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HIGH-PURITY GLASSES BASED ON ARSENIC CHALCOGENIDES

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Low impurity content is the essential requirement to many applications of vitreous arsenic chalcogenides as a material for optoelectronics. Investigations carried out in last ten years increased the knowledge volume about the nature and origin of impurities in chalcogenide glasses, their effect on glass properties, especially on the transmittance in middle IR region and on radiation strength. These properties are most sensitive to impurity presence. The minimum calculated content of impurities, leading to observation of impurity contribution to the property value, is 0.1 - 100 ppb at. for different impurity groups. The effective methods of preparations and analysis of high - purity glasses are developed. The best glass samples contain the impurities of widespread metals and silicon on the level of 0.1 ppm wt., optically active hydrogen - 0.2 -0.05 ppm at., oxygen and carbon - 0.5 - 1 ppm wt., submicron size heterogeneous inclusions - 10^4 - $5*10^6$ cm^{-3}. Impurity content in the glasses of ordinary quality is 10 - 100 times higher. The presence of impurities should be taken into account while investigating both well-known and developed properties and applications of glasses.

1. Introduction

The vitreous arsenic chalcogenides are effective optical materials. They have different attractive properties such as a wide transparency region, low optical losses in the 2-12 μm interval, stability to the atmospheric moisture etc.

Transparency region of glasses measured at the absorption coefficient level of 1 cm^{-1} is 0.62-11.5 μm for As_2S_3 ; 0.85-1.75 μm for As_2Se_3 and 0.75-12.25 μm for $As_2S_{1.5}Se_{1.5}$. The minimum optical losses in As_2S_3 and As_2Se_3 are evaluated as $(6-7)*10^{-2}$ dB/km between 4 and 6 μm. For this reason vitreous arsenic chalcogenides are applicable for the manufacture of optical fibers. There are other fields of arsenic chalcogenides application both traditional and newly developed. Because of stable scientific and applied interest to these glasses the problem of their purity is very actual. The possible effect of impurity presence on the glass properties, which is of especially delicate nature, is relatively not often taken into account.

In the present paper the modern level of purity for the vitreous arsenic chalcogenides and impurity effect on glass properties are considered.

2. Preparation of vitreous arsenic chalcogenides

Bulk samples of vitreous arsenic chalcogenides of optical grade are produced by solidification of the glass forming melt. The initial charge with definite composition is melted in evacuated sealed ampoules made of quartz glass at the time-temperatures modes, which exclude the crystallization, liquation and stria formation. These conditions are individual for different glass systems and determined additionally by mass of the charge melted. For example the values of critical cooling rate for the vitreous As_2S_3, As_2Se_3 and As_2Te_3 approximately differ by three orders of magnitude and equal to $2.4*10^{-6}$; $9*10^{-3}$ and 28 K/s, respectively [1]. It was reflected at the choice of conditions for synthesis and treatment of these glasses.

Different variants for the preparation of initial charge for the glass forming chalcogenide synthesis are possible [2]: from chemical elements (the traditional method); through the decomposition of volatile inorganic hydrides; through the arsenic monosulfide as an arsenic-containing component of charge.

The layers of arsenic selenide may be prepared by plasmochemical decomposition of arsine and selenium hydride [3]. The prepared glass contains a noticeable quantity (several atomic percent) of hydrogen. It is a serious obstacle during heat treatment of glass while manufacturing it into fiber due to blowing up of the melt by hydrogen bubbles evolved. It is serious obstacle at the heat treatment of glass into fiber because of melt distending by hydrogen bubbles evolved. Nevertheless this method may be perspective for the thin films preparation of arsenic selenide. The dependence of the content of arsenic and selenium of different valence states in the layers, prepared at the experimental conditions was established for this process [4].

3. The nature and origin of impurities

The elemental composition, aggregation and chemical forms of impurity presence in vitreous arsenic chalcogenides depend on their macrocomposition, and on conditions of their synthesis. The preparation method and purity degree of initial substances (arsenic, chalcogens) are of importance. A few impurity groups may be isolated at the classification in accordance with element nature and the form of impurity presence in the glass (table 1).

