

ON THE COMPOSITIONAL TRENDS IN IR IMPURITY ABSORPTION OF Ge–As(Sb)–S GLASSES

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IR impurity absorption spectra in 4000–1000 cm^{-1} (2.5–10 μm) region for chalcogenide glasses of pseudobinary stoichiometric $\text{As}_2\text{S}_3(\text{Sb}_2\text{S}_3)\text{--GeS}_2$ and non-stoichiometric $\text{As}_2\text{S}_3(\text{Sb}_2\text{S}_3)\text{--Ge}_2\text{S}_3$ cross-sections are studied. The compositional features of the main absorption bands of the various impurity structural fragments are compared for the investigated As-based and Sb-based glassy systems.

1. Introduction

Chalcogenide glasses (ChG) owing to high transmittance in near and medium IR spectral regions belong to important class of disordered materials perspective for IR optics [1-7]. Their simplicity and cheapness in technological preparation route in comparison with conventional crystalline substances are especially attractive for industrial device manufacturers. That is why the ChG have being under a high attention of researchers for a long period of time [7].

It is well known that application possibilities of ChG in IR optics are sufficiently restricted by vibrational absorption bands of impurities, they being introduced with initial chemical ingredients used for glass synthesis [5]. The above disadvantage can be eliminated, in part, with special purification methods [3]. Nevertheless, a small amount of impurity remainders, in the first hand O- and H-based ones such as molecular H_2O , H_2S , As_4O_6 , etc., sorbed mainly near the glass surface, in structurally-intrinsic nanovoids and imperfections (bubbles, pores, cracks etc.) are always present in ChG whichever technological modification or additional post-technological treatment would be performed [5,8]. The only way to overcome this obstacle is to choose the best ChG compositions with minimal ability of covalent-bonded glass-forming network to chemical interaction with absorbed impurities. In other words, the best specimens of ChG perspective for IR device application should be prepared by varying their covalent connectivity owing to purposeful change in chemical composition within a whole glass-forming region.

With this in mind, we shall try to establish the compositional features of IR impurity absorption spectra for ternary Ge–As(Sb)–S ChG taken along two typical glass-forming sections, the first one being restricted by stoichiometric (ST) arsenic (or antimony) trisulphide $\text{As}_2\text{S}_3(\text{Sb}_2\text{S}_3)$ and germanium disulphide GeS_2 (i.e. so-called ST cross-sections: $\text{As}_2\text{S}_3\text{--GeS}_2$ and $\text{Sb}_2\text{S}_3\text{--GeS}_2$), and the second one being restricted by ST $\text{As}_2\text{S}_3(\text{Sb}_2\text{S}_3)$ and non-stoichiometric (NST) Ge_2S_3 sulphides (i.e. so-called NST cross-sections: $\text{As}_2\text{S}_3\text{--Ge}_2\text{S}_3$ and $\text{Sb}_2\text{S}_3\text{--Ge}_2\text{S}_3$).

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2. Experimental

The investigated bulk samples of Ge–As(Sb)–S systems were prepared by standard melt quenching method using high purity (99,999 %) initial elements. After preparation, all ingots were sliced to disks of about 1 mm thickness and polished for optical measurements. The ST $\text{As}_2\text{S}_3(\text{Sb}_2\text{S}_3)\text{–GeS}_2$ ($2.43 \leq Z \leq 2.63$) and NST $\text{As}_2\text{S}_3(\text{Sb}_2\text{S}_3)\text{–Ge}_2\text{S}_3$ ($2.55 \leq Z \leq 2.76$) glass compositions were chosen for IR spectroscopic investigations (Table 1). The values of average coordination number Z were calculated as the average number of covalent chemical bonds per atom of formula unit.

Table 1. Chemical compositions and corresponding values of Z for the investigated Ge–As(Sb)–S ChG.

