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Mid-IR impurity absorption in As_2S_3 chalcogenide glasses doped with transition metals

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Abstract. Room temperature IR impurity absorption spectra in $4000-7000\ \text{cm}^{-1}$ ($1.4-25\ \mu\text{m}$) region for chalcogenide glasses of As_2S_3 doped with chromium (0.5, 1 wt.%) and manganese (0.1, 1, 2, 5 wt.%) have been studied. The effects of chromium and manganese impurities on the transmission spectra are discussed.

Keywords: arsenic sulfide, transmission spectra, transition metals.

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1. Introduction

The chalcogenide glasses (ChG) based on sulfides and selenides are very promising materials for various IR device application [1-6] due to their transparency in the middle infrared spectrum and low phonon energies which lead to the shifting of the multi-phonon absorption edge to longer wavelengths ($\sim 330-380\ \text{cm}^{-1}$) compared to fluoride ($\sim 440-650\ \text{cm}^{-1}$) or silicate glasses ($\sim 1150\ \text{cm}^{-1}$) making ChG suitable as materials for infrared fiber optics operating in the 2–10 μm wavelength [3-7]. Higher values of the refractive index and high degree of covalent bonding in ChG increase the probability of radiative transitions in comparison with other basic materials [3, 6].

Special interest for applications is related with glassy As_2S_3 doped with optically active rare-earth and transition metal ions, because they alter electrical, thermophysical, mechanical, magnetic (for ChG as a whole the diamagnetic effect is characteristic but introduction of the chromium or manganese impurities of different concentration facilitates the transition from the diamagnetic state into the paramagnetic or ferromagnetic one [9]) and optical properties of the host material due to structural and electronic changes of the glass network [10, 11].

The main problem is preparation of these glasses with high chemical and physical purity, low O-, H- and C-containing group concentration in the glass matrix and low physical defects and clusters. It is known that insufficiently high purity of the initial chemical ingredients and the intensive environment influence on these materials directly after their synthesis are the reasons for the appearance of impurity bands in the middle IR spectral region. The above-mentioned impurity absorption processes depend on the average covalent-ionic bonding and structural-topological features of the ChG [7, 12].

In this work, the following glassy system was investigated: As – S undoped and doped with manganese and chromium in various concentrations.

2. Experimental procedure

The binary As-S glasses doped with Mn (concentration 0.1, 1, 2, 5 wt.%) and Cr (concentration 0.5, 1 wt.%) were synthesized by using elements (As, S, Mn, Cr) of high purity, which were melted in evacuated ($p \sim 10^{-5}\ \text{Torr}$) and sealed silica ampoules at

850…900 °C for 24 hours and subsequently quenched in air. The prepared bulk glasses were cut into plates of 1 mm in thickness and polished to yield samples with high quality flat surfaces suitable for optical measurements. The amorphous nature of the bulk samples was confirmed by the absence of peaks in the X-ray diffraction pattern using X-ray diffractometer SEIFERT XRD 3000 PTS with CuK_α ($\lambda = 1.5418$ Å) emission source.

Room temperature transmission spectra in the $700 - 4000\ cm^{-1}$ region were recordered using FT spectrometer "Perkin Elmer" Spectrum BXII.

3. Results and discussion

The typical IR transmission spectra of the investigated ChG are presented in Figs. 1 and 2, respectively. The As – S – Mn(Cr) glassy systems are generally characterized by the similar behavior of impurity absorption processes for pure As_2S_3 and doped with transitional metals 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, 11 – 19]. Isolated (free) molecular water H_2O IR vibrational bands at $3600 - 3450\ cm^{-1}$are the most intensive in the obtained transmission spectra. The absorption band at $2488\ cm^{-1}$, associated with – S – H (sulphur-hydrogen) complexes, molecular-adsorbed water H_2O ($1589\ cm^{-1}$), sulfoxide groups ($1158\ cm^{-1}$) and different forms of arsenic oxide (1048 and $792\ cm^{-1}$), absorption band at $982\ cm^{-1}$ associated with As – O and/or As – H bonds show comparatively weaker intensities. Other researchers [17, 18] identify this band as vibration of As – S and/or S – S bonds. The small double peak at 2362 and $2346\ cm^{-1}$ is caused by the presence of CO_2 molecules. The absorption band of molecular H_2S ($2323\ cm^{-1}$) linked with the atoms of the ChG structural network, has the lowest intensities. However, authors in [17] assert that band $2323\ cm^{-1}$ corresponds to the vibrational band of CO_2 molecule.

