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GLASS FORMATION AND PROPERTIES OF THE GLASSES OF THE Ho-As-S SYSTEM ALONG As_2S_3-Ho AND AsS-Ho CROSS-SECTIONS

Teymur Ilyasly, Dunya Hasanova*, Humay Huseynova

Department of General and Inorganic Chemistry, Baku State University, Baku, Azerbaijan

Abstract. Holmium and its chalcogenides are considered to be promising materials for electronic technology, like luminescent and photovoltaic materials. The Ho-As-S system has been studied along the As_2S_3-Ho and AsS-Ho cross-sections by complex methods of physicochemical analysis. A glass area appeared on the basis of arsenic sulfides As_2S and AsS in various cooling modes, it has been determined that the glass formation region is wider on the basis of As_2S_3 than AsS. When studying the properties of glasses, it has been found that the values of macroscopic properties increase with increasing holmium concentration. It is assumed that new structural units are formed in glasses according to the results of differential thermal analysis (DTA), X-ray phase analysis (XRD), microstructural analysis (MSA), measurements of microhardness, electrical.

Keywords: *glass, synthesis, alloy, structural unit, quenching, temperature.*

Corresponding Author: *Dunya Hasanova, Department of General and Inorganic Chemistry, Baku State University, 23 H. Javid ave., AZ-1148, Baku, Azerbaijan e-mail: dunyahesenova93@mail.ru*

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1. Introduction

Chalcogenide glassy semiconductors based on arsenic chalcogenides exhibit significant photoinduced changes in optical, photoelectric and physicochemical properties, which make these compounds promising materials for obtaining new type photoresistors for the needs of microelectronics (Reinfelde *et al.*, 2011; Ashok *et al.*, 2012; 2013; Kandpal & Kushuana, 2007; Bonazzi & Bindi, 2008; Hari *et al.*, 2000; Efimov *et al.*, 2001).

It is known that the fraction of ionic bond does not exceed 10% in chalcogenide glasses (Minayev, 1991; Borisova, 1972). The proportion of the ionic bonds increases when rare earth elements are included in the composition of the glasses, which reduces the region of glass formation.

The covalent structure of chalcogenide glasses blocks the formation of ionic bonds, which explains the absence of impurity conductivity in them.

There are numerous works in the literature on the interaction of arsenic chalcogenides and lanthanide chalcogenides (Gahramanova, 2020; Ilyasly *et al.*, 2018; Efendiyev *et al.*, 1987; Khudiyeva *et al.*, 2016; Rustamov *et al.*, 1987; Ilyasly & Mammadov, 1987), but there are scarce data on the compounds with participation of holmium (Ilyasly *et al.*, 2021).

2. Experiments and results

The purpose of this work is to determine the glass formation regions in the Ho-As-S system along the As_2S_3-Ho and AsS-Ho cross-sections and to study some physicochemical properties of glasses.

The initial samples of the system have been synthesized from elements with a high purity grade As - B5, Ho - A1 sulfur with chemical grade of pure for analysis.

The synthesis mode has been chosen according to the physicochemical properties of the initial components and the recording results of the synthesis of the initial ligatures. Synthesis has been carried out in quartz containers evacuated to 10^{-3} Hg. The synthesis mode was stepwise: at a temperature of 750K for 2 hours, at 950K for 2 hours, and at a temperature of 1200K for 4 hours. The melts have been cooled by hardening in air and in cold water. This resulted in obtaining the samples of cherry-red color in a glassy form. In the As_2S_3-Ho and AsS-Ho systems, the glass formation region reaches 10at% Ho and 5at% Ho, respectively, during cooling by 10 deg/min.

The synthesized alloys have been subjected to research using a set of methods of physicochemical analysis.

Differential thermal analysis (DTA) has been carried out on a "Thermoscan-2" device using the chromel/alumel thermocouple.

X-ray phase analysis has been performed on a D-2 PHSEP diffractometer using CuK_α radiation with a Ni filter. Microstructural analysis (MSA) of the alloys of the system has been studied using the МИН-8 and МИМ-7 microscopes on etched samples ground and polished with GOI paste.

The etching agent was a mixture of the composition HNO_3:H_2O_2=1:1, the etching time was 10-15 seconds. The microhardness of alloys (glasses) has been measured on a ПМТ-3 device at the loadings of 0.10–0.20N. Depending on the composition, the measurement error was 2.2–4.3%. The density of the alloys of these systems has been determined by the pycnometer method; toluene served as a filler.