Table 1. Impurity groups in vitreous arsenic chalcogenides.

Principle of classification	Impurity group	Impurity in the group	Typical impurity content, ppm.at.
By elements	Light elements (gas-forming impurities)	Hydrogen, oxygen, carbon, nitrogen	10-100
	Metals	Transition and other metals, silicon	0.1 – 1.0
	Analogues of elements-macrocomponents	Phosphorus, antimony, sulfur, selenium	1 - 100
By the form of presence	Embedded in the glass network	Hydrogen, oxygen, nitrogen, halogens, (OH, SH, SeH, NH, AsH-groups)	0.001 - 10
	Dissolved compounds	CO_2, COS, H_2O, N_2	0.01 - 10
	Heterogeneous inclusions	Carbon, silicon dioxide	$10^6 – 10^9$ cm^{-3}

There are three basic sources of impurities in chalcogenide glasses. First of them is the initial substances used for the glass-forming compound synthesis. Arsenic, chalcogens as pure materials were developed for the semiconductor application. Electrically active impurities, e.g. metallic impurities, were the main object of attention in the first line. For this reason commercial samples of As, S, Se, Te contain of 0.1-0.01 ppm.wt of metallic impurities and more high (1-10 ppm.wt) content of hydrogen, oxygen, carbon and silicon.

The second source of impurities is the material of container used for the synthesis of glass-forming compounds. Impurities having high value of diffusion coefficient, especially hydrogen, enter the chalcogenide melt. It was established [5] that hydrogen from quartz glass, containing 100 ppm of hydrogen, enters the melt of chalcogenide glass starting from 650 °C. The dependence of hydrogen entry rate, υ (g cm^{-2}s^{-1}), on temperature is described by the expression

$$\ln \upsilon = -11,2 - (15300/T)$$

<div align="right">(1)</div>

$$(873 \text{ K} \le T \le 1023 \text{ K})$$

Chemical interaction of chalcogenides and some impurities (CS_2, TeO_2) with the quartz glass at high temperature leads to the thin layers formation of new compounds on the inner surface of container and to the appearance of heterogeneous inclusions in chalcogenide melt.

The third source of impurities is the surrounding atmosphere and residual gas of vacuum used at the glass synthesis and glass treatment procedures.

Arsenic and chalcogens have tendency to oxidation at elevated temperature. As it follows from thermodynamic evaluation and from mass-spectrometric investigations of oxide vapors, the equilibrium partial pressure of oxygen at dissociation of arsenic, selenium and tellurium oxides at ~1000 K is at the level of 10^{-4} - 10^{-6} Pa (10^{-6} -10^{-8} mm of Hg). This value will be lower at temperature decrease. For this reason the oxidation of chalcogens and arsenic in the open vacuum system will be excluded at the vacuum better then 10^{-4} - 10^{-6} Pa.

Impurities in vitreous arsenic chalcogenide are present in different forms (Table 1). Atoms of impurity elements may be embedded in glass networks as non-bridging and bridging atoms. The stable impurity compounds (CO_2, CS_2, COS, N_2 etc.) are present in dissolved state in the form of instant solution. Both these forms are well known. Heterogeneous inclusions are the less studied impurity form. They consist of substances which are hardly soluble in the melts of chalcogenides. The particle size depends on the glass sample origin and is distributed between 0.05 and several microns (see Fig.1). Inclusions in arsenic chalcogenide consist of carbon and silicon dioxide. Impurities in this form enter the glasses from initial substances and are also formed by interaction of chalcogen, arsenic, chalcogenides with the apparatus material [6,7].
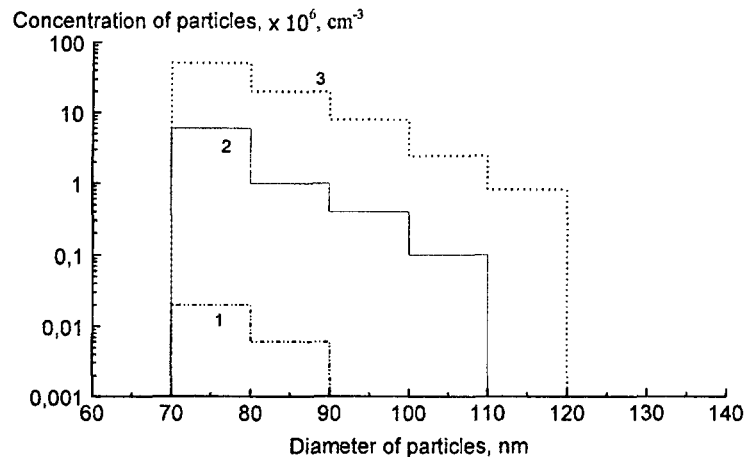

