Laser Desorption Ionization Time-of-Flight Mass Spectrometry of Silver-Doped (GeS$_2$)$_{50}$(Sb$_2$S$_3$)$_{50}$ Chalcogenide Glasses

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ABSTRACT: Mass spectra of (GeS$_2$)$_{50}$(Sb$_2$S$_3$)$_{50}$ glass and Ag-doped glasses [5% Ag (GeS$_2$)$_{50}$(Sb$_2$S$_3$)$_{50}$ and 15% Ag (GeS$_2$)$_{50}$(Sb$_2$S$_3$)$_{50}$] obtained using laser desorption ionization (LDI) time-of-flight coupled with quadrupole ion trap mass spectrometry were studied. The analysis of the mass spectra indicated the formation of Ag$_2$Sb$_2$S$_4$ clusters. In addition to the Sb$_2$S$_4$' (d = 1 and 2), Sb$_2$S$_4$' (d = 1–3), Sb$_2$S$_4$' (d = 1–5), Sb$_2$S$_4$' (d = 3 and 4), Sb$_2$S$_4$' (d = 3 and 5), Sb$_2$S$_4$' (d = 3 and 5) clusters, various clusters containing Ag, such as AgSb$_2$S$_4$' (a = 1 and 2), AgGe$_2$S$_4$', AgSb$^{+}$' (c = 1, 2, and 4), AgSb$^{+}$' Sb$_2$S$_4$' (d = 1–5), AgSb$_2$S$_4$' Sb$_2$S$_4$' (d = 3 and 5), AgSb$_2$S$_4$' Sb$_2$S$_4$' (d = 4 and 5), AgSb$_2$S$_4$' Sb$_2$S$_4$' and AgSb$_2$S$_4$' were generated. Moreover, in spite of the five-ninth purity of all glass components, several hydrogenated clusters (Sb$_2$H$_4$', Sb$_2$H$_4$', Sb$_2$H$_4$', AgH$_{11}$', Ag$_2$Sb$_2$H$_4$', Ag$_2$Sb$_2$H$_4$', Ag$_2$Sb$_2$H$_4$' and Ag$_2$Sb$_2$H$_4$') and some low-intensity oxidized clusters, such as Sb$_2$O$^{+}$ and Sb$_2$O$_5$' were also detected. When applying LDI on (GeS$_2$)$_{50}$(Sb$_2$S$_3$)$_{50}$ glass, no Ge-containing clusters were detected in the positive ion mode, and mass spectrometry was complemented with Raman spectroscopy. The knowledge gained concerning cluster stoichiometry contributes to the elucidation of the structure of Ag-doped Ge--Sb--S chalcogenide glasses. It should be noted that some of the clusters were considered to be structural fragments. Furthermore, mass spectrometry was complemented with Raman spectroscopy.

INTRODUCTION

Crystalline and amorphous chalcogenides are high-tech materials that have strategic importance. The Ge--Sb--S system is an important member of the chalcogenide glass family. The properties of Ge--Sb--S glasses have already been studied, including their optical, mechanical, and structural properties. Ag-doped materials are already widely used in many fields. The incorporation of Ag into Ge--Sb--S materials changes their optical transmittances, optical gaps, reflectivity, and so forth. Higher indexes of refraction, decreased sensitivities to alkaline etching, and red-shifted absorptions have been observed in such glasses in comparison with silver-free chalcogenide glasses. Ag-doped Ge--Sb--S glasses are utilized in RAM memory and are also widely used in many other fields, for example, as solid electrolytes, optical waveguides, holographic devices, and electrochemical sensors. Inorganic hydrides represent a wide class of compounds that have been described extensively. The role of hydrogen in impairing the optical and emission properties of chalcogenide glass fibers has been studied. When hydrogenated chalcogenide glasses were deliberately prepared, they show some unique and improved properties. Because Ag acts to form a high number of hydrides, the formation of silver hydrides in glasses follows. Recently, the thermokinetic behaviors of Ag-doped (GeS$_2$)$_{50}$(Sb$_2$S$_3$)$_{50}$ glasses have been studied, along with the influence of Ag on their structures and physical properties.

