Effects of oxides on optical absorption and homogeneity of GeS$_2$-Sb$_2$S$_3$-based glass

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ABSTRACT
We investigated the effects of oxide impurities on the optical absorption, glass structure, and homogeneity of a sulfide glass that is a potential candidate for use as an infrared-transmitting material. We prepared glasses based on the pseudo-binary GeS$_2$-Sb$_2$S$_3$ system by a conventional method using metals and sulfur as raw materials in an evacuated silica glass ampoule. The oxygen impurity content according to oxygen analysis was 0.034 mass% (340 ppm) for 20GeS$_2$-80SbS$_3$/glass. The oxygen impurities were distributed as oxides bonded to Ge and Sb with a distribution constant, although most of the oxygen was bonded to Ge. In addition, oxysulfide glasses were prepared by substituting GeO$_2$ or SbO$_2$ for the corresponding sulfides. In this case, the oxygen of the added oxides bonded mainly to Ge in the glasses. When more than 2 mol% of the oxides was substituted for the corresponding sulfides in the 20GeS$_2$-80SbS$_3$/glass, the glass became translucent or opaque. Microscopy observation revealed that droplet phases with diameters of 2 to 4 μm were precipitated. These phases were rich in germanium and oxygen. The inhomogeneity is induced by the addition of oxides to the glasses, particularly, in those with a large fraction of Sb$_2$S$_3$ in the composition.

1. Introduction
Because of their high transmissivity in the near- and mid-infrared regions, chalcogenide glasses are considered to be practical candidates for application in optical systems such as night vision and surveillance cameras as infrared-transmitting materials [1–3]. For instance, high-quality selenium-based glasses are available for commercial use because of the high glass formability and transparency at wavelengths beyond 14 μm [2–4]. In addition, moldable glasses based on tellurium have been developed recently for infrared optics [5]. A number of sulfide glass systems, including As-S-based, Ge-S-based, and Ga-S-based systems, have been reported [6–11]. Among them, glasses composed of GeS$_2$ and Sb$_2$S$_3$ have received attention as As- and Se-free glasses [10,11]. The glass system has a high glass-forming ability in a wide compositional range. Furthermore, the glasses are transparent even in the visible region, especially when the GeS$_2$ fraction is larger than the Sb$_2$S$_3$ fraction [10,12]. However, GeS$_2$-based glasses suffer from the presence of an infrared absorption edge, which is usually located at 10 to 11 μm, and they cannot completely cover the atmospheric window. This limit is attributed to the absorption assigned to oxide impurities bonded to Ge, i.e. Ge-O stretching vibration. In fact, Ge-free glasses based on Ga$_2$S$_3$-Sb$_2$S$_3$ have an absorption edge around 13 μm, which is shifted by 1 to 1.5 μm in the long-wavelength direction from those of Ge$_2$-based glasses. Consequently, this system almost covers the atmospheric window [13–18].

Much effort has been made to investigate and eliminate the effects of oxygen impurities on the properties of chalcogenide glasses, particularly the effects on the optical absorption in the infrared region [19–25]. Many studies have focused primarily on selenium- and tellurium-based glasses for application in infrared-transmitting fibers [21,23–25]. In addition, oxygen impurities in sulfide glasses have been studied to investigate their effects on the glass formability and stability, and physicochemical properties [26–28]. Furthermore, oxysulfide glasses containing oxides as a component of glasses have been investigated [29–32]. However, few studies of the effects of oxygen impurities in sulfide glasses on the optical absorption and quantitative analyses of the oxygen content have been reported.

In this work, we conducted a quantitative estimation of the effects of oxygen impurities on the optical absorption and homogeneity of GeS$_2$-Sb$_2$S$_3$-based...
glasses. We found that addition of oxides induced the clustering of germanium oxide, resulting in phase separation in the glass.