The study of the glass formation region in the As_2S_3-Ho and AsS-Ho systems was started with the synthesis of initial components and alloys based on arsenic sulfides. The authors of [10] proposed thermodynamic theory on neutral structural vacancies (SV_s) predetermined by unshared electron pairs sp^3 of hybrid clouds of X atoms directed towards structural vacancies studying heterodesmic compounds of the $A_2^{III}X_3^{VI}$ type.

The presence of structural vacancies in crystals predetermines the unusual mechanism of impurity distribution, whereas glass is essentially a stable state of the structural vacancies. Let us consider the issue of holmium dissolution in arsenic trisulfide based on the thermodynamic theory of structural vacancies.

The followings develop out of the theory.

1. The solubility limit of impurities is determined by the value of U_v - the elastic stress on structural vacancies (this value is constant for each crystal) and U_i - the elastic stress on the impurity ion, which in turn is controlled by the size of the impurity atom R=18.5 sm^3/g atom, the including holmium in the glasses is energetically favorable and favors glass formation.

When a non-ionized impurity is included in the glass, only the size factor of the impurity ion matters. In this case the elasticity concept of stress on the structural vacancies for glass loses its meaning.

2. The solubility of holmium increases with increasing temperature, which has been established by us, plotting the microdiagram of the As_2S_3-Ho system according to the experiment results (Fig. 1).
3. Higher thermodynamic stability of the phase with a nonzero- concentration of the impurities is expected than that of the purest phase, which we have observed in the practice.

Thus, the chemical inertness of holmium atoms when included them in glassy arsenic trisulfide is theoretically possible. Investigating the As_2S_3-Ho and AsS-Ho systems, the boundaries of the glass formation region have been established and microdiagrams of these systems have been plotted (Fig.1, 2)

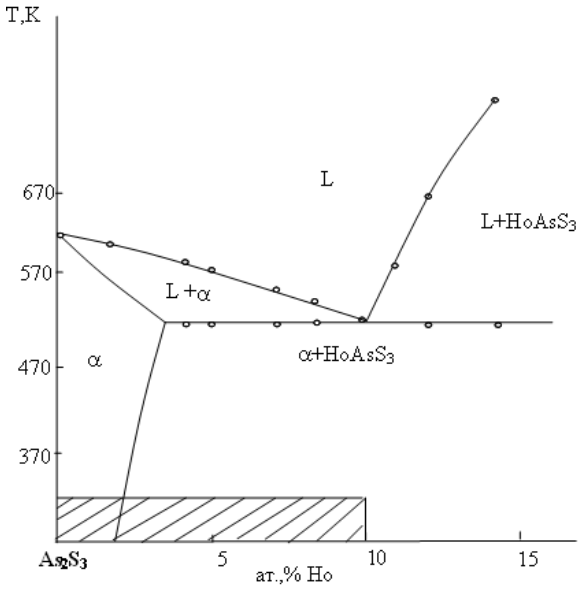


Fig. 1. Microdiagram of the As_2S_3-Ho cross-section
The hatched area is the glass formation region

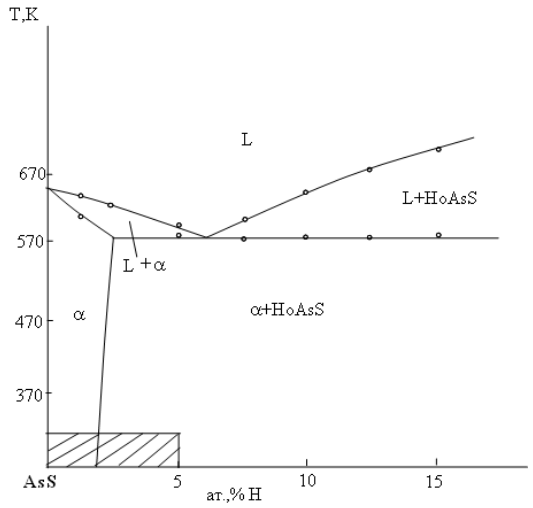


Fig. 2. Microdiagram of AsS-Ho cross-section

Hardenings of the samples based on As_2S_3 and AsS with the participation of holmium has been carried out at 900K by water quenching and air cooling, the results are given in Table 1 and Table 2.