Fig. 1. Histograms of the distribution of impurity particles in glasses: 1- As_2S_3; 2 - As_2Se_3; 3- $As_2Se_{1.5}Te_1$.

Some impurities may present in the glasses in several forms. Carbon compounds (oxides, sulfide and oxysulfide) are dissolved in the glass. Elementary carbon has low solubility in arsenic chalcogenide melts and is present as heterogeneous inclusions.

The oxygen in arsenic selenide present as a cage molecule As_4O_6 and as a polymer formed by structural units $AsO_{3/2}$. In the As_2Se_3 melt monomeric and polymeric forms are in equilibrium, that is frozen at the cooling melt. Taking into account the peculiarities of mutual solubility of polymers it will be reasonable to assume the presence of polymeric arsenic oxide in the form of inclusions. At the melt solidification polymeric arsenic oxide may crystallize. The evidence to this follows from observation of absorption bands characteristic of the transmission spectra of individual arsenic oxide in the form of glass, claudetite and As_4O_6 molecules in the transmission spectra of oxygen containing As_2Se_3 [8-10].

4. Impurity effect on optical properties of glasses

In general case the property of solid material of a given macrocomposition depends on the content of impurities and structural defects. Property value may be presented as the sum

$$P = P_0 + Pi + P_d + P_{ii} + P_{dd} + P_{id}, \qquad (2)$$

where P_0 is the value for the impurity and defect free hypothetical substance, P_i and P_d — increments caused by impurities and defects, respectively, P_{ii}, P_{dd} - increments caused only by mutual interaction of impurities and defects, P_{id} — increment caused by the interaction of impurities and defects.

P_0 is calculated usually on the base of model conception. For example, the calculated theoretical value of the minimum optical losses in As_2S_3 and As_3Se_3 are equal to (6-7) 10^{-2} dB/km between 4 and 6 μm [11]. The impurities, embedded into the glass network or the dissolved impurities, manifest themselves in the spectra of the total optical loss of optical fibers as the bands of selective absorption. Position of the absorption band is determined by the nature of impurity. Table 2 gives the positions of the maxima of impurity absorption bands in vitreous arsenic sulfide and arsenic selenide.

Table 2. The maxima of absorption bands for the main impurities in As-S and As-Se glasses [12].

Compound or functional group leading to absorption	Position of the maximum of the absorption band, μm
OH⁻	2.92
S-H	4.01; 3.65; 3.11; 2.05
Se-H	7.8; 4.57; 4.12; 3.53; 2.32
Ge-H	4.95
As-H	5.02
P-H	4.35
H_2O	6.31; 2.86; 2.79
Ge-O	12.8; 7.9
P-O	8.3
CO_2	4.33; 4.31; 15.0
COS	4.95
CSe_2	7.8
CS_2	6.68; 4.65
Arsenic oxides (different forms)	15.4; 12.7; 9.5; 8.9; 7.9; 7.5
Se-O	10.67; 11.06
Si-O	9.1-9.6
Non-identified bands supposedly due to carbon presence	4.65; 5.17; 5.56; 6.0

It follows from Table 2 that a considerable number of impurity absorption bands are present in the transparency range. The extinction coefficient is a quantitative measure for estimation of impurity effect on the optical loss in glasses. The values for the extinction coefficient are known only for the limited number of impurities in chalcogenide glasses (Table 3).