2. Experimental procedures

Glasses were prepared by a conventional melting-cooling method for chalcogenide glass in an evacuated silica glass tube. The metals Ge (4 N) and Sb (4 N) (Kojundo Chemical Laboratory Co. Ltd.), and sulfur (6 N), reagent grade GeO₂ and Sb₂O₃ (FUJIFILM Wako Pure Chemical Corp.) were used as raw materials. Sulfur was distilled in a vacuum at 130°C to remove water impurities. The raw materials were weighed and placed in a silica glass tube in a glove box filled with Ar gas. The silica tube was sealed by a H₂–O₂ flame burner under evacuation using a vacuum pump. The sealed silica tube was heated to 950°C for more than 70 h in a rocking furnace and then quenched in air. The vitrification of the prepared samples was confirmed by naked-eye observation and X-ray diffraction (XRD) measurements (Rigaku, RINT2500) using Cu Ka X-rays at 40 kV and 50 mA. The obtained glasses were annealed at a temperature 5 K below the glass transition temperature for 4 h. The glass transition and crystallization temperatures were measured using differential thermal analysis (DTA) (Shimadzu, DTG-60) at a heating rate of 10 K/min. The density was measured by Archimedes’ method using kerosene as the immersion liquid.

The composition was systematically varied in three series. In series I, the content ratio of GeS₂ and Sb₂S₃ was varied as (100 – x)GeS₂·xSb₂S₃/₂ (x = 10, 20, 40, 60, 70, or 80 mol%). In series II, the oxide GeO₂ or Sb₂O₃ was added to the 60GeS₂·40Sb₂S₃/₂ glass to replace the corresponding sulfide as (60 – y)GeS₂·(40 – z)Sb₂S₃/₂·yGeO₂·zSb₂O₃/₂ (y or z = 0.1–10 mol%). Finally, in series III, the oxide GeO₂ or Sb₂O₃ was added to the 20GeS₂·80Sb₂S₃/₂ glass as (20–x)GeS₂·(80–z)Sb₂S₃/₂·yGeO₂·zSb₂O₃/₂ (y or z = 0.2–10 mol%). Hereafter, the compositions of the glasses are denoted as, for example, 20–75–SbO₃/₂ for the 20GeS₂·75Sb₂S₃/₂·5SbO₃/₂ glass. In this paper, we present mainly the results for series III, although the first and second series are also discussed.

The glasses were cut to an appropriate shape and both sides were polished for spectroscopy measurements. Transmission spectra were obtained using a visible-near-infrared spectrometer (Hitachi, U-3000 or Shimadzu, U-3000) and a FT-IR spectrometer (JEOL, JIP-WINSPEC50). The absorption edge at the short wavelength side was defined as the wavelength at which the absorbance reaches 5 for the samples with 0.65 mm thickness; the absorbance is given by ln(100/T), where T (%) is the transmittance in the visible-near-infrared region.

The oxygen impurity content was measured using an oxygen elemental analyzer (LECO, ONH836) for the glasses with some compositions in series I and III. The measurements were performed for three samples with the same composition; these three samples were taken from glasses prepared in different silica glass ampoules. Oxygen impurity data were acquired by five measurements of the individual samples, and the obtained values were averaged.

Glasses having inhomogeneous structure were observed by scanning electron microscopy (SEM; JEOL, JSM-7600 F) with energy-dispersive X-ray (EDX) microanalysis (Oxford, INCA).

3. Results

The compositions of the glasses prepared in this study are summarized in Table 1 for series III and in Table S1 in the Supporting Information for series I and II, along with their glass transition and crystallization temperatures, density, and absorption edge on the short-wavelength side. The samples marked with asterisks in the absorption edge column in Table 1, which have high oxide contents, did not have glassy luster and were

| Composition (mol%) | [O⁺]⁺(at) | T_g (°C) | T_c (°C) | Density (g/cm³) | Absorption edge (nm) |
|-------------------|----------|----------|----------|-----------------|---------------------|
| Series III        |          |          |          |                 |                     |
| GeS₂              |          |          |          |                 |                     |
| Sb₂S₃/₂           |          |          |          |                 |                     |
| GeO₂              |          |          |          |                 |                     |
| Sb₂O₃/₂           |          |          |          |                 |                     |
| 20                 | 80       | 0        | 0        | 0               | 251                 |
| 20                 | 79.8     | 0        | 0.2      | 0.2             | 250                 |
| 20                 | 79.7     | 0        | 0.3      | 0.3             | 251                 |
| 20                 | 79.5     | 0        | 0.5      | 0.5             | 249                 |
| 20                 | 79.3     | 0        | 0.7      | 0.7             | 249                 |
| 20                 | 79.0     | 0        | 1.0      | 0.9             | 249                 |
| 20                 | 78.7     | 0        | 1.3      | 1.2             | 251                 |
| 20                 | 75.0     | 0        | 5.0      | 4.7             | 247                 |
| 20                 | 70       | 0        | 10       | 9.4             | 243                 |
| 19                 | 80       | 1.0      | 0        | 1.3             | 247                 |
| 18                 | 80       | 2.0      | 0        | 2.5             | 250                 |