Table 1. States of alloys of the As_2S_3-Ho system under different cooling modes

№	Composition of the alloys in mole %		at%, Ho		Hardening by air cooling	Hardening by water quenching	Temperature of the hardening, K
	As_2S_3	Ho	As_2S_3	Ho			
1	100	0	100	0	glass	glass	900
2	97	3	99,3853	0,6147	glass	glass	900
3	95	5	99,9374	1,0626	glass	glass	900
4	93	7	98,517	1,4830	glass	glass	900
5	90	10	97,8261	2,1739	crys. glass	glass	900
6	85	15	96,9584	3,0416	crys. glass	glass	900

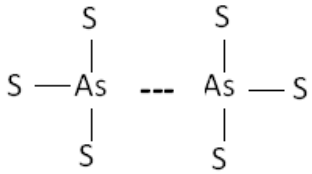
Table 2. States of alloys of the AsS-Ho system under different cooling modes

№	Composition of the alloys in mole %		at%, Ho	Hardening by air cooling	Hardening by water quenching	Temperature of the hardening, K
	As_2S_3	Ho				
1	100	0	0	glass	glass	900
2	97	3	0,5025	glass	glass	900
3	95	5	2,5641	glass	glass	900
4	90	10	5,2631	crys. glass	glass	900
5	85	15	13,0434	crys. glass	crys. glass	900

As is seen from the diagram, there are solubility regions based on As_2S_3 and AsS. Solubility increases with increasing temperature. (Fig. 1, 2)

The existence of the solubility region confirms that atomic and ionized holmium can be dissolved in As_2S_3 and AsS.

As indicated, alloys based on monosulfide and trisulfide are quenched starting from 900K at various rates, and for this case the state of the alloys is indicated in Table. 3.4. As is seen from the table, the values of the macroscopic properties T_g (glass transition temperature), d (density), Hμ (microhardness) increase. This fact indicates that new structural units are formed in glasses corresponding to the following composition:



The electrical conductivity of the obtained glasses has been studied (Fig. 3,4) after determining the glass formation boundary and stabilizing the glasses of the As_2S_3-Ho and AsS-Ho system. As is seen from the figure, the impurity region in glasses is absent within the studied temperature range.

Homogenizing isothermal annealing of holmium doped glasses is quite less than the duration of annealing of pure arsenic trisulfide. The holmium doped glasses

crystallize even during Differential Thermal Analysis (DTA), and it was possible to crystallize arsenic trisulfide at a temperature of 465K for 750 hours.

Thus, the chemical inertness of holmium atoms when included them in glassy arsenic trisulfide is theoretically possible.

Alloys obtained on the basis of As_2S_3 and AsS have been investigated using complex chemical-physical analysis, the results of which are presented in Tables 3 and 4.

Table 3. The values of some physicochemical properties of the glasses of the As_2S_3-Ho system

№	Composition of the alloys, mole %		T_g, K	T_{crys}, K	T_{melt}, K	Microhardness, Hμ, N/m^2. 10^7	Density 10^3 kg/m^3
	As_2S_3	Ho					
1	100	0	450	-	-	128	4,53
2	99	1	450	455	650	135	4,60
3	97	3	455	460	645	135	4,65
4	95	5	460	475	645	140	4,73
5	90	10	465	495	640	145	4,75
6	85	15	480	498	655	148	4,81

Table 4. The value of some physicochemical properties of the glasses of the AsS – Ho system

№	Composition of the alloys, mole %		T_g, K	T_{crys}, K	T_{melt}, K	Microhardness, Hμ, N/m^2, 10^7	Density 10^3 kg/m^3
	AsS	Ho					
1	100	0	-	-	645	118	4,40
2	99	1	440	450	645	120	4,45
3	97	3	450	465	650	125	4,50
4	95	5	465	478	645	128	4,55
5	90	10	470	485	640	135	4,67

The study of electrical properties during a period of time is one of the most important issues in the study of the glassy state. The greatest difference between the crystalline and glassy states is that the electrical conductivity of glasses is less sensitive to impurities and their intrinsic conduction region dominates at lower temperatures. The temperature dependence has been measured on the basis of As_2S_3. The samples of the composition have been synthesized to measure the electrical conductivity of glasses; synthesized samples are presented in Table 5 intended to the developed synthesis for each composition, the cooling of the melts has been carried out with a rate of 10 deg/min.

The electrical conductivity of glasses has been measured within the temperature range 570–720 K.