ST: $\text{As}_2\text{S}_3\text{–GeS}_2$		NST: $\text{As}_2\text{S}_3\text{–Ge}_2\text{S}_3$	
Chemical composition	Z	Chemical composition	Z
$\text{As}_{34.8}\text{Ge}_{4.3}\text{S}_{60.9}$	2.43	$\text{As}_{24}\text{Ge}_{16}\text{S}_{60}$	2.56
$\text{As}_{28.6}\text{Ge}_{9.5}\text{S}_{61.9}$	2.48	$\text{As}_{16}\text{Ge}_{24}\text{S}_{60}$	2.64
$\text{As}_{21.05}\text{Ge}_{15.79}\text{S}_{63.16}$	2.53	$\text{As}_8\text{Ge}_{32}\text{S}_{60}$	2.72
$\text{As}_{6.25}\text{Ge}_{28.125}\text{S}_{65.625}$	2.63	$\text{As}_4\text{Ge}_{36}\text{S}_{60}$	2.76
ST: $\text{Sb}_2\text{S}_3\text{–GeS}_2$		NST: $\text{Sb}_2\text{S}_3\text{–Ge}_2\text{S}_3$	
$\text{Sb}_{25}\text{Ge}_{12.5}\text{S}_{62.5}$	2.50	$\text{Sb}_{25}\text{Ge}_{15}\text{S}_{60}$	2.55
$\text{Sb}_{21.05}\text{Ge}_{15.79}\text{S}_{63.16}$	2.53	$\text{Sb}_{20}\text{Ge}_{20}\text{S}_{60}$	2.60
$\text{Sb}_{16.67}\text{Ge}_{19.44}\text{S}_{63.89}$	2.55	$\text{Sb}_{15}\text{Ge}_{25}\text{S}_{60}$	2.65
$\text{Sb}_{11.8}\text{Ge}_{23.5}\text{S}_{64.7}$	2.59	$\text{Sb}_{13}\text{Ge}_{27}\text{S}_{60}$	2.67
$\text{Sb}_{6.25}\text{Ge}_{28.125}\text{S}_{65.625}$	2.63	$\text{Sb}_5\text{Ge}_{35}\text{S}_{60}$	2.75

Double-beam spectrophotometer “Specord 75 IR” (Germany) was used for investigation of impurity absorption processes in $4000\text{--}1000\text{ cm}^{-1}$ ($2.0\text{--}10\text{ }\mu\text{m}$) region at the ambient temperature. The intensities I (a.u.) of the main absorption bands of impurity complexes were calculated as:

$$I = \log(T_1/T_2), \quad (1)$$

where T_1 and T_2 – transmissions of sample in the minimum and maximum of the chosen absorption band, respectively [1].

We shall suppose that changes in the intensity of impurity absorption bands correspond to changes in the concentration of respective impurity complexes incorporated into glass matrix.

3. Results and discussion

The typical IR transmission spectrum of the investigated ChG is presented in Fig. 1. The Ge–As(Sb)–S glassy systems are generally characterized by the similar behaviour of impurity absorption processes for ST and NST cross-sections, but some difference in compositional features of the main impurity absorption bands is detected.

The observed absorption bands were identified using previous experimental results (Table 2) [1–8]. The absorption band at 2490 cm^{-1} , associated with –S–H (sulphur-hydrogen) complexes, is the most intensive in the obtained transmission spectra. The molecular-adsorbed H_2O (3500 cm^{-1}), H_2S sulphur-hydrogen groups (2330 cm^{-1}), molecular As_4O_6 and –S–O– complexes (1300 cm^{-1}) have comparatively lower intensities. The band of 3240 cm^{-1} corresponding to the stretching modes of OH hydrogenous groups connected with ChG structural network has the weakest intensity. The absorption vibrational modes of $\equiv\text{C}\text{–O}\text{–S}\text{–}$ type carbon-containing groups at 2050 cm^{-1} reveal only in IR transmission spectra of NST glass compositions. It should be noted that for all

investigated glasses, except of the Ge-enriched ternary samples, the H₂O molecular-adsorbed vibrational bands in 1580 cm⁻¹ region of IR spectra are observed.