a) Nominal oxide ion mol% to total anions (sulfide + oxide ions). b) A wavelength and energy, at which the absorbance, ln(100/T), (transmittance (%)), at the short wavelength side, reaches 5 for the samples with 0.65 mm thickness. c) Since the samples marked with asterisks did not have glassy luster and were opaque, the absorption edges were not able to be measured.
opaque. However, they had a halo pattern in the XRD data, as shown in Figure 1, along with other typical halo patterns of glasses [see the halo patterns c and d in Figure 1]. Furthermore, because these samples had clear glass transition and crystallization peaks in the DTA results, they were judged to be vitrified. All the samples in Table S1 were transparent and had a halo pattern in the XRD data, indicating that they were vitrified.

Figure 2 shows the visible and infrared transmission spectra of the 20–80, 20–79.5-0.5SbO$_{3/2}$, 20–78.7–1.3SbO$_{3/2}$ and 20–75-5SbO$_{3/2}$ glasses listed in Table 1. On the short-wavelength side of the spectra, the transmission limits of the 20–80, 20–79.5-0.5SbO$_{3/2}$ and 20–78.7–1.3SbO$_{3/2}$ glasses were almost the same regardless of Sb$_2$O$_3$ content. In fact, the absorption of the glasses in series III containing oxides (Table 1) changed very little up to oxide contents of $y = 1.0$ mol% or $z = 1.3$ mol%. For the glasses in series II, in which the oxides were added to the 60GeS$_2$·40SbS$_{3/2}$ glass, the absorption edge did not change up to $y = 2.0$ mol% or even $z = 10$ mol%, as shown in Table S1. The band gap of the GeS$_2$·Sb$_2$S$_3$ glass is thought to be determined by the energy levels of the 5s lone pair electrons and 5p vacant orbitals of the Sb$^{3+}$ ion, which contribute mainly to the top of the valence band and bottom of the conduction band, respectively. Therefore, the absorption edge on the short-wavelength side of the GeS$_2$·Sb$_2$S$_3$ glass depends strongly on the concentration ratio of GeS$_2$ to Sb$_2$S$_3$. It varied from 459 nm for the 90–10 glass to 625 nm for the 20–80 glass, as presented in Table S1. Thus, the addition of oxides does not affect the absorption edge for the same ratio of Ge and Sb contents. However, the transmittance of the 20–75-5SbO$_{3/2}$ glass decreased dramatically in the entire spectral range; in the visible and near-infrared regions in particular, the glass exhibited no transmission. The transmittance of the 20–70–10SbO$_{3/2}$ and 18–80–2GeO$_2$ glasses (not presented) was also zero or very low. This result is indicated by the appearance of these samples, as mentioned above. This is due to the inhomogeneity induced by the precipitation of heterogeneous phases, which will be discussed in detail later.

In the infrared region, four bands designated A (7.72 µm, 1296 cm$^{-1}$), B (12.5 µm, 798 cm$^{-1}$), C (16.3 µm, 613 cm$^{-1}$), and D (19.3 µm, 517 cm$^{-1}$) from the short-wavelength side are clearly observed. All of them originated from oxide impurities although they appeared on the multiphonon absorption tail from the

**Figure 1.** XRD patterns of samples showing halo, a: 20–80, b:20–79-1SbO$_{3/2}$, c: 20–75-5SbO$_{3/2}$, d: 20–70-10SbO$_{3/2}$.

