa. Table 1 shows some physicochemical properties of alloys of the $TlAsSe_2$-InSe system after heat treatment.

Table 1.

Composition of alloys of the $TlAsSe_2$-InSe system, results of DTA, density and microhardness measurements.

Composition, mol %		Thermal effects, ºC	Density, q/cm^3	Microhardness, MPa	
				δ	α
$TlAsSe_2$	InSe			P=0,10 N	P=0,15 N
100	**0.0**	265	7,45	920	–
97	**3,0**	225,265	7,46	1050	–
95	**5,0**	200,250	7,40	1050	–
90	**10**	170,240	7,27	–	–
80	**20**	170	7,07	Eutek.	Eutek.
70	**30**	170,275	6,88	–	–
60	**40**	170,370	6,66	–	680
50	**50**	170,440	6,50	–	680
40	**60**	170,510	6,32	–	680
30	**70**	170,560	6,12	–	680
20	**80**	170,600	5,94	–	680
10	**90**	170,625	5,74	–	680
5,0	**95**	410,650	5,65	–	670
0,0	**100**	660	5,56		600

Conclusion

The T-x phase diagram of the $TlAsSe_2$-InSe system was constructed based on the results of physicochemical analyses. The phase diagram of the system is quasi-binary, eutectic type. Cocrystallization of $TlAsSe_2$ and InSe compounds ends at the double eutectic point of composition 20 mol % InSe, temperature 170°C. In the $TlAsSe_2$-InSe system at room temperature, solid solutions based on the $TlAsSe_2$ compound reach 5 mol % InSe, and based on InSe compounds - up to 2.5 mol % $TlAsSe_2$. In the $TlAsSe_2$-InSe system, upon slow cooling based on the $TlAsSe_2$ compound, the glass transition region expands to 20 mol % InSe.

References:

1. Lovu M., Shutov S., Rebeja S., Colomeyco E., Popescu M. Effect of metal additives on photodarkening kinetics in amorphous As_2Se_3 films. Journal of Optoelectronics and Advanced Materials 2000. V. 2, Issue: 1. P 53-58.

2. 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.

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

4. Shiryaev V.S., Smetanin S.V., Ovchinnikov D.K., Churbanov M.F., Kryukova E.B., and Plotnichenko V.G. Effects of Oxygen and Carbon Impurities on the Optical Transmission of As_2Se_3 Glass. Inorgan. materials. 2005. T.41. № 3. P. 308-312.

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

6. 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.

7. 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.

8. 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. 7637.

9. Fu L.B., Rochette M., Ta'eed V., Moss D., and 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.

10. Pudo D., Mägi E.C., and Eggleton B.J., "Long-period gratings in Chalcogenide fibers. Opt. Express. 2006. V.14. P. 3763-3766.

11. 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.

12. 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.

13. Kazim-zade A.G., Agaeva A.A., Salmanov V.M., Mokhtari A.G. Optical radiation detectors based on layered crystals and InSe. Technical Physics. 2007. T.7. Issue 4. P. 80-82.

14. Gasanova L.G. Kyazym-zade A.G., Salmanov V.M., Guseinov A.G., Optical nonlinearities in GaSe and InSe crystals under laser excitation. Optics and Spectroscopy. 2014. T. 116. No. 4. P. 130-133.

15. Aliyev I.I., Gamidova Sh.A., Suleymanova M.G., Kahramanov Sh.T., Ahmedova C.A. The nature of chemical interaction and glass formation in the As_2Se_3-TlS system. Scientific journal. Archivist. 2022, T: 7, No.: 9(63), P.18-22.

16. Rzaev R.M., Aliyev1 I.I., Gashimov Kh.M.. Ahmedova C.A**.** Synthesis and investigation of physico-chemical properties alloys of the As_2S_3-Tl_2Te_3 system UNEC. Journal of Engineering and Applied Sciences Vol. 2, No. 2, 2022, P. 45-50.

17. Aliyev I.I. , Ragimova V.M., Ahmedova C.A., Shakhbazov M.G., Gashimov Kh.M. Investigation of phase formation and glass formation in the As_2Se_3-TlTe system. Norwegian Journal of development of the International Science, 2022, № 88, P. 3-10.

18. Aliyev I.I., RzayevR.M., Hashimov Kh.M., Ahmedova C.A., Naghiyev T.G. An investigation of structural, thermo-physical, and photoelectric properties ofglassy As_2Se_3–Tl_2Te_3 alloys Modern Physics letters B, Online Ready https://doi.org/10.1142/SO217984924502324

19. Farzaliev A.A., Aliyev I.I., Aliyev O.M., Aliyev I.G. Study of phase formation in the As_2Se_3–TlSe system. Chemical Problems. 2006. No. 2. P. 284-287.

20. Ahmedova C. A. Investigations of Chemical interaction and glass formation in the system As_2S_3 – $TlGaTe_2$. Sciences of Europe # 127, (2023). P. 8-12.

21. Kirilenko V.V., Nikitna V.K., Dembschvski S.A. Glass formation and features of chemical interaction in chalcogenide systems As_2X_3-Tl_2X. Inorg. materials. 1975. T.11. No. 11. S. 1929-1935.

22. State diagram of binary metal systems. Directory: In 3 volumes: T. 3. Book. 1/ Sub.general ed. N.P. Lyakisheva.-M.: Mechanical Engineering, 2001.-872 p.