The intensity of all absorption bands in Ge-As(Sb)-S ChG essentially depends on their chemical composition or average coordination number *Z*. The compositional dependences of intensity of the main impurity absorption bands in ChG of ST As₂S₃(Sb₂S₃)-GeS₂ and NST As₂S₃(Sb₂S₃)-Ge₂S₃ cross-sections are presented in Table 2.

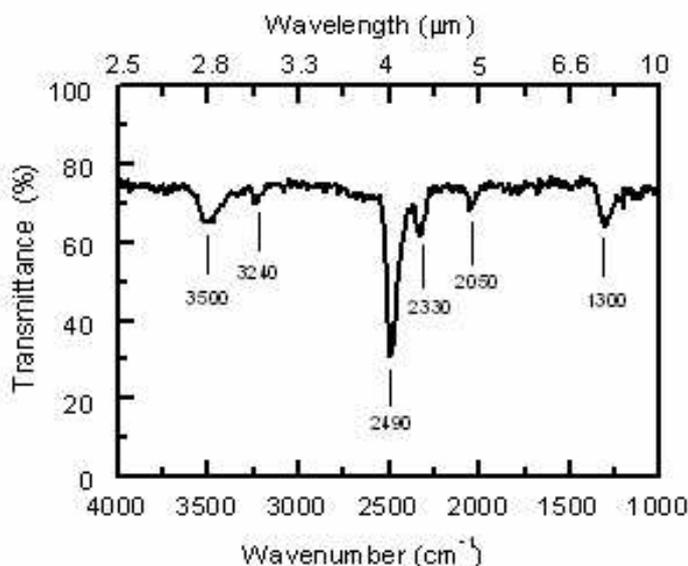


Fig. 1. IR transmission spectrum of Ge-Sb-S NST glass composition at $Z=2.75$. Lines show the main absorption bands.

Following to Table 2, it can be seen that the molecular H₂S are not observed for As-based ChG, whereas for Sb-based ones these impurity groups are detected being practically *Z*-independent. The same compositional features correspond to OH-related impurity complexes. The amount of ≡C-O-S- impurity groups, observed only for NST compositions, is similar in both As- and Sb-based ChG and these complexes are preferentially occurred for Ge-enriched samples. The intensity of impurity band at 1300 cm⁻¹ is linear function on chemical composition in the case of Sb-based ChG that seen especially well in the case of NST cross-section, whereas non linear one with slight saturation within ST cross-section and with clear maximum at $Z=2.72$ within NST cross-section for As-based samples. Because of two vibrational modes corresponding to the -S-O- impurity complexes and molecular As₄O₆ can be detected in this IR region, the observed differences in the compositional trends of this band for Sb- and As-based materials are obvious. Among impurities which are strongly dependent on the ChG chemical composition, the molecular-adsorbed water H₂O (3500 and 1580 cm⁻¹) and sulphur-hydrogen groups -S-H (2490 cm⁻¹) must be distinguished being compositionally opposite. So the H₂O decreasing is accompanied by the -S-H increasing, however, no any peculiarities (extremes, thresholds, etc.) are observed on the compositional trends of H₂O, while the sharp maximum in concentration of -S-H impurity complexes in the range of $2.64 < Z < 2.72$ can be seen for NST samples.

Table 2. Intensities I (a.u.) of the main impurity absorption bands in the investigated Ge-As(Sb)-S ChG.