**Figure 2.** Visible and infrared transmission spectra of 20–80, 20–79.5-0.5SbO$_{3/2}$, 20–78.7–1.3SbO$_{3/2}$, and 20–75-5SbO$_{3/2}$ glasses. The thickness of glasses was 0.65 mm.
long wavelength side; bands B and D are assigned to Ge-O vibration, and band A is assigned to a combination of bands B and D [20,21,23–25,33,34]. Band C is assigned to Sb-O stretching vibration [33]. Figure 3 (a) and (b) show the infrared absorption spectra of the glasses in series I and III, respectively. The relative intensity of bands B and C clearly depends on the Ge and Sb contents of the glasses, as shown in Figure 3 (a). As shown in Figure 3 (b), however, the intensity of band B increased rapidly with the addition of the oxides, whereas that of band C showed little variation. To confirm this observation, the integrated intensities were evaluated by the decomposition of the three bands between 1000 to 500 cm\(^{-1}\) into three Gaussian curves (corresponding to bands B, C, and D) by a fitting procedure. The variation of the integrated intensities of bands B and C is plotted against the nominal content of the added oxides in Figure 4 (a). In the inset of Figure 4 (a), the peak decomposition for the 20–79.5-0.5SbO\(_{1.2}\) glass is presented as an example. Figure 4 (a) indicates that only the intensity of band B, which is assigned to Ge-O vibration, increased in proportion to the amount of the added oxides up to \(z = 1.0\) mol\%, although the intensity of band C, which is assigned to Sb-O stretching vibration, scarcely changed. This result indicates that the additional oxide ions bonded mainly with Ge. The increment in band B tended to be saturated beyond a content of \(z = 1.0\) mol\%, which corresponds to a nominal number density of oxygen of \(2.1 \times 10^{20}\) cm\(^{-3}\).

![Figure 3](image-url)  
**Figure 3.** Absorption spectra in the infrared region of glasses in (a) series I and (b) series (III).

![Figure 4](image-url)  
**Figure 4.** (a) Dependences of integrated absorption intensities of band B and C on the nominal number density of oxygen, (b) dependence of integrated absorption intensity of band B on the analytical number density of oxygen in samples. Inset in (a) shows an example of peak decomposition of an absorption spectrum using three Gaussian curves.

To clarify the relationship between the absorption bands and the oxide content, the amount of oxygen in the glasses was measured using an oxygen elemental analyzer for glasses. Figure 4 (b) shows the relationship between the measured concentration (not the nominal concentration) of oxygen and the integrated intensity of band B. The relationship is proportional although the points are a little scattered. The least-squares fit shows a linear relationship described by eq. (1)

\[
A_{\text{Ge-O}} = a \times [O] + b 
\]

where \(A_{\text{Ge-O}}\) (cm\(^{-1}\)) and [O] (cm\(^{-3}\)) are the integrated absorption intensity of band B and the number density of oxygen measured by the oxygen elemental analyzer, respectively. Note that the extrapolation of the linear line runs near the origin. We will discuss this point in more detail later.

The analytical concentration of oxygen in the 20–80 glass, i.e. the concentration of oxygen impurities incorporated into the glass from the raw materials and during glass preparation, was in the range from
of 3.37 x 10^19 to 6.15 x 10^19 cm^-3, and the average was (5.0 ± 1.1) x 10^19 cm^-3 that corresponds to 0.034 mass \% (340 ppm) or 0.34 mol\% to 100 mol\% of the glass.

Figure 5 shows Raman spectra of the glasses with different GeS_2 and Sb_2S_3 contents [Figure 5(a-c), series I] and the 20–80 glasses with additional oxides [Figure 5(d), series III]. These spectra were corrected for thermal population effects [35,36]. After the background scattering was subtracted, the spectra shown in Figure 5(a–c) were well decomposed using several Gaussian-Lorentzian curves assigned to the vibrational modes presented in Table 2. The spectra presented in Figure 5(d) show no variation with the addition of oxides. Among the Raman bands constituting the spectra, as shown in Figure 5(b and c), the main band (band G) is assigned to the vibrational mode associated with the Sb-S bond. This band is almost unaffected by the addition of oxides because the added oxygen bonds mainly with Ge, as mentioned above.

In series III, the glasses with more than 2 mol\% added oxides became opaque and had neither a glassy appearance nor luster. The transmittance was significantly decreased, although they had the typical halo pattern in the XRD data, indicating that the samples were still amorphous. Thus, SEM observations and EDX analyses of the completely opaque 20–70–10SbO_3/2 glass were performed, as shown in Figure 6. Inhomogeneous structure consisting of droplet phases 2 to 4 \(\mu\)m in diameter was observed in the SEM image in Figure 6. Figure 7 shows EDX mapping images of the SEM image in Figure 6(b), which indicate that the precipitated phases are rich in germanium and oxygen and poor in antimony and sulfur compared with those of the matrix phase. This phase-separated structure was characteristic of the glasses with a high Sb_2S_3 content and a high oxide content. In fact, homogeneous 60GeS_2 · 40SbS_3/2 glasses were obtained even though 10 mol\% of SbS_3/2 was replaced by the oxide (see Table S1 in the Supporting Information).

