IR studies of impurities in chalcogenide glasses and thin films of the Ge-Sb-S-Te system

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Abstract. Chalcogenide glasses with composition Ge_xSb_{40-x}S_{50}Te_{10} (x = 10, 20 and 27 at.% ) were synthesized and thin films from these parent materials were evaporated onto glass substrates. The vibrational properties of the impurities in the powdered glasses and the corresponding films were studied by FTIR spectroscopy. Vibrational modes attributed to O-H hydroxyl groups, molecular H_2O and carbon impurity atoms were detected in the IR spectra of powdered glasses, but were absent in the IR spectra of the films. Vibrational modes of oxygen atoms bonded to basic elements, such as Ge-O and Te-O bonds, were present in the IR spectra of both kinds of samples.

1. Introduction
In general, chalcogenide glasses transmit longer IR wavelengths than silica and fluoride glasses and thus find applications in civil, medical and military areas [1,2,3]. The transparency range of these glasses depends on their composition. For example, for S-based glasses the transparency is located within the 0.5 – 7 μm spectral range; for Se-based glasses it is within 0.8 – 12 μm; and for telluride glasses this range is 1.2 – 16 μm. The applications of chalcogenide glasses in the IR optics are mainly restricted by vibrational absorption bands of impurities introduced during and/or after the glass synthesis [4]. Therefore, choosing proper glass compositions for which the ability for chemical interaction between the absorbed impurities and the covalent-bonded glass-forming network is minimal is of great importance. Useful information about the impurity atoms properties and their chemical bonding can be obtained by IR spectroscopy.

Recently, we started studying the physico-chemical properties of a new quaternary chalcogenide glassy system, namely Ge-Sb-S-Te [5,6]. We report here the results of an IR spectroscopic study of synthesized Ge_xSb_{40-x}S_{50}Te_{10} (x = 10, 20 and 27 at. %) glasses and of thin films evaporated from these parent materials, focusing on the impurities present in the samples. The information obtained on the IR absorption observed for various bonded impurity atoms is discussed in terms of the samples composition.
2. Experimental details

The glassy alloys of Ge\textsubscript{x}Sb\textsubscript{40-x}S\textsubscript{50}Te\textsubscript{10} (x = 10, 20, 27) were synthesized from 5N purity elements by the conventional melt-quenching method. The synthesis was performed in a rotary furnace, the glass components of a proper composition being placed in a quartz ampoule evacuated down to 10\textsuperscript{-3} Pa. The ampoules were loaded in the furnace and heated up to 950°C. They were kept at this temperature for 24 h rotating the furnace for homogeneous melting and, upon ending the process, the ampoules were pulled out and quenched in ice water.

Part of the bulk glasses thus synthesized was powdered. For IR measurements, the powdered glasses (~1 mg each) were mixed with spectroscopic grade KBr (200 mg each) and the mixtures were pressed into pellets and dried at 100°C for one hour. The other part served as a parent material for thermal vacuum evaporation of corresponding thin films onto ordinary glass substrates. The thickness of the films (~1 µm) was controlled in situ by a MIKI FFV quartz sensor device.

The pellets were measured on a Nicolet 6700 Fourier Transform Infrared (FTIR) Spectrometer, while the thin films, on a SHIMADZU FTIR Prestige-2 operating with a high-energy ceramic light source (350 – 7800 cm\textsuperscript{-1}) and a high signal-to-noise ratio of 40000:1. For both apparatuses, the FTIR measurements were performed at room temperature in the spectral range of 4000 – 400 cm\textsuperscript{-1} and 4000 – 350 cm\textsuperscript{-1}, respectively, with a resolution of 4 cm\textsuperscript{-1}. The spectral range of these apparatuses allows one to detect the infrared absorption bands for various bonded impurity atoms.

3. Results and discussion

Generally, mainly oxide and hydride impurities may be present in chalcogenide glasses. Most of the absorption bands observed in the IR spectra could be assigned to vibrational bands of these impurity bonds. The IR spectra of powdered glasses and the corresponding thin films are presented in figures 1 and 2, respectively, while the position of the detected absorption bands are summarized in tables 1 and 2. The bands were identified on the basis of experimental observations reported in refs [9-17].

