The formation and properties of glasses based on Ga$_2$S$_3$-Bi$_2$S$_3$ system

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ABSTRACT
The formation and properties of glasses based on a stoichiometric pseudo-three-component system, Ga$_2$S$_3$-Bi$_2$S$_3$-SnS$_2$, were investigated for the application as an infrared transmitting material. Glasses were obtained in the compositional range from 30 to 40 mol% of GaS$_2$, 30 to 50 mol% of BiS$_2$, and 10 to 30 mol% of SnS$_2$. Glasses were also obtained for a system in which some parts of the Bi$_2$S$_3$ were replaced by the same molar amount of Sb$_2$S$_3$. The glass transition temperatures of the obtained glasses were within a range of 260 to 305°C. Thermally stable glasses were obtained although the glass system contained neither selenium nor arsenic and less amount of antimony, which are commonly used for typical chalcogenide glasses. The difference between crystallization and glass transition temperatures was close to 90 K for the glass with a composition of 40GaS$_2$·40BiS$_2$·20SnS$_2$, and it was extended beyond 100 K by replacing a part of the bismuth with antimony. The transmission spectra of the glasses showed that they have a wide optical window covering a wavelength region from 1.4 μm to 13 μm.

1. Introduction
With increased attention on security and safety in society, the demand for infrared surveillance systems is growing rapidly. These infrared systems generally use infrared radiations in wavelengths ranging from 3 to 5 μm and 8 to 13 μm; these wavelength ranges are known as atmospheric windows [1–4]. The radiation from a black body at approximately 310 K, the human body temperature, has a spectrum with a peak at 9.4 μm expanding a tail to the long-wavelength side. Thus, it is very important to build up infrared systems composed of optics, utilizing materials that are transparent in the infrared region covering the latter range of the atmospheric windows. To date, crystal materials, i.e. germanium and zinc selenide, have been conventionally utilized to fabricate these optics. However, the lower formability of the crystals causes the poor cost performance of these materials.

Because of their good formability and the excellent transmissivity in the infrared region, chalcogenide glasses have become increasingly popular as materials for infrared transmitting optics. In fact, high-quality glasses based on germanium arsenic selenide and germanium antimony selenide are used in practical applications [5]. On the other hand, several types of glasses based on sulfide systems have been reported as infrared transmitting materials [6]. Among them, Ga-Ge-Sb-S-based and Ge-Sb-Sn-S-based glasses are interesting because the glass systems have high thermal stability and contain no toxic elements [7,8]. However, the transmission limit of the glasses in the infrared region is located at around 10 to 11 μm, and therefore, the optical transmitting range cannot completely cover the atmospheric window. This is owing to the absorption that is attributed to the stretching vibration of the bond between the germanium and the oxygen impurity. The absorption band has a peak at around 12.8 μm that determines the transmission limit of the germanium sulfide-based glasses [9,10]. Recently, Ge-free Ga-Sb-S-based glass systems have been reported as potential materials that can be applied to infrared optics [11–17]. These glasses exhibit sufficient thermal stability and mold-shaping ability. In addition, because the glasses have no absorption assigned to the Ge-O vibration, the transmission limit of the glasses shifts to the long-wavelength direction by 1 to 2 μm in comparison with that of the germanium sulfide-based glasses [14,17]. As a result, the transmission window of the gallium sulfide-based glasses can almost cover the atmospheric window.

Although gallium sulfide is regarded as a glass-forming compound, it needs other sulfides to be vitrified through a conventional melting-cooling procedure. Various sulfide glass systems containing gallium have been reported to date [18–28]. Among them, however, the Ge-free glass systems are still limited, and glasses reported as infrared transmitting materials contain a high content of Sb [13–17]. Here, we introduce a new glass system based on Ge and Sb-free gallium bismuth sulfide that can be used as an infrared-transmitting material with mold-shaping ability. The glass-forming region and fundamental glass properties are reported.
2. Experimental procedures

Glasses were prepared by the conventional method for chalcogenide glass in a vacuum-evacuated silica glass ampule using gallium (7 N), bismuth (4 N), tin (4 N), and sulfur (5 N) as starting materials. Sulfur was distilled at 130°C in a vacuum to remove impurity water. Details of the preparation method were described elsewhere [17]. Vitrification was determined by naked eye observation and X-ray diffractometry (XRD). Glass transition and crystallization temperatures were measured by differential thermal analysis (DTA). Thermal expansion coefficient was measured by thermomechanical analysis (TMA). Both thermal analyses were performed at a heating rate of 10 K/min under nitrogen gas flow. Density was measured by Archimedes’ method using kerosene as an immersion liquid. Refractive index was measured by means of spectroscopic ellipsometry. Vickers hardness was measured at an ambient temperature using a hardness tester. The indentation load and dwell time at the maximal load were 500 g and 15 s. The Vickers hardness, \( H_v \) (kg/mm\(^2\)) was evaluated by the next equation.

\[
H_v = \frac{2P \sin(68^\circ)}{a^2} = 1.8544 \times \frac{P}{a^2} \tag{1}
\]

Here, \( P \) (kg) is the applied load and \( a \) (mm) is the diagonal length of the indent.