4. Discussion

Oxide impurities in chalcogenide glasses used as optical materials in the infrared region are an important issue. Analytical and quantitative studies have been conducted mainly for selenium- and tellurium-based glasses. For instance, the relationship between the absorption bands assigned to Ge-O stretching vibration and the oxygen impurity content were investigated for GeSe_2 and Ge-Se-Te glasses. In the Ge-Se-Te

Table 2. Assignments for Raman bands appeared in the spectra shown in Figure 5.

| Band | Wavenumber (cm\(^{-1}\)) | Assignment | Reference |
|------|--------------------------|-------------|-----------|
| E    | 222                      | S-Sb-S vibration | 37        |
| F    | 263                      | \(\nu_3\)Ge-GeS \_2 stretching | 39        |
| G    | 294                      | SbS \_2 bending vibration | 37, 38, 40 |
| H    | 327                      | \(\nu_1\)GeS \_2 vibration | 37, 39, 40 |
| I    | 359                      | \(T_g\) mode of Ge_S\_3 \_4 unit | 41        |
| J    | 390                      | edge-shared GeS \_2 stretching and \(\nu_1\) \(\nu_2\) | 39        |
| K    | 416                      | \(S_v\)S \_2-GeS \_2 stretching | 39, 40    |

Figure 5. Raman spectra of (a) 90–10 glass, (b) 60–40 glass, (c) 20–80 glass, and (d) (i): 20–80, (ii): 20–79.5–0.5SbO_3/2, (iii): 20–79–15SbO_3/2, (iv): 20–70–10SbO_3/2 glasses. The spectra were corrected for thermal population effect and back ground scattering was subtracted for (a) to (c), in which peak decomposition was performed using five to seven Gaussian-Lorentzian curves and calculated spectra by the fitting are shown with circles.
glasses, the absorption coefficient for 1 ppm oxygen in the 765 cm⁻¹ band, which corresponds to band B in this study, was estimated as 0.228 cm⁻¹ ppm⁻¹ [21,23]. We calculated this value as 0.080 cm⁻¹ ppm⁻¹ for our 20–80 glass, which is reasonable, considering the difference in the refractive indices of the Ge-Se-Te and Ge-Sb-S glasses.

The oxide impurities are distributed as germanium oxide and antimony oxide in the present glass systems. In fact, in the glasses of series I, without additional oxides, the ratio of the absorption intensities of the bands assigned to Ge-O and Sb-O was well correlated to the ratio of the Ge and Sb contents as shown in Figure 8. Then it is considered that the equilibrium reaction (2) is established for the glasses without additional oxides. We define the distribution constant as an equilibrium constant of the reaction (2), assuming that all of the oxygens in the glass are bonded with either Ge or Sb, as shown in eq. (3):

$$\text{Ge} \text{– S} + \text{Sb} \text{– O} \rightleftharpoons \text{Ge} \text{– O} + \text{Sb} \text{– S} \quad (2)$$

$$K \approx \frac{[\text{Ge} \text{– O}] [\text{Sb} \text{– S}]}{[\text{Ge} \text{– S}] [\text{Sb} \text{– O}]} \approx \frac{[\text{Ge} \text{– O}] [\text{Sb}]}{[\text{Sb} \text{– O}] [\text{Ge}].} \quad (3)$$

Here, Sb – O and Ge – O denote oxygen atoms distributed or bonded to Sb and Ge atoms, respectively, and Ge – S and Sb – S represent the structural
units of the glass matrix. Because the oxide impurity content is low, the [Sb−S]/[Ge−S] ratio is approximately equal to the [Sb]/[Ge] ratio of the glass.