The aim of the present study is to use mass spectrometry (MS) to elucidate the chemistry of these materials, especially in terms of their basic structural items, via the study of the clusters generated by laser desorption ionization (LDI) in both undoped and silver-doped (GeS$_2$)$_{50}$(Sb$_2$S$_3$)$_{50}$ chalcogenide glasses. Complementary structural information on these glasses was acquired via Raman spectroscopy.

RESULTS AND DISCUSSION

The formation of clusters generated from (GeS$_2$)$_{50}$(Sb$_2$S$_3$)$_{50}$ glass, as well as from the same glass doped with 5 or 15% Ag via LDI, was studied. A reflectron or linear mode was employed to record the mass spectra in both positive and negative ion modes. It was shown that the clusters produced in the positive ion mode were of high intensity, and mass spectra indicated that they...
occurred in higher numbers than the clusters in the negative ion mode. Therefore, the discussion to follow will be based largely on the results from the positive ion mode.

**LDI of (GeS$_2$)$_{50}$(Sb$_2$S$_3$)$_{50}$ Chalcogenide Glass.** An example of the mass spectra of (GeS$_2$)$_{50}$(Sb$_2$S$_3$)$_{50}$ chalcogenide glass generated via LDI at laser energy 170 a.u. is given in Figure S1. Sb$_5$S$_4$$^+$ (d = 1 and 2), Sb$_3$S$_2$$^+$ (d = 1–3), Sb$_3$S$^+$ (d = 1–5), Sb$_2$S$_3$$^+$, and Sb$^+$ (c = 1 and 2), Ag$^{+}$, and AgSb$^{+}$ were detected. Some hydrogenated Sb$_3$H$_5$$^+$ clusters were detected. Some hydrogenated clusters containing antimony, sulfur, or both elements, for example, Sb$_3$H$_5$$^+$, were also identified. No clusters containing Ge were detected in the positive ion mode. However, GeSbS$^+$, GeSbS$_3$$^+$, and GeSbS$_5$$^+$ clusters were observed in the negative ion mode, as shown in Figure 1. A comparison of the experimental and theoretical isotopic patterns demonstrated that the most intensive cluster was Sb$_5$S$_4$$^+$, as shown in Figure S2, and a good agreement between the experimental and theoretical mass spectra was observed.

**Effect of Laser Energy on 5% Ag-Doped (GeS$_2$)$_{50}$(Sb$_2$S$_3$)$_{50}$ Chalcogenide Glass in Negative Ion Mode.** A comparison of the mass spectra generated for 5% Ag-doped (GeS$_2$)$_{50}$(Sb$_2$S$_3$)$_{50}$ chalcogenide glass at different laser energies is shown in Figure S7. The spectra for the negative ion mode differ from those for the positive ion mode. The most intense peak in the negative ion mode was for Sb$^-$ clusters, while the most intense peak corresponded to the Sb$^-$ cluster for 10% silver-doped material and the AgSb$^-$ cluster for 15% silver-doped glass. In the 410–500 m/z range, the most intense peak was for AgSb$_2$$^-$, and Sb$_2$$^-$ were observed after conducting LDI on 5% Ag-doped glass, but they were not detected for 15% silver-doped glass. Most of the hydrogenated clusters were observed in the 500–800 m/z range. The intensities of the mass spectra for the 5% Ag-doped glass were higher than those for the 15% Ag-doped glass (which is opposite to what was observed in the 100–160 m/z range).