Fig.2 gives the spectral dependence of the extinction coefficient of SeH-group, As_2O_3 and of sulfur in As_2Se_3. It follows from the Tables 2, 3 and from Fig.2 that the impurity effect of hydrogen-containing substances is mostly pronounced at 2.5-6.5 μm spectral range, and of the oxygen impurity in the longer wave range (7 – 14 μm). The effect of sulfur impurity, embedded in the network of selenide and selenide-telluride glass, is substantially weaker than in the form of SH-groups. In view of experimental values of the extinction coefficient for SH, the SeH-group, CO_2, COS, CS_2 and As_2O_3 the content of these impurities in glasses with optical losses at the level of the intrinsic values should not exceed 0.1 – 10 ppb (see Table 3).

Table 3. The values of extinction coefficients for the impurities in chalcogenide glasses.

Impurity compound or functional group	Glass	The maximum of absorption band, μm	Extinction coefficient, dB/km/ppm*	Calculated content of impurity leading to the optical loss equal to the intrinsic one, ppb*
SH	As_2S_3	4.0	2500	0.3
SeH	As_2Se_3	4.5	1000	0.1
CO_2	As_2S_3	4.33	15625	0.05
COS	-"-	4.95	10^5	0.008
CS_2	-"-	6.68	477400	0.2
As_2O_3	As_2Se_3	12.65	43560	100
		9.5	1030	400
Se-O	-"-	10.6	380	2000
S	-"-	10.6	0.52	10^6
S	$As_2Se_{1.5}Te_{1.5}$	14.5	32	10^4

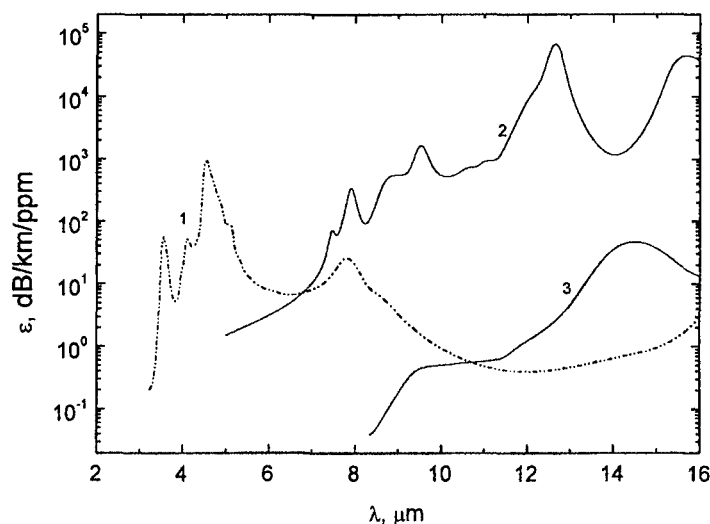I* - the intrinsic loss of glass is estimated accounting for "the weak absorption tail" [14]

Fig. 2. Spectral dependence of the extinction coefficient of SeH groups (1) [12], oxygen (2) [13] and sulfur (3) [14] in As_2Se_3 glass.

The presence of impurities in the form of heterophase inclusions of submicron size leads to additional optical loss due to absorption and scattering which effect depends on the content of particles and on their distribution by size. Mechanical strength and especially damage threshold of optical fibers are also sensitive to presence of impurities in the form of heterophase inclusions. The energy threshold of the volume damage of As_2S_3 glass increases by two orders of magnitude under the effect of YAG-Er-laser pulse radiation with lowering of the content of submicron-size particles in glass from 10^6 to 10^4 cm^{-3} (see Fig.3). The As_2S_3 glass samples with the particle content lower than the detection limit were not damaged by the pulses with energy more than 1 J [15].