Figure 4(b) shows the proportional relationship between the oxygen impurity content measured by the oxygen elemental analyzer and the absorption intensity of the Ge−O stretching band. All of the oxygen atoms bonded to Ge are considered to contribute to the absorption of the Ge−O band. Therefore, the x-axis intercept of the extrapolated line of the least squares fit theoretically gives a content of oxygen atoms which are not bonded to Ge, but bonded to Sb. As mentioned above, the extrapolation of the line runs near the origin, which means that the content of oxygen atoms bonded to Sb is low. In fact, we estimated the content from the x-axis intercept as $6 \times 10^{18}$ cm$^{-3}$, although the errors of the least-squares fit are large. Even if this value is overestimated, it becomes about $1.6 \times 10^{19}$ cm$^{-3}$. Considering that the total number density of oxygen impurities that is approximately, $5.0 \times 10^{19}$ cm$^{-3}$, in the 20–80 glass, the number density of oxygen bonded to Ge was estimated as more than $3.4 \times 10^{19}$ cm$^{-3}$. Then, in spite of the ratio, [Sb]/[Ge] = 4, the equilibrium of the reaction (2) shifts to the right hand side; the equilibrium constant, $K$, could be estimated as more than approximately 9, and the oxide impurities are more likely to exist as germanium oxide.

Although it is shifted to the Ge side, the oxygen impurities were distributed in the Ge and Sb with a distribution constant that is independent of the Ge/Sb content ratio in the glasses containing no additional oxides. However, when oxides were added, most of them were selectively bonded with Ge. This result can be explained by the clustering of GeO$_2$. When the oxide content exceeds a critical value, GeO$_2$ starts to form clusters and become more stable. Then, the added oxides, which selectively bond with Ge, are aggregated into clusters, and become increasingly stable. At higher oxide contents, the clusters grow, and eventually phase separation occurs. It has been found that nanoscale heterogeneous structures are formed in the GeS$_2$−GeO$_2$ glass system [29,30].

Finally, we discuss the source of the oxygen impurities. It is rather surprising that the oxygen content exceeded a few hundred ppm even though the glasses were prepared from high-purity raw materials by careful processing. In the literature, absorption due to Ge−O is also reported in the infrared transmission spectra of Ge-Sb-S glasses [37,38,39,40,41,42,43]. It may be difficult to attribute the impurities only to contaminants in the starting materials. These large quantities of oxide impurities, and the resulting strong absorption band assigned to Ge−O stretching, seem to be characteristic to the sulfide glasses. In Figure 9, the transmission spectra of Ga-Ge-S and Ga-Ge-Te glasses are compared. Both glasses were prepared from the same raw metals, Ga and Ge, by the same process. Nevertheless, the Ga-Ge-Te glass has no absorption bands assigned to oxides, indicating that the source of the oxygen impurities is sulfur and/or sulfides. One possibility is a reaction with silica glass during the melting process. Sulfides are more ionic than selenides and tellurides, and thus promote reactions such as that in the equation below.

$$\text{Si} - \text{O} + \text{Ge} - \text{S} \rightleftharpoons \text{Si} - \text{S} + \text{Ge} - \text{O}.$$

The existence of Si in glasses is sometimes suggested by the fact that the absorption band at approximately $9.1 \mu$m ($1.1 \times 10^3$ cm$^{-1}$) observed in Figure 9 is often assigned to Si−O stretching vibration [24,34–43]. In fact, a small quantity of silicon impurities was detected in the GeS$_2$−Sb$_2$S$_3$ glasses by X-ray fluorescence spectroscopy, as reported in Fig. S1 in the Supporting Information.
5. Conclusions

Glasses based on GeS$_2$-Sb$_2$S$_3$ and glasses including oxides, which were substituted for part of the corresponding sulfides, were prepared. The effects of oxygen impurities and the added oxides on the optical absorption and glass homogeneity were investigated. The variation in the intensities of the infrared absorption bands assigned to Ge-O and Sb-O stretching vibration and quantitative oxygen analyses revealed that the oxygen impurities were distributed in the oxides bonded with Ge and Sb with a distribution constant, although oxygen was more likely to be bonded with Ge than with Sb. Furthermore, the oxygen of the oxides that were substituted for the sulfides bonded mainly with Ge, regardless of the type of oxide. Then, the substitution of antimony oxide for antimony sulfide at more than 5 mol% of Sb$_{3/2}$ induced phase separation in the 20GeS$_2$·80SbS$_{3/2}$ glass, in which droplets of Ge and O-rich phases were precipitated. The measured oxygen impurity content of the 20GeS$_2$·80SbS$_{3/2}$ glass was approximately 340 ppm. A significant source of impurities seems to be the SiO$_2$ used in the silica glass ampoule, which can react with sulfides during glass melting.

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Disclosure statement

No potential conflict of interest was reported by the author(s).