**Comparison of (GeS$_2$)$_{50}$(Sb$_2$S$_3$)$_{50}$ 5% Ag-Doped (GeS$_2$)$_{50}$(Sb$_2$S$_3$)$_{50}$ and 15% Ag-Doped (GeS$_2$)$_{50}$(Sb$_2$S$_3$)$_{50}$ Mass Spectra.** Figure 2A–D shows the mass spectra of (i) (GeS$_2$)$_{50}$(Sb$_2$S$_3$)$_{50}$ (ii) 5% Ag-doped (GeS$_2$)$_{50}$(Sb$_2$S$_3$)$_{50}$ and (iii) 15% Ag-doped (GeS$_2$)$_{50}$(Sb$_2$S$_3$)$_{50}$ glasses measured at the same laser energy (160 a.u.). In the 100–160 m/z range, it was observed that when silver is incorporated into (GeS$_2$)$_{50}$(Sb$_2$S$_3$)$_{50}$ glass and its percentage is increasing from 5 to 15%, the intensities of the mass spectra also increase (indicating the decreasing stability of silver-doped chalcogenide glass). In the 190–410 m/z range, the most intense peak for nondoped glass was for the Sb$^-$ cluster, while the most intense peak was for the Sb$^-$ cluster for the 5% silver-doped material and the AgSb$^-$ cluster for 15% silver-doped glass. In the 410–500 m/z range, the most intense peak for nondoped glass was for AgSb$_2$$^-$, which contrasts with the findings for the positive ion mode, where Sb$^-$ had the most intense peak (cf. Figure S3). In this mass range, the exception of AgSb$_2$$^-$, Sb$_2$$^-$ (d = 2, 3), Sb$_3$$^-$ (d = 3–5), and AgSbS$_3$$^-$ (d = 3–5) clusters, which were also generated in the positive ion mode, the other clusters are missing. The spectra below 250 and over 550 m/z at low intensity are not provided (only two clusters, namely, Ag$_2$SbS$^-$ and Ag$_2$Sb$_2$$^-$, were detected). Figure S7 demonstrates that the intensities of the clusters increase when the laser energy increases from 150 to 160 a.u., but the same intensities decrease when the laser energy is further increased to 170 a.u., except in the case of AgSb$_2$$^-$ clusters. A comparison of the experimental and theoretical isotopic patterns for the AgSb$_2$$^-$ cluster is given in Figure S8, and there is good agreement between the experimental results and the theoretical model.

In conclusion, the glasses’ structural disorder allows the random formation of homopolar bonds (Ge–Ge, Sb–Sb, and S–S). It is also clear that silver reacts with sulfur and forms preferential Ag–S bonds, which results in sulfur depletion and the formation of Ge–Ge and Sb–Sb bonds. The LDI technique is powerful enough to ionize all the Ge–Ge and Sb–Sb bonds.

**Hydrogen Presence in Clusters.** Even though the studied materials were made from elements (Ag, Ge, Sb, and S) with five-ninths (SN) purity, several hydrogenated clusters, namely, SbS$_3$$^+$, Sb$_2$S$_4$$^+$, Ag$_3$Sb$_2$$^+$, Ag$_2$SbH$_4$$^+$, Ag$_3$Sb$_2$H$_4$$^+$, Ag$_3$Sb$_2$H$_4$$^+$, Ag$_2$SbH$_4$$^+$, Ag$_3$Sb$_2$H$_4$$^+$, and Sb$_2$S$_3$H$_4$$^+$ were detected. The hydrogen detected in the studied glasses is most probably from elements used for synthesis. Even when SN purity standards are used, traces of hydrogen can be present because H$_2$ is used as a reduction agent during the preparation of the pure elements.
Raman Spectra of Glasses. The Raman spectra of prepared undoped and Ag-doped (GeS2)50(Sb2S3)50 glass samples are shown in Figure 3. All Raman spectra were scaled by area and decomposed into a series of Raman peaks. Raman spectroscopy was performed to analyze the structures in a nondestructive way, unlike MS. Moreover, MS was not able to detect any structural units of clusters related to $\text{Ge}^{\equiv}\text{S}^{\equiv}$ or $\text{Ge}^{\equiv}\text{Ge}$ in undoped Ge–S glass. These structural units were identified via Raman spectroscopy.

The Raman spectra of (GeS2)50(Sb2S3)50 glass are shown in Figure 3A. These spectra are in good agreement with those for similar glasses in the Ge–Sb–S system.23–26 The Raman band between 200 and 450 cm$^{-1}$ can be decomposed into seven bands with maxima near 250, 290, 318, 343, 360, 390, and 415 cm$^{-1}$.