The glass designated for power optics applications, in the ideal case should not contain any particle in the volume illuminated by intense radiation flux. The value of $10^3 - 10^4$ cm^{-3} may be accepted as the upper limit of particle content at present time.
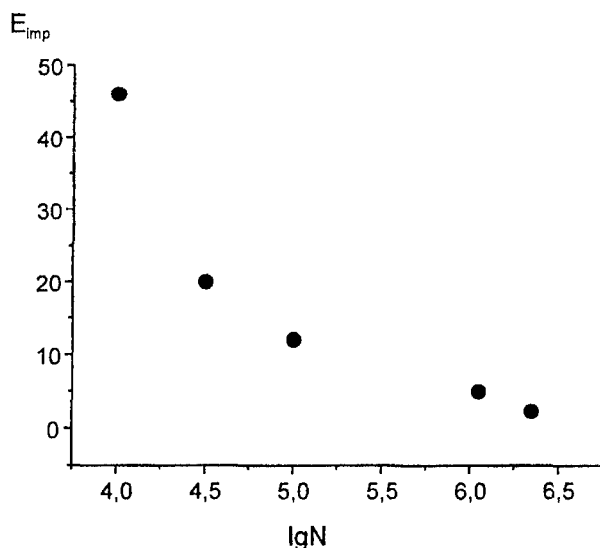
Fig. 3. The dependence of YAG-Er-laser damage threshold upon the content of submicron particles in As-S glass. N - particle content, cm^{-3}, E_{imp} - pulse energy, mJ.

5. Preparation of high purity glasses based on arsenic chalcogenides

At the present time there are two efficient ways for the preparation of arsenic chalcogenide melts with low content of impurities, solidification of which gives the homogeneous high-purity glasses. First of them is synthesis of glass forming compounds or their mixture by vacuum melting of the charge prepared by the above-mentioned methods. This variant can be used while manufacturing all chalcogenide glasses.

The existing problems are connected with a rather high (up to tens ppm) content of the impurities of oxygen, carbon and hydrogen in the commercial samples of specially pure chalcogens and arsenic. Selenium, tellurium and arsenic can oxidize at the contact with environment even at room temperature. That is why the starting high-purity substances are loaded into the container for glass synthesis by evaporation under oil-free vacuum.

Ultrapurification of arsenic and selenium from submicron particles, consisting mainly of carbon, by the method of vacuum sublimation or distillation is of low efficiency at the acceptable evaporation rates [16]. Arsenic monosulfide As_4S_4 was used as an arsenic-containing component of the charge to manufacture the glasses with the ratio of As/S equal to 1/1 and less. This compound is more suitable for the ultrapurification from submicron particles because of low viscosity of melts. Two- and three-component glasses were manufactured by melting the purified arsenic monosulfide with the required amount of chalcogens, e.g.

$$As_4S_4 + S_2 \rightarrow 2 As_2S_3 \tag{3}$$

$$As_4S_4 + Se_2 \rightarrow A As_2S_2Se \tag{4}$$

The second way includes the purification of glass-forming arsenic compounds of technical quality by chemical and distillation methods, melting of some distillate fractions up to homogeneous state achievement and melt solidification. Vacuum distillation in an open and closed system allows a 3-10 times decrease of the content of impurities of highly volatile substances and of submicron particles [17]. Particles behave themselves as hardly volatile impurities, and their content is increased in the lost fraction of a distillate. The purification efficiency is very sensitive to the evaporation rate and to the melt viscosity. Depending on the type of distillate fraction taken for the subsequent treatment it is possible to prepare the glasses with different content of different impurities. The glass from the first distillate fraction is enriched by hydrogen and oxygen compounds, from the lost one - by heterogeneous particles. To remove some impurities (carbon, oxygen) the preliminary chemical treatment of arsenic chalcogenide may be used. To remove the oxygen, chemically bound with glass macrocompo-