3.1. IR transmittance spectra of powdered glasses

The glasses showed good transparency in the entire spectral range studied. The transmittance values showed a weak tendency to decrease with decreasing the Ge content. The IR transmittance spectra of all three glassy compositions were similar; thus, only the IR spectra of Ge\textsubscript{10}Sb\textsubscript{30}S\textsubscript{50}Te\textsubscript{10} and Ge\textsubscript{27}Sb\textsubscript{13}S\textsubscript{50}Te\textsubscript{10} compositions, i.e. the glasses with the lowest and highest Ge amount, are illustrated in figure 1. Various absorption bands are seen, which are related to chemical bonds of different extrinsic impurities present in the glassy material. The position of these impurity bands are summarized in table 1. It should be noted that the vibrational bands related to the basic chemical bonds in the glassy compositions are below the measurement limit of 400 cm\textsuperscript{-1} and, therefore, cannot be detected.

For all three compositions, the most intensive and broadest band appeared within the range 3300–3700 cm\textsuperscript{-1} with a minimum centered at around 3446 cm\textsuperscript{-1}. This absorption band can be associated with the vibrational modes of O-H hydroxyl groups bonded with external hydrogen and/or atoms of the chalcogenide structural network [9-11]. The other, much weaker band, associated with adsorbed molecular H\textsubscript{2}O [10] appeared around 1640 cm\textsuperscript{-1}. The reason for the appearance of these two absorption bands most probably is moisture absorbed by the sample from the environment during the samples preparation (powdering, pressing etc) and during the IR measurements.

\begin{figure}[h]
\centering
\includegraphics[width=1\textwidth]{image1.png}
\caption{IR transmittance spectra of Ge-Sb-S-Te powdered glasses with compositions, inserted.}
\end{figure}
Table 1. Position of impurity bands in the IR spectra of powdered Ge-Sb-S-Te glasses.

| Vibrational modes | Vibrational band position (cm⁻¹) |
|-------------------|---------------------------------|
|                   | Ge₂₇Sb₁₃S₅₀Te₁₀ | Ge₂₀Sb₂₀S₅₀Te₁₀ | Ge₁₀Sb₃₀S₅₀Te₁₀ |
| ν₂O-H             | 3448             | 3431             | 3444             |
| ν₂C-H             | 2920             | 2920             |                  |
| ν₂C-O-S           | 2050             | 2051             |                  |
| ν₂O-H             | 1639             | 1637             | 1640             |
| ν₂C-H             | 1430             | 1440             |                  |
| ν₂C-O ; ν₂C-H     | 1160             | 1106             |                  |
| ν₂Ge-O            | 1032             | 1048             | 1047             |
| ν₂Te-O            | 668              | 663              | 529              |

The intensity of water and O-H related vibrational bands depends on the glassy composition. S-based chalcogenides have larger affinity to absorbing water-related particles and the absorbed impurities bind structurally with S atoms [18]. In our case, the S amount is constant and, therefore, the variation observed of the intensity of these two bands can be explained by the difference in Sb atomic concentration [18]. By increasing the Sb content, the metallic character of chemical bonds increases and, thus, the probability increases of Sb atoms interacting with these impurities [18].

The oxides are among the impurities that are strongly dependent on the chemical composition of chalcogenide glasses. In all IR spectra, absorption bands are present related to vibration of oxygen atoms bonded to basic elements or to carbon impurity atoms. A band has been reported in the spectral range 700 – 800 cm⁻¹ assigned to phonon absorption of Ge-O bonds within mixed chalcogenide germanium tetrahedra [14]. Therefore, the shoulder observed around 800 – 730 cm⁻¹ can be due to the presence of Ge-O bonds in the powders. In addition, the weak band around 1040 cm⁻¹ can also be related to the Ge-O vibration mode [16]. The broad and asymmetric band centered between 668 – 529 cm⁻¹ can be, dependent on the composition, attributed to vibrational mode of Te-O bonds [13].
All other absorption bands detected in the IR spectra are very weak and do not dependent on the glass composition. They can be assigned to vibrations of carbon impurities in different configurations. The absorption bands in the ranges 2860 – 2922 cm\(^{-1}\) and 1430 – 1383 cm\(^{-1}\) are assigned to stretching and bending vibration of C-H bonds, respectively, in CH\(_2\) and/or CH\(_3\) impurity groups [10, 19]. Absorption bands in the range 1160-1106 cm\(^{-1}\) can be assigned to vibrations of the C-O ester groups and/or the CH\(_2\) group [20]. The broad and very weak band centered at 2050 cm\(^{-1}\) has been assigned to C-O-S impurity groups due to contamination of the raw materials [10,12].