Figure 3. Raman spectra of (A) (GeS2)50(Sb2S3)50, (B) 5% Ag-doped glass, and (C) 15% Ag-doped glass and (D) comparison of the integral intensities of the Raman bands at 212, 318, 343, and 415 cm$^{-1}$.
The main Raman bands, which are located at 343, 318, and 290 cm\(^{-1}\), have been attributed to the symmetric stretching vibrations of corner-sharing \([\text{GeS}_4]\) tetrahedra and asymmetric and symmetric stretching vibrations of \([\text{SbS}_3]\) pyramids. The smaller bands at 360, 390, and 415 cm\(^{-1}\) can be ascribed to edge-shared \([\text{GeS}_4]\) tetrahedral symmetric stretching vibrations, asymmetric stretching vibrations of corner-shared \([\text{GeS}_4]\) tetrahedra, and bridging sulfur vibrations in the \(\text{S}_3\text{Ge}^–\text{S}\text{GeS}_3\) structural units, respectively. Finally, the band at 250 cm\(^{-1}\) can be assigned to vibrations of the \(\text{Ge}^–\text{Ge}\) bonds in the \(\text{S}_3\text{Ge}^–\text{S}\text{GeS}_3\) ethane-like structural units.

The low-intensity broad band in the region 100–200 cm\(^{-1}\) can be decomposed into three bands at 110, 140, and 170 cm\(^{-1}\) corresponding to bending vibrations (\(\nu_2\) and \(\nu_4\) mode) of \(\text{GeS}_4\) tetrahedra and \(\text{Sb}^–\text{Sb}\) vibrations in \((\text{S}_2)\text{Sb}–\text{Sb}(\text{S}_2)\) bipyramidal units.

The addition of silver to \((\text{GeS}_2)_{50}(\text{Sb}_2\text{S}_3)_{50}\) glass causes several changes:

1. The addition of silver at 5\% (Figure 3B,D): The intensity of the band connected to the vibrations of the \(\text{SbS}_3\) pyramids (318 cm\(^{-1}\)) decreases, while the intensity of the band corresponding to the vibrations of the \(\text{Sb}–\text{Sb}\) bonds (170 cm\(^{-1}\)) increases. The new band at 212 cm\(^{-1}\) appears when the silver is added to the glass matrix. This band indicates the formation of \(\text{Ag}^–\text{S}\) bonds dispersed in glass structure. A similar band was found in the Raman spectra of \(\text{Ag}_2\text{S}\) amorphous thin film.\(^{27}\)

2. The addition of silver at 15\% (Figure 3C,D): The intensity of the band at 318 cm\(^{-1}\) decreases progressively, while the intensities of the bands corresponding to the corner-sharing \([\text{GeS}_4]\) tetrahedra (343 and 390 cm\(^{-1}\)) decrease slightly. The intensities of the bands at 170, 212, 250, 360, and 415 cm\(^{-1}\) increase.

We assume that silver is first incorporated into the host structure via its interactions with the sulfur atoms in the \([\text{SbS}_3]\) pyramids. Thus, the concentration of \(\text{Sb}–\text{Sb}\) bonds grows. The intense growth of the band at 250 cm\(^{-1}\) shows that more ethane-like structural units have been formed. The reduction of the band near 343 cm\(^{-1}\) and the growth of bands at 360 and 415 cm\(^{-1}\) indicates that the addition of silver leads to the breaking of \(\text{Ge}^–\text{S}–\text{Ge}\) bridges and the creation of nonbridging sulfur \(\text{Ge}^–\text{S}\) terminal bonds \([\text{pyro-}(\text{GeS}_3.5^–\text{S}), \text{meta-}(\text{GeS}_5^–\text{S})]\), and di-