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References

[1] Zakery A, and Elliott SR. Optical properties and applications of chalcogenide glasses: a review. J Non-Cryst Solids. 2003;330(1–3):345-346.
[2] Bureau B, Zhang XH, Smektala F, et al. Recent advances in chalcogenide glasses. J Non-Cryst Solids. 2004;345&346:276–283.
[3] Xh Z, Bureau B, Lucas P, et al. Glasses for seeing beyond visible. Chem Eur J. 2008;14:432–442.
[4] Zhang XH, Guimond Y, Belley Y. Production of complex chalcogenide glass optics by molding for thermal imaging. J Non-Cryst Solids. 2003;326&327:519–523.
[5] Wilhelm AA, Boussaud-Plédel C, Coulombier Q, et al. Development of far-infrared-transmitting Te based glasses suitable for carbon dioxide detection and space optics. Adv Math. 2007 Matsushita Y, Infrared Array Sensor Forum, 2019, Ibaraki Osaka, Ritsumeikan Univ;19:3796–3800.
[6] Kawamoto Y, Tsuchihashi S. The properties and structure of glasses in the system As$_2$S$_3$–Sb$_2$S$_3$. Yokogawa-Kyokai-Shi. 1969;77:328–335.
[7] Kawamoto Y, Tsuchihashi S. Glass-forming regions and structure of glasses in the system Ge- S. J Am Ceram Soc. 1969;52:626–627.
[8] A-m L-L, Guittard M, Flahaut J. Mat Res Bull. 1976;11:1489–1496.
[9] Popescu MA. “Non-Crystalline Chalcogenides,” Ch. 1, Dordrecht. The Netherlands: Kluwer Academic Publishers; 2001. p. 4–102.
[10] Ichikawa M, Wakasugi T, Kadono K. Glass formation, physico-chemical properties, and structure of glasses based on Ga$_2$S$_3$·GeS$_2$·Sb$_2$S$_3$. J Non-Cryst Solids. 2010;356(43):2235–2240.
[11] Tani K, Suetsugu T, Kaga N, et al. U.S. Patent 8,603,928 B2, 2013.
[12] Hosoya K, Tokuda Y, Okada A, et al. Preparation, properties, and photodoping behavior of GeS$_2$, Ga$_2$S$_3$, and Sb$_2$S$_3$-based glasses with excess sulfur and CsCl. J Mat Res. 2019;34:2747–2756.
[13] Ashida T, Wakasugi T, Okada A, et al. Glass formation and properties of the glasses based on As- and Ge-free sulfide systems for infrared transmitting materials. Chem Lett. 2016;45:63–65.
[14] Yang A, Zhang M, Lei L, et al. Ga-Sb-S chalcogenide glasses for mid-infrared application. J Am Ceram Soc. 2016;99:12–15.
[15] Qiu J, Yang A, Zhang M, et al. Ga$_2$S$_3$–Sb$_2$S$_3$–CsI chalcogenide glasses for mid-infrared applications. J Am Ceram Soc. 2017;100:5107–5112.
[16] Zhang M, Yang Z, Zhao H, et al. Glass forming and properties of Ga$_2$S$_3$·Sb$_2$S$_3$·CsCl chalcohalide system. J Alloys Comp. 2017;722:166–172.
[17] Ashida T, Okada A, Wakasugi T, et al. Glass formation and properties of glasses based on Ga$_2$S$_3$·Sb$_2$S$_3$ systems incorporated with CsX (X=Cl, Br, I) and AgCl. J Ceram Soc Jpn. 2018;126:452–461.
[18] Kadono K, Furukawa M, Yamamoto S, et al. The formation and properties of glasses based on Ga$_2$S$_3$·Bi$_2$S$_3$ system. J Asian Ceram Soc. 2020;8:284–290.
[19] Ma DS, Danielson PS, Moynihan CT.Bulk and impurity infrared absorption in 0.5As$_2$Se$_3$–0.5GeSe glass. J Non-Cryst Solid. 1980;37:181–190.
[20] Vlček M, Tichý L, Klikorka J, et al. Influence of oxygen traces on physical properties of glassy GeSe$_2$. J Mat Sci. 1987;22:2119–2123.
[21] Nishii J, Yamashita T, Yagamishi T. Oxide impurity absorption in Ge-Se-Te glass fibres. J Mat Sci. 1989;24:4293–4297.
[22] Reitter AM, Sreekaram AN, Varshneya AK, et al. Modified preparation procedure for laboratory melting of multi-component chalcogenide glasses. J Non-Cryst Solids. 1992;139:121–128.
[23] Nishii J, and Yamashita T. Chalcogenide glass-based fibers. In: Sanghera JS, and Aggarwal ID, editors. Chapter 4 in infrared fiber optics boca raton. Boca Raton, FL, CRC Press; 1998. p. 143–184.
[24] Shinyaev VS, Churbanov MF. Preparation of high-purity chalcogenide glasses. In: Chalcogenide glasses. Adam J-L, Zhang X ed. Chapter 1. Oxford: Woodhead Publishing; 2014. p. 3–35.
[25] Meneghetti M, Caillaud C, Chahal R, et al. Purification of Ge-As-Se ternary glasses for the development of high quality microstructured optical fibers. J Non-Cryst Solids. 2019;503:504–84–88.