In conclusions, it is shown that the influence of O- and C- containing complexes (–C–O–, =C–O–S– and –C–H–) on the IR transmittance spectra is insignificant in comparison with that of water related impurities. Since all these impurities are present in powdered chalcogenides, one would expect that they will transferred into the growing film during evaporation of powdered glasses.

### 3.2. IR reflectance spectra of evaporated films

The IR reflectance spectra of the films are presented in figures 2a and 2b. The positions of the absorption bands of the corresponding chemical bonds are summarized in table 2.

In the spectral range 1200 cm\(^{-1}\) – 4000 cm\(^{-1}\) (figure 2a), interference fringes appeared, with the vibrational bands of the proper chemical bonds being superimposed on them. Absorption bands of water-related impurities in the IR spectra can be observed neither at ~3600 cm\(^{-1}\) nor at ~1640 cm\(^{-1}\), which is evidence that the films are free from these impurities.

The doublet observed in the spectral range 2340 – 2365 cm\(^{-1}\) (figure 2) is due to the presence of H\(_2\)S molecules in the film surface region [10]. The intensity of this band has a tendency to increase with increasing the Ge content as a result of compositional variations and structural compactness [5]. Such a vibrational band is not observed in the IR spectra of the corresponding parent glasses (figure 1) because the parent materials are with better stoichiometry and higher compactness.

Concerning the oxygen related impurities, some weak vibrational bands are present in the IR spectra of the evaporated films as well. According to literature data [21], the vibrational bands in the spectral ranges 400 – 500 cm\(^{-1}\) (figure 2b) and 720 – 780 cm\(^{-1}\) (figure 2a) are attributed to intermolecular vibrations of Te-O chemical bonds. In our case, weak bands were detected at 419, 668 and 746 cm\(^{-1}\) which could be related to Te-O bond vibrations. The band at 900-912 cm\(^{-1}\) was more

### Table 2. The position of vibrational bands in the IR spectra of Ge-Sb-S-Te thin films.

| Vibrational modes | Vibrational band position (cm\(^{-1}\)) |
|-------------------|-------------------------------|
|                   | Ge\(_{27}\) Sb\(_{13}\) S\(_{50}\) Te\(_{10}\) | Ge\(_{20}\) Sb\(_{20}\) S\(_{50}\) Te\(_{10}\) | Ge\(_{10}\) Sb\(_{30}\) S\(_{50}\) Te\(_{10}\) |
| \(v_{\text{H-S-H}}\) | 2364 | 2364 | 2364 |
| \(v_{\text{Ge-O-Ge}}\) | 2344 | 2344 | 2344 |
| \(v_{\text{Ge-S}}\) | 912 | 906 | 900 |
| \(v_{\text{Te-O}}\) | 746 | 746 | 746 |
| \(v_{\text{GeS}_{4/2}}\) | 668 | 668 | 668 |
| \(v_{\text{GeO}}\) | 419 | 419 | 419 |
| \(v_{\text{GeS}}\) | 466 | 460 | 444 |
| \(v_{\text{GeS}}\) | 392 | 392 | 397 |
| \(v_{\text{GeS}}\) | 381 | 381 | 386 |
| \(v_{\text{GeS}}\) | 374 | 373 | 375 |
| \(v_{\text{GeS}}\) | 370 | 370 | 370 |
| \(v_{\text{GeS}}\) | 366 | 366 | 361 |
intense and could be assigned to the stretching mode of oxygen in Ge-O-Ge bonds [15]. The presence of oxygen atoms binding to basic elements is quite realistic since the films have been exposed to air after sample loading from the vacuum chamber, as well as during storage and IR measurements. Our earlier XPS studies of chalcogenide films with other compositions [22] revealed some degree of oxidation of the surface layer.

For all three film compositions, a strong and broad band with several superimposed small minima in the spectral range 350 – 500 cm\(^{-1}\) was detected (figure 2b). The broad band centered around 460 – 446 cm\(^{-1}\) is related to the vibrational mode of Ge-S chemical bonds [12, 17]. The small peaks, superimposed on this band, centered at different positions (table 2) can be assigned to the stretching mode of the basic GeS\(_{4/2}\) tetrahedral units with possible different configurations [8, 23].