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**Table 1. Clusters Generated from \((\text{GeS}_2)_{50}(\text{Sb}_2\text{S}_3)_{50}\) and Its Ag-Doped Chalcogenide Glasses**

| Ag doping | Clusters Generated |
|-----------|-------------------|
| 5%        | \(\text{SbS}^+\) | \(\text{SbS}_2^+\) | \(\text{Sb}_2\text{S}_2^+\) | \(\text{Sb}_3\text{S}_3^+\) | \(\text{Sb}_3\text{S}_4^+\) | \(\text{Sb}_3\text{S}_5^+\) |
|           | \(\text{SbS}^+\) | \(\text{SbS}_2^+\) | \(\text{Sb}_2\text{S}_2^+\) | \(\text{Sb}_3\text{S}_3^+\) | \(\text{Sb}_3\text{S}_4^+\) | \(\text{Sb}_3\text{S}_5^+\) |
|           | \(\text{SbS}^+\) | \(\text{SbS}_2^+\) | \(\text{Sb}_2\text{S}_2^+\) | \(\text{Sb}_3\text{S}_3^+\) | \(\text{Sb}_3\text{S}_4^+\) | \(\text{Sb}_3\text{S}_5^+\) |
|           | \(\text{SbS}^+\) | \(\text{SbS}_2^+\) | \(\text{Sb}_2\text{S}_2^+\) | \(\text{Sb}_3\text{S}_3^+\) | \(\text{Sb}_3\text{S}_4^+\) | \(\text{Sb}_3\text{S}_5^+\) |
| 15%       | \(\text{SbS}^+\) | \(\text{SbS}_2^+\) | \(\text{Sb}_2\text{S}_2^+\) | \(\text{Sb}_3\text{S}_3^+\) | \(\text{Sb}_3\text{S}_4^+\) | \(\text{Sb}_3\text{S}_5^+\) |
|           | \(\text{SbS}^+\) | \(\text{SbS}_2^+\) | \(\text{Sb}_2\text{S}_2^+\) | \(\text{Sb}_3\text{S}_3^+\) | \(\text{Sb}_3\text{S}_4^+\) | \(\text{Sb}_3\text{S}_5^+\) |

*Bold*: clusters containing silver; *Italics*: clusters containing both silver and hydrogen.
(GeS$_2$)$_2$ thiogermainate tetrahedra). The presence of metathiogermaine tetrahedra can indicate the formation of the Ag,Ge,S amorphous phase, which then becomes an inherent part of the amorphous network. Our results are in good agreement with those given in Fraenkle et al.22

Another aim of this work was to study the silver doping of glasses using MS. LDI time-of-flight MS decomposes glass into ionic fragments in contrast to Raman spectroscopy, which is a nondestructive technique. The identified fragments (clusters) are listed in Table 1. In contrast to the similar (GeSe$_2$) (SbSe$_2$) system,31 there were no Ge-containing clusters detected when LDI was applied to generate the mass spectra of nondoped glasses in the positive ion mode. A possible explanation could be that the bond energy of Ge -- S is higher than that of Sb -- S (Ge -- S = 534 kJ/mol, Sb -- S = 199 kJ/mol)22 and also higher than the bond energy of Ge -- Ge and Sb -- S (Ge -- Ge = 188 kJ/mol). Another possible explanation is that the electronegativity of S is greater than that of Se. Regardless, the presence of Ge-containing structural units and Ge and Sb bonds was confirmed by Raman spectroscopy, which also clearly identified Ge -- Ge and Sb -- Sb bonds when silver was added to the glass structure. Comparison of the results of Raman spectroscopy with MS is shown in Table 2. Germanium-contained structural units were detected by Raman spectroscopy but not observed by MS. This might be because these structural units are too stable (tetrahedral structure and high bond energy of Ge -- Ge or Ge -- S bonds) to be decomposed by MS. There are no Ag -- S -- Sb structural units detected by Raman, but they were observed by MS. This is, for example, because of the possible reactions that happened between the ions in the plasma plume. In conclusion, while Raman spectroscopy detects the basic structural units, MS shows mostly their fragments. Thus, the combination of these two techniques provides a more complex image of the glass structure and bond strengths when the glass is exposed to laser beams with different energies and intensities.

## CONCLUSIONS

LDI can generate clusters in Ge -- Sb -- S and its Ag-doped chalcogenide glasses efficiently, and the simultaneous use of a time-of-flight mass spectrometer yields mass spectra that can be analyzed to provide cluster compositions. This methodology has been shown to be a powerful method for studying the formation of various clusters in inorganic compounds. No Ge-containing clusters were detected when LDI of nondoped (GeS$_2$)$_{50}$ (SbS$_2$)$_{50}$ glass was done. When (GeS$_2$)$_{50}$ (SbS$_2$)$_{50}$ glass was doped with silver, only one Ge-containing cluster was generated. Because of a trace concentration of hydrogen, Raman spectroscopy was not detecting any hydrogenated clusters. The hydrogen in the studied glasses most probably originated from the elements used for the synthesis of these glasses. Although 5N purity standards were used, traces of hydrogenated clusters are detectable by MS.