nents, a small amount of magnesium (aluminum, rare-earth elements) was added to the melt of the compound being purified which binds oxygen into magnesium oxide. After heating at 700-800°C the melt was subjected to vacuum distillation. To reduce the carbon content similar procedures with addition of small amounts of arsenic and selenium oxides may be applied. A special feature of the process is the difference in macrocomposition of the distillate and of the initial chalcogenide melt. Arsenic chalcogenide evaporate with dissociation and it leads to separation of vapour components at their condensation. In Fig.4 the average distillate composition is given as function of the part of evaporated loading at the As_2S_3 vacuum distillation in the closed system. It is seen that As_2S_3 distillate is enriched with arsenic during vacuum distillation. This phenomenon should be taken into account at the preparation of arsenic chalcogenide layers by condensation of their vapour.
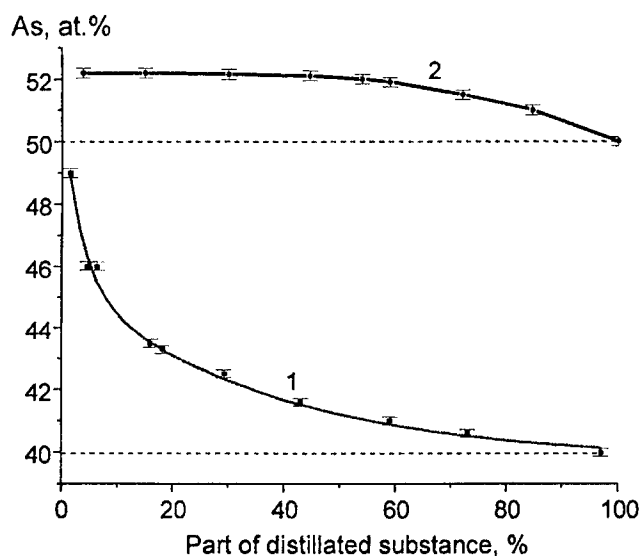

Fig. 4. Average distillate composition as a function of evaporated substance at vacuum distillation of As_2S_3 (1) and As_4S_4 (2).

A practically important question is the stable reproducibility of the glass properties from one sample to another one. The background for the variation of the glasses properties from synthesis to synthesis is a high sensitivity of the glass properties to impurities.

An absolute and relative content of impurity compounds and groups in the glasses can change because of variations in the impurity content in the initial substances and difference in conditions of the glass synthesis and melt solidification (vacuum quality, time-temperature modes). The relative content of the glass network defects, such as "chalcogen-chalcogen" and "arsenic-arsenic" bonds is also affected by the variations of the conditions. For example, the presence of sulfur at the level of several at.% in selenide glass will not noticeably effect its transparence in the 7-11 μm wavelength region. But the impurity hydrogen will change its chemical form. The main part of hydrogen will be bounded with sulfur atoms because of the higher strength of the S-H bond as compared to that of the SeH bond. The intensity of SeH band will reduce considerably but the intensity of SH band will increase. Fig.5 shows the spectra of absorption in the range from 3000 to 1500 cm^{-1} for As_2Se_3 (1), As_2S_3 (2) and $(As_2Se_3)_{0.95}(As_2S_3)_{0.05}$ (3) prepared from glasses 1 and 2. [18].

Thus, for the preparation of vitreous arsenic chalcogenide with the reproducible optical properties a strict identity of the impurity content in the initial substances as well as of the glass preparation conditions should be provided.

In Table 4 the content of impurities in the arsenic chalcogenide glasses is given. It is seen that the content of wide-spreaded metals and silicon is of 0.1-1.0 ppm wt. The content of oxygen and carbon determined by reaction gas-chromatography method and by activation method for the best glass samples is equal to 0.2-0.6 ppm at. Hydrogen content in the form of SH, SeH and OH groups determined by IR-spectroscopy of bulk samples and fibers is equal to 0.02-0.2 ppm at. The content of particles with diameter of 0.1 μm and lower is less then $1 \cdot 10^4$ cm^{-3} for As_2S_3 glass as a result of addi-