Fig. 3 shows the dependence curves $\sigma \sim f(10^3/t)$ for the initial As_2S_3 and holmium-containing glasses. As is seen from the curve of dependence, the values of the specific electrical conductivity of the samples increase with an increase in the concentration of holmium in As_2S_3. A semiconductor conductivity is observed over the entire investigated interval. According to the results of our research, the electrical conductivity at 300 K is $1.8 \cdot 10^{-11}$ $Ohm^{-1} \cdot cm^{-1}$, and the values of the thermal band gap ΔE=2.1 eV for glassy As_2S_3.

Table 5. The synthesis mode of the glasses of the Ho-As-S system

№	Composition of the alloys at%	Synthesis temperature, K		Annealing temperature, K	Temperature stabilization, K
		I stage	II stage		
1	$Ho_2As_{15}S_{83}$	970	1170	540	440
2	$Ho_5As_{20}S_{75}$	990	1190	565	450
3	$Ho_{10}As_{22}S_{68}$	1020	1220	580	460
4	$Ho_{12}As_{26}S_{62}$	1050	1245	590	465
5	$Ho_{14}As_{30}S_{56}$	1080	1260	600	470

It has been established that hole (p) - type of conductivity dominates in the glasses. It has been found that impurities included in the matrix of chalcogenide glass in an amount of up to 10^{-1}% also do not affect the electrical conductivity. As is seen from Fig. 4, AsS has no "impurity" slopes. This can be explained by the presence of a large number of local centers in AsS arising from the loss of long-range order and having a quasi-continuous energy distribution. These local centers provide "recharging" of impurity centers, which makes impurities electrically inactive.

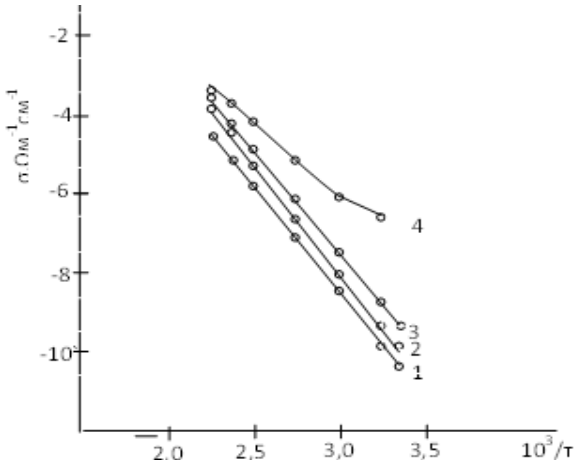


Fig. 3. Dependence of electrical conductivity of the glasses on the basis of As_2S_3:
1 - As_2S_3; 2 - 1 at % Ho; 3 - 3 at % Ho; 4 - 5 at % Ho

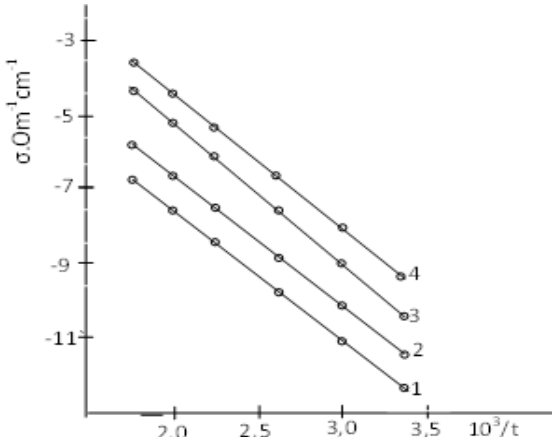


Fig. 4. Dependence of electrical conductivity of the glasses on the basis of AsS
1 - AsS; 2 - 1 at % Ho; 3 - 3 at % Ho; 4 - 5 at % Ho

3. Conclusion

Replaces arsenic at certain concentrations. In As_2S_3-Ho_2S_3 the system, after glass crystallization, a solid solutions based on As_2S_3 and the $HoAsS_3$ compound are formed. And in the As_2S_3-HoS system, after glass crystallization, solid solutions based on As_2S_3 and the HoAsS compound are formed. When studying the As_2S_3-Ho and AsS-Ho systems, it has been established that there are glass formation areas along the cross-sections. Macroscopic properties such as T_g (glass transition temperature), T_{cr} (crystallization temperature), T_{melt} (melting temperature), H_μ (microhardness), d (density) have been determined and it has been found that the values of these parameters increase when inclusion in the composition of the glasses. It is supposed that new structural units are formed in glasses. It has been established that the glass formation region reaches 10 at% on the basis of As_2S_3, while the glass formation region on the basis of AsS is up to 5 at% at the same cooling rate.

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