[26] Morgan SP, Furniss D, Seddon AB, et al. Effect of glass purity on the glass stability and physical properties of Ga-La-S glasses. J Non-Cryst Solids. 1997 213&214;213–214:72–78.

[27] Li R, Furniss D, Bagshaw H, et al. Effects of oxide content on the glass-forming ability of the Ga2S3–Na2S system. J Am Ceram Soc. 1998;81:3353–3356.

[28] Morgan SP, Reaney IM, Buckley RB, et al. Crystallization in 70Ga2S3·30La2S3 (mol%) glasses as a function of oxide/hydroxide concentration. J Am Ceram Soc. 2000;83:617–622.

[29] Kim Y, Saienga J, Martin SW. Preparation and characterization of germanium oxy-sulfide GeS2–GeO2 glasses. J Non-Cryst Solids. 2005;351:1973–1979.

[30] Maurel C, Petit L, Dussauze M, et al. Processing and characterization of new oxysulfide glasses in the Ge-Ga-As-S-O system. J Solid St Chem. 2008;181:2869–2876.

[31] Terakado N, Tanaka K. The structure and optical properties of GeO2–GeS2 glasses. J Non-Cryst Solids. 2008;354:1992–1999.

[32] Terakado N, Tanaka K. Nanoscale heterogeneous structures in GeO2–GeS2 glasses. Jpn J Appl Phys. 2008;47:7972–7974.

[33] Lezal D. Chalcogenide glasses – survey and progress. J Optoelectron Adv Mat. 2003;5:23–34.

[34] Snopatin GF, Shiryaev VS, Plotnichenko VG, et al. High-purity chalcogenide glasses for fiber optics. Inorg Mat. 2009;45:1439–1460.

[35] Kobliška RJ, Solin SA. Temperature dependence of the Raman spectrum and the depolarization spectrum of amorphous As2S3. Phys Rev B. 1973;8:756–768.

[36] Lucovsky G, Galeeiner Fl, Keezer RC, et al. Structural interpretation of the infrared and Raman spectra of glasses in the alloy system Ge1–xSx. Phys Rev B. 1974;10:5134–5146.

[37] Jiang C, Wang X, Zhu M, et al. Preparation of chalcogenide glass fiber using an improved extrusion method. Opt Eng. 2016;55:056114.

[38] Lee JH, Lee WH, Choi JH, et al. High refractive index dispersion of compositionally optimized Ge-Ga-Sb-S sulfide glass for use as molded lens in the long-wave-length infrared range. Ceram Inter. 2018;44:21956–21961.

[39] Koudelka L, Frumar M, Pisárčík M. Raman spectra of Ge-Sb-S system glasses in the S-rich region. J Non-Cryst Solids. 1980;41:171–178.

[40] Watanabe I, Noguchi S, Shimizu T. Study on local structure in amorphous Sb:S films by Raman scattering. J Non-Cryst Solids. 1983;58(1):35–40.

[41] Heo J, Yoon JM, Ryu S-Y. Raman spectroscopic analysis on the solubility mechanism of La2+ in GeS2–Ga2S3 glasses. J Non-Cryst Solids. 1998;238:115–123.

[42] Frumarová B, Némec P, Frumar M, et al. Synthesis and optical properties of the Ge–Sb–S:PrCl3 glass system. J Non-Cryst Solids. 1999 256&257;256–257:266–270.

[43] Mei Q, Saienga J, Schrooten J, et al. Preparation and characterization of glasses in the Ag2S+B2S3+GeS2 system. J Non-Cryst Solids. 2003;324:264–276.