Z	3500 cm ⁻¹ (H ₂ O)	3240 cm ⁻¹ (-S-OH)	2490 cm ⁻¹ (-S-H)	2330 cm ⁻¹ (H ₂ S)	2050 cm ⁻¹ (≡C-O-S-)	1580 cm ⁻¹ (H ₂ O)	1300 cm ⁻¹ (-S-O- or As ₄ O ₆)
ST: As ₂ S ₃ -GeS ₂							
2.43	0.28	0	0.28	0	0	0.20	0.05
2.48	0.29	0.01	0.37	0	0	0.10	0.12
2.53	0.16	0.03	0.50	0	0	0.02	0.11
2.63	0.04	0.03	0.56	0	0	0	0.09
ST: Sb ₂ S ₃ -GeS ₂							
2.50	0.22	0	0.30	0.10	0	0.10	0.05
2.53	0.15	0	0.39	0.12	0	0.05	0.05
2.55	0.09	0.03	0.45	0.10	0	0.02	0.06
2.59	0.06	0.04	0.60	0.11	0	0	0.06
2.63	0.04	0.05	0.67	0.12	0	0	0.06
NST: As ₂ S ₃ -Ge ₂ S ₃							
2.56	0.15	0.04	0.90	0	0	0.04	0.08
2.64	0.12	0.06	1.10	0	0.01	0.02	0.11
2.72	0.07	0.04	0.86	0	0.01	0.01	0.16
2.76	0.05	0.04	0.80	0	0.03	0	0.10
NST: Sb ₂ S ₃ -Ge ₂ S ₃							
2.55	0.22	0	0.28	0.09	0	0.11	0.03
2.60	0.10	0.03	0.40	0.15	0	0.05	0.02
2.65	0.08	0.03	0.40	0.09	0	0.02	0.04
2.67	0.07	0.03	0.38	0.08	0.01	0.02	0.06
2.75	0.06	0.03	0.39	0.09	0.04	0	0.07

Such compositional behaviour of the impurity absorption can be connected with structural-topological features of the investigated ChG. Indeed, taking into consideration the principally same technological conditions of samples preparation, we suppose that preferential factors affected on the impurity processes in ChG should be found within structural and chemical parameters of glassy-like materials, such as glass compactness or free volume, nature of chemical elements and bonds, dimensionality of glassy matrix and so on.

The content of molecular-adsorbed water (H₂O) agrees with change of As(Sb) atoms concentration. Somewhat larger concentration of H₂O (1580 cm⁻¹) for Sb-based ChG (see Table 2) can be explained by higher degree of metallization of chemical bonds, proper to Sb [9] or, in other words, by better possibility of Sb atoms to interact with impurities.

The compositional dependences of sulphur-hydrogen complexes (-S-H) for both investigated systems are in good agreement with compositional changes of ChG atomic compactness. It is known that compactness decreases with Z increasing for all glasses. But in the case of ST glasses it decreases monotonously at the whole range of Z variation, while in the case of NST ones it decreases non-monotonously with sharp peculiarities in the range of $2.65 < Z < 2.72$ [10-13]. The decreasing of the compactness leads to the increasing of free volume that is obviously accompanied by presence of voids in the structural network [13]. Therefore, we can suppose the formation of -S-H groups on the internal surfaces of voids, which are created in the process of melt quenching. Because of peculiarities in compositional behaviour of compactness or free volume in the range of $2.65 < Z < 2.72$ are better expressed for the investigated NST As-based ChG in comparison with NST Sb-based ones

[10-13], the compositional features in concentration of –S–H impurity complexes are revealed better for NST As-based ChG as well (see Table 2).

It is not clear yet exactly why molecular H₂S does not reveal for the investigated As-based ChG, but it can only be supposed that such complexes in the case of NST cross-section in Ge–As–S family are included into –S–H groups, which are essentially intensive (about in two times) for these glass compositions in comparison with ChG of NST cross-section in Ge–Sb–S family (see Table 2).

The compositional behaviour of the intensity of OH-groups strongly correlates with concentration of S atoms for the investigated ST and NST cross-sections. We can assume that these impurity complexes are structurally connected with S atoms. That is why the concentration of OH impurities practically does not differ for the investigated As- and Sb-based ChG with similar content of S atoms (see Tables 1 and 2).

It can be supposed that –S–H and –S–OH impurity groups are stabilised in the glass structural network as the products of closing of S (chalcogen) “dangling” bonds. Besides, at the ChG synthesis the parallel process of closing of S “dangling” bonds by O atoms is observed (–S–O–, 1300 cm⁻¹).