The vibrational modes of the other basic chemical bonds are beyond the IR measurement limit (350 cm\(^{-1}\)) and, thus, cannot be detected.

Conclusions
Extrinsic impurities in the powdered glassy alloys of Ge\(_{x}\)Sb\(_{40-x}\)S\(_{50}\)Te\(_{10}\) (x = 10, 20, 27) and of films evaporated in vacuum from these parent materials were studied by FTIR spectroscopy. The FTIR transmittance spectra of powdered glasses revealed water related impurities, which are dominant over the impurities of O- and C- containing complexes. The evaporated films are free from water impurities but absorption bands related to Ge-O and Te-O chemical bonds are detected, most probably due to oxidation of the surface region.

References
[1] Keirsse J, Boussard-Pledel C, Loreal O, Sire O, Bureau B, Leroyer, P, Turlin B and Lucas J
2003 Vibrational Spectrosc. 32
[2] Busse L, Moon J, Sanghera J and Aggarwal I 1996 Laser Focus World 32 143
[3] Sanghera J, Shaw L, Busse L, Nguyen V, Pureza P, Cole B, Harbison B, Aggarwal I, Mossadegh R, Kung F, Talley D, Roselle D and Miklosh R 2000 R Fiber Integr. Opt. 19 251
[4] Seddon A 1995 J. Non-Cryst. Solids 184 44
[5] Pamukchieva V, Szekeres A, Todorova K, Fabian M, Svab E, Revay Zs and Szentmiklosi L
2009 J. Non-Cryst. Solids 355 2485
[6] Pamukchieva V, Szekeres A, Todorova K, Svab E and Fabian M 2009 Opt. Mater. 32 45
[7] Kamitso E I, Kapartsis J A, Culeas I P and Iovu M S 1997 J. Phys. Chem. B 101 11061
[8] Mei Q, Siaienga J, Schrooten J, Meyer B and Martin S W 2003 J. Non-Cryst. Solids 324 264
[9] Mironov V A and Yankovskii S A 1985 Spectroscopy in Organic Chemistry (Moscow: Khimiya)
[10] Kavetsky T S, Kovalskiy A P, Pamukchieva V D and Shpotyuk O I 2000 Infrared Phys. Tech. 41 41
[11] Efimov M and Pogareva V G 2000 J. Non-Cryst. Solids 275 189
[12] Smith C, Jackson J, Petit L, Rivero-Baleine C and Richardson K 2010 J. Solid St. Chem. 183 1891
[13] Munoz-Martín D, Villegas M A, Gonzalo J and Fernandez-Navarro J M 2009 J. Eur. Ceram. Soc. 29 2903
[14] Tikhomirov V K, Furniss D, Seddon A B, Savage J A, Mason P D, Orchard D A and Lewis K L
2004 Infrared Phys. Technol. 45 115
[15] Rath S, Kabiraj D, Avasthi K D, Tripathi A, Jain K P, Kumar M, Mavi H S and Shukla A K
2007 Nucl. Instr. Meth. Phys. Res. B 263 419
[16] Ito F, Nakanaga T, Takeo H, Essig K and Jones H 1995 J. Molecular Spectr. 174 417
[17] Nakamoto K 2009 Infrared and Raman Spectra of Inorganic and Coordination Compounds Part A (Wiley, New York)
[18] Kavetsky T, Golovchak R, Shpotyuk O, Filipiecki J and Swiatek J 2004 J. Optoelectron. Adv. Mater. 6 1141
[19] Bellamy L J 1958 The Infra-Red Spectra of Complex Molecules (London: Methuen)
[20] Trif M, Ansorge-Schumacher M and Socaciu C 2007 Proc. XI\(^{th}\) Int. Workshop Bioencapsulation (6-8 Sept. Vienna Austria)
[21] Frumarova B, Oswald J, Kremer P, Frumar M, Cerny V and Smrcka V 1996 Opt. Mater. 6 217
[22] Pamukchieva V, Skordeva E, Arsova D, Guimon M F and Gonbeau D 2005 J. Optoelectron. Adv. Mater. 7 1265
[23] Julien C, Barnier S, Massot M, Chbani N, Cai X, Loireau-Lozac’h A and Guittard M 1994 Mater. Sci. Eng. B 22 191