tional efforts directed on particles removing [19]. In As-Se and As-Se-Te glasses the particle content is equal to $1 \cdot 10^5$ - $5 \cdot 10^6$ cm^{-3}. The level of transparency in the middle IR-region corresponding to the achieved purity degree of arsenic chalcogenide glasses is given in Table 5. It is obvious that the difference between predicted and real optical losses is of two orders of magnitude.
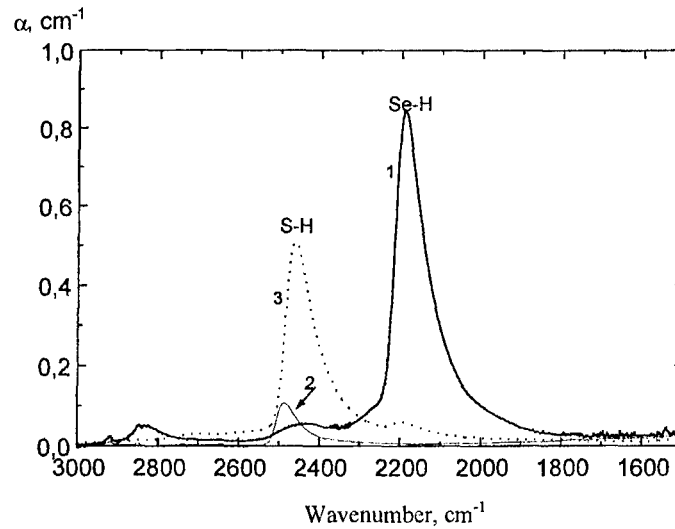

Fig. 5. A hydrogen transfer from Se to S in the mixed As_2S_3-As_2Se_3 glasses. 1, 2 ,3 - absorption spectra of As_2Se_3, As_2S_3 and $(As_2Se_3)_{0,95}(As_2S_3)_{0,05}$ glasses, respectively.

Table 4. Impurity content in the prepared arsenic chalcogenides.

Impurity	Method of determination	Impurity content, in:		
		As_2S_3	$As_2S_{1.5}Se_{1.5}$	As_2Se_3
Hydrogen in the form of SeH- and SH-groups	Spectroscopy of a fiber	0.05 ppm at.	1 ppm at.	0.5 ppm at.
Carbon	Radioactivation and Gas-Chromatographic	≤ 0.2 ppm wt.		6 ppm wt.
Oxygen	Radio-activation analysis	1 ppm wt.		0.9 ppm wt.
Submicron size particles 0.06-0.2 μm	Laser ultramicroscopy	≤ $2 \cdot 10^4$ cm^{-3}	$1 \cdot 10^7$ cm^{-3}	$2 \cdot 10^6$ cm^{-3}
Al, Fe, Ni, Cr, Mg Mn, Ni	Emission spectroscopy	1-100 ppb wt.	<0.2-2 ppm wt	1-100 ppb wt.

Table 5. Optical transparence of the best samples of vitreous arsenic chalcogenides.

Glass	Minimum optical losses		At laser wavelength, dB/km				
	β, dB/km	λ, μm	2.08 μm	2.9 μm	3.7 μm	5.6 μm	10.6 μm
As_2S_3	23	2.4	400	160	140	230	-
$As_2S_{1.5}Se_{1.5}$	190	4.8	1000	3800	400	200	-
As_2Se_3	78	4.2	160	160	80	85	650
$As_2Se_{1.5}Te_{1.5}$						1000	3500

6. Conclusions

The accordance with theoretical evaluation of the impurity effect on optical properties of glasses may be observed at the impurities content from 1 to 0.01 ppb. The content of limiting impurities in chalcogenide glasses obtained up-to-date is not less than 50-100 ppb. That is why the impurities contribution into the investigated glass properties is considerable. For the development of optoelectronic materials, based on high purity arsenic chalcogenides, the 1-2 order decrease in the impurities content is required now. It will become possible if the efforts will be concentrated on the preparation of arsenic and chalcogens with the lower content of impurities, on the development of more sensitive method of the impurities determination and on the improvement of the glass preparation technique.

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