Raman scattering results are helpful in understanding the structure of the original material prior to MS. Raman spectroscopy observes the structure in short-range order, and all bonds, for example, Ag -- S, Sb -- Sb, Ge -- Ge, Ge -- S, and Sb -- S bonds, in identified structural units agree well with those structural units and fragments identified by MS, with the exception that no Ge -- Ge and Ge -- S units in undoped glasses were identified via MS. The results enable an understanding of the structural motifs of the Ag-doped Ge -- Sb -- S chalcogenide glasses, and the findings could contribute to proposals of new thin films to be manufactured by pulsed laser deposition. Such films could lead to more efficient conductive bridge RAM memory materials and devices.

## EXPERIMENTAL SECTION

### Chemicals

Acetonitrile was purchased from Sigma-Aldrich (Steinheim, Germany). Germanium, antimony, sulfur, and silver of 5N purity were purchased from VUK Panenské Brézany s.r.o. (Panenské Brézany, Czech). Ultrapure double-distilled water was produced with a quartz apparatus from Heraeus Quarzschmelze (Hanau, Germany). All other reagents were of analytical grade purity.

Samples of Ag(aGeS$_2$)$_{50}$ (SbS$_2$)$_{50}$ glass for x = 0, 5, and 15 were prepared. Appropriate amounts of elements (Ge, Sb, S, and Ag) of 5N purity were sealed in an evacuated silica ampule. Each batch weighed about 10 g. The syntheses were done in a quartz furnace at a temperature of 970 °C for 36 h. Then, the temperature was decreased to 700 °C, and the samples were quenched in water and annealed for 3 h ca. 20 °C under glass transition temperature. The compositions and glass homogeneities were tested via a scanning electron microscopy microscope Lyra 3 (Tescan) equipped with the energy-dispersive X-ray analyzer AZtec X-Max 20 (Oxford Instruments).

### Mass Spectrometry

Mass spectra were recorded in both the positive and negative ion modes via AXIMA Resonance or CFR mass spectrometers from Kratos Analytical Ltd. (Manchester, UK). Both instruments were equipped with a nitrogen laser (337 nm) and coupled with time-of-flight detection. The AXIMA Resonance mass spectrometer had a quadrupole ion trap. The laser repetition rate was set to 5 Hz with a pulse time width of 3 ns. The maximum laser pulse energy was 250 μJ.
Software and Computations. The stoichiometries of the clusters were determined via comparisons of theoretical and experimental isotopic envelopes on Launchpad software (Kompact version 2.9.3, 2011) from Kratos Analytical Ltd. (Manchester, UK).

Sample Preparation for MS and Raman Spectroscopy. Selected pieces were powdered in an agate mortar in a nitrogen atmosphere, and the powders were then suspended in acetonitrile (1 mg/mL). Next, 2.5 μL of each suspension was deposited on a target, dried, and used to measure mass spectra. Pieces of bulk glasses were used to measure Raman spectra.

Raman Spectroscopy. The room-temperature Raman spectra were measured by a MultiRam Raman spectrophotometer (Bruker). Spectra were excited with a laser operating at 532 nm and the powders were then suspended in acetonitrile (1 mg/mL). Next, 2.5 μL of each suspension was deposited on a target, dried, and used to measure mass spectra. All parameters were fixed, with only changes in band areas and the ratios between the Gauss and Lorentz parts allowed, and individual bands were attributed to structural units.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c02561.

Mass spectra of (GeS)25(Sb2S3)15 glass; comparison of experimental and theoretical isotopic patterns; mass spectra of 5% and 15% Ag-doped (GeS)25(Sb2S3)15 glass; effect of laser energy; and experimental and theoretical isotopic patterns (PDF).

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Notes
The authors declare no competing financial interest.

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