The observed difference in compositional trends of the band at 1300 cm⁻¹, connected with –S–O– impurities and molecular As₄O₆, can be explained by different amount of –S–O– and As₄O₆ complexes for As-based ChG within ST and NST cross-sections, whereas in the case of Sb-based ChG clearly understandable is existing only –S–O– groups. It can be suggested that –S–O– concentration is dominant for As-based ST ChG, because for this cross-section no existing of wrong homopolar As–As bonds is expected which could be potential candidates to interact with oxygen, while in the case of As-based NST ChG the molecular As₄O₆ is preferentially formed being here in a good compositional agreement with a fraction of homopolar As–As bonds, structurally possessed for these glasses, having the similar maximum on Z dependence nearby Z=2.72 (see Table 2 and Ref. [14]). Thus, we can interpret the practically same compositional trends in the intensity of the band at 1300 cm⁻¹ for ST compositions of As- and Sb-based ChG, where in the both cases slight saturation of the band intensity for Ge-enriched samples is detected (see Table 2).

The appearance of ≡C–O–S– impurity groups for both investigated NST cross-sections at high Z values may be caused by the pollution of initial raw materials (Ge first of all), because these complexes are only revealed in the case of the highest Ge content.

So, the analysis of compositional trends in IR impurity absorption of the investigated Ge–As(Sb)–S ChG shows that Ge-enriched glass compositions are characterized by minimum content of impurities associated with molecular water H₂O, i.e. these ChG possess the highest transmittance in 4000-3500 cm⁻¹ and 2000-1500 cm⁻¹ regions within Ge–As(Sb)–S families. At the same time, IR transmittance of Ge-enriched ChG is sufficiently limited by larger concentration of –S–H impurity complexes in comparison with As and Sb-enriched ones in 3500-2500 cm⁻¹ region. The influence of O- and C-containing complexes (–S–O–, As₄O₆, ≡C–O–S–) on IR transmittance of the investigated ChG is insufficient in comparison with H₂O and –S–H impurities. That is why the compositional features of molecular adsorbed water and sulphur-hydrogen complexes should be taken into account for practical application of the investigated ChG in IR optics. With this aim, the using of Ge-enriched glass compositions is recommended in 4000-3500 and 2000-1500 cm⁻¹ IR regions.

4. Conclusion

Therefore, the investigations of IR impurity absorption spectra of ternary Ge–As(Sb)–S ChG show that the intensity of vibrational absorption bands of various impurity structural fragments essentially depends on chemical composition of glasses or average coordination number Z. It has been established that As(Sb) atoms are responsible for absorption of molecular water H₂O, whereas S atoms – for hydrogenous groups (OH). The –S–H and –S–OH are stabilised in the glass structural network as the products of closing of S “dangling” bonds and –S–H groups are formed on the internal surfaces of voids, created technologically during samples preparation. The molecular H₂S complexes

are only detected for ChG in Ge–Sb–S family, explanation of compositional features of which needs additional investigations. It has only been suggested that in the case of NST cross-sections the disappearance of molecular H₂S for As-based ChG can be caused by appearance of about in two times intensive –S–H groups for these glasses in comparison with NST Sb-based ChG. In addition to the process of closing of S “dangling” bonds by hydrogen atoms, the parallel process of their closing by oxygen atoms are observed as well. The analysis of the IR data in the range of 1300 cm⁻¹ for the investigated Sb- and As-based ChG testifies about different amount of –S–O impurities and molecular As₄O₆ for As-related samples within ST and NST cross-sections, effecting on the compositional trends of the intensity of this band. It is observed the preferential forming of molecular As₄O₆ for NST As-containing compositions, being structurally connected with homopolar As–As chemical bonds. The ≡C–O–S– impurity groups appear only at the highest Ge concentration for NST glass compositions. These results obtained should be taken into account with aim of practical application of the investigated ChG in IR optics, where Ge-enriched glasses are recommended to be used in 4000-3500 and 2000-1500 cm⁻¹ IR regions.

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