According to Figs. 1 and 2, the intensity, spectral position and shapes of all impurity absorption bands in pure and doped ChG depend on their chemical compositions, i.e. on the doping level.

The intensities of the molecular-adsorbed water bands (band at 3450 and $1589\ cm^{-1}$) increase a little in the case of As – S systems doped with 0.5% Cr and 0.1% Mn. Essentially, the intensities of the bands for hydroxyl-containing groups (band $\sim 3601\ cm^{-1}$) slightly increase in the ChG of the As – S system doped with chromium and remain almost constant for the samples of As – S system doped with manganese.

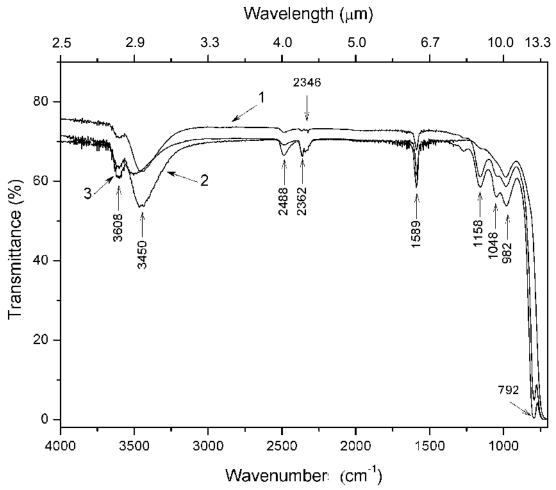

Fig. 1. Mid-infrared transmission spectra of glasses As_2S_3 (*1*), As_2S_3 + 0.5% Cr (*2*), As_2S_3 + 1% Cr (*3*).

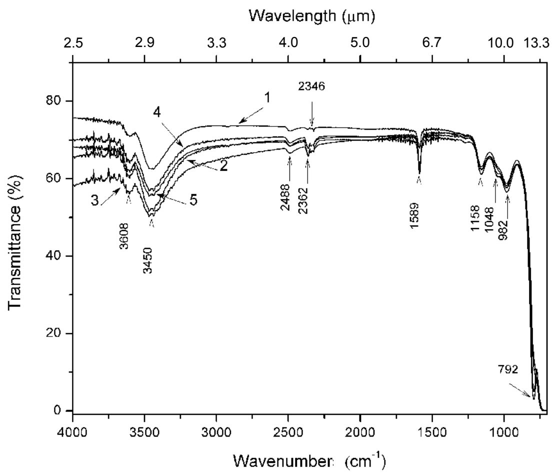

Fig. 2. Mid-infrared transmission spectra of glasses As_2S_3 (*1*), As_2S_3 + 0.1% Mn (*2*), As_2S_3 + 1 % Mn (*3*), As_2S_3 + 2% Mn (*4*), As_2S_3 + 5% Mn (*5*).

Thus, the concentration changes of the OH group do not coincide in both ChG systems. One can assume that the OH impurity complexes by their origin are structurally connected with S atoms, the relative content of which changes with the nature of dopant and doping level [12, 13, 19].

The content of molecular adsorbed water was estimated using the values of vibrational band intensities. The As atom content is responsible for the existence of H_2O impurities in the investigated ChG, limiting considerably their transparence within the 2.5–3.3 μm ($4000 - 3000\ cm^{-1}$) range [12, 13].

The absorption band at $2323\ cm^{-1}$ corresponds to the presence of molecular H_2S characteristic for pure As_2S_3 and vanishes after doping with Cr up to 1% and Mn up to 2%. For As_2S_3 + Mn 2% and 5%, the intensity rises up to the double value in comparison with pure As_2S_3. However, the intensity of the vibrational band at

Table. Assignments of characteristic vibrational bands for vitreous As_2S_3 doped with Cr and Mn.

Glass composition and characteristic atomic groups	Infrared peaks (cm^{-1}) and assignments										
	O – H	H_2O	S – H	CO_2	CO_2	H_2S [9, 10] or CO_2 [15, 16]	H_2O	SO_2	As – O [15, 16]	As – O As – H [9] or As – S S – S [15, 16]	AsO_4
As_2S_3	3601	3450	2488	–	2346	2323	1589	1158	1048	982	792
As_2S_3+0.5% Cr	3608	3451	2488	2362	2344	–	1588	1158	1047	981	793
As_2S_3+1% Cr	3604	3489	2486	2362	2344	–	1589	1159	–	984	–
As_2S_3+0.1% Mn	3608	3451	2488	2362	2342	–	1587	1158	1048	980	792
As_2S_3+1% Mn	3608	3450	2487	2361	2342	–	1587	1159	–	981	–
As_2S_3+2 % Mn	3605	3451	2486	2361	2343	2324	1588	1158	–	982	–
As_2S_3+5% Mn	3607	3451	2488	2362	2343	2324	1588	1157	1048	981	792

$2488\ cm^{-1}$ associated with $-S-H$ complexes increases monotonously for the samples doped with Cr, but for the samples of $As-S$ system doped with Mn the intensity band at $2323\ cm^{-1}$ practically does not change. Only a small increase of this band is observed. These features agree entirely with the concentration changes of the structural compactness in the investigated glasses [20]. The compactness decrease implies "free volume" formation in the glass structural network owing to the appearance of the specific "microvoids". One can suppose that $-S-H$ complexes are formed on the internal surfaces of these microvoids created technologically during rapid quenching the glass melt. It is also known that a lot of "dangling" S bonds appear in the process of ChG formation [21]. These bonds become non-active or saturate their main valence at the final stage of this process. So, saturation of ''dangling'' sulphur bonds takes place not only due to bonding of sulphur into its own structural chains, but also due to bonding with H atoms.

At the ChG synthesis, the parallel process of making the S "dangling" bonds closed by oxygen atoms (absorption band at $1158\ cm^{-1}$, attributed to the SO_2 impurity, 1048 and $792\,cm^{-1}$ associated with $As-O$ bonds), adsorbed from atmosphere or formed at the high-temperature H_2O decomposition, also occurs. Another possibility for the formation of $As-O$ and $S-S$ in the glass is incorporation of SO_2 molecules into the glass network through the breaking of $As-As$ bonds and formation of $>As-O-S-O-As<$ linkages [17–19]. The intensity of the $As-O$ and $S-S$ bands increases with decreasing of SO_2 bands. It is clear that these processes are comparatively weak, because the glass structural chains are not closed fully, but only partially, forming some bridges between neighboring atoms, fragments or blocks [21].

As it was found previously [20, 22], chromium or manganese dopants embedded to arsenic sulfide glasses influence on their structure and thermal properties. Introduction of Cr and Mn leads to the intensity increase of the main band at $346\ cm^{-1}$ that corresponds to antisymmetric As – (S) – As stretching vibrations in $As(S)_{3/2}$-pyramids and 192, 227, 236, $365\ cm^{-1}$ bands, which correspond to the presence of As_4S_4 nanophase. The intensity of $496\ cm^{-1}$ band characteristic for the vibrations of $S-S$ bonds is decreased with Cr and Mn introduction. On the other hand, the presence of Cr and Mn admixtures gives rise to decreasing the T_g value [22].

4. Conclusion

The effect of transition metal (Mn and Cr) impurities on the optical properties of As_2S_3 glass is studied in the mid-infrared spectral region. The investigations of IR impurity absorption spectra of $As-S-Mn(Cr)$ ChG show that the intensity of vibrational absorption bands of various impurity structural fragments essentially depends on chemical composition of glasses. The observed changes upon doping with Mn and Cr in the mid-infrared region are most likely related to interactions of a portion of the introduced metal ion impurities with the inherent impurities of the host glass, such as hydrogen and oxygen atoms. It has been ascertained that As atoms are responsible for absorption of molecular water H_2O, whereas S atoms – for hydroxyl groups (OH). The $-S-H$ and $-S-OH$ groups are stabilized in the glass structural network as the products of closing the S "dangling" bonds, and $-S-H$ groups are formed on the internal surfaces of microvoids created technologically during preparation of the samples.

The obtained results must be taken into account in the fabrication process of the investigated ChG for IR optical devices.

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