3. Results

Figure 1 shows the glass-forming region and the glass transition temperatures (\( T_g \)) for the Ga\(_3\) S\(_{3/2}\)Bi\(_2\) S\(_3\)-SnS pseudo-three-stoichiometric-component system. The composition was represented as mol% of cations. In the Ga\(_2\)S\(_3\)-Bi\(_2\)S\(_3\) two-component system, all samples investigated for glass formation were devitrified by air-quenching although the samples of the compositions 50GaS\(_{3/2}\)·50BiS\(_{3/2}\) and 40GaS\(_{3/2}\)·60BiS\(_{3/2}\) were partially vitrified by water-quenching. This partial glass-forming range in the two-component system is consistent with that previously reported [21,22]. However, in the three-component system with the addition of SnS, some samples with appropriate compositions were vitrified more easily; glasses were obtained in the compositional region ranging from 30 to 40 mol% of GaS\(_{3/2}\), 30 to 50 mol% of BiS\(_{3/2}\), and 10 to 30 mol% of SnS. In SnS crystal, Sn\(^{2+}\) ions are coordinated by six S\(^{-}\) ions and the Sn-S bond is more ionic than that of the Bi-S bond according to the electronegativities of these elements. Therefore, SnS probably plays a role of glass modifier in the GeS\(_2\)-BiS\(_3\)-SnS system. The glass transition temperatures ranged from 260 to 310°C. Table 1 presents the properties of the glasses with those of the GeS\(_2\)-SbS\(_3\)-SnS-based and GaS\(_2\)-SbS\(_3\)-SnS-based glasses for comparison. The thermal stability index, i.e. the difference between the glass transition and crystallization temperatures, \( \Delta T = T_c - T_g \), were within 40 to 90 K. The replacement of a part of BiS\(_3\) by SnS-SnS made the glass more stable, and the stability index, \( \Delta T \), reached a value beyond 100 K. Figure 2 shows typical DTA and thermal expansion curves for the 40GaS\(_{3/2}\)·40BiS\(_{3/2}\)·20SnS glass as an example for the GaS\(_2\)-BiS\(_3\)-SnS-based glass. In Table 2, the glass transition and dilatometric softening temperatures, along with the thermal expansion coefficient, measured by thermomechanical analysis, are listed with those of the glasses of other systems. The Vickers hardness of the 40GaS\(_{3/2}\)·40BiS\(_{3/2}\)·20SnS glass was 281 ± 21 kg/mm\(^2\). This value was similar to those reported for other sulfide glasses [29] though the strict comparison is inadequate because of the different conditions of the measurement. The hardness of the sulfide glasses is half or less than half of the typical value of oxide glasses, e.g. 500 to 600 kg/mm\(^2\) for soda-lime silicate glass. The improvement of the mechanical properties is an important subject for the practical application of the glasses. The refractive indices of the 40GaS\(_{3/2}\)

![Figure 1](image)

**Figure 1.** Glass-forming region and glass transition temperatures (\( T_g \)) for the Ga\(_3\) S\(_{3/2}\)Bi\(_2\) S\(_3\)-SnS pseudo-three-stoichiometric-component system. \( \Delta \): partially vitrified by water-quenching, \( x \): devitrified.

| Composition (mol%) | \( T_g \) (°C) | \( T_c \) (°C) | \( \Delta T \) (K) | \( \rho \) (g/cm\(^3\)) | Reference |
|-------------------|----------------|----------------|------------------|---------------------|-----------|
| 40 GaS\(_{3/2}\) | 50 BiS\(_{3/2}\) | 30 SbS\(_{3/2}\) | 10 SnS | 388 | 89 | 5.25 | This work |
| 40 GaS\(_{3/2}\) | 70 BiS\(_{3/2}\) | 30 SbS\(_{3/2}\) | 20 SnS | 338 | 75 | 4.88 | [14] |
| 30 GaS\(_{3/2}\) | 50 BiS\(_{3/2}\) | 30 SbS\(_{3/2}\) | 20 SnS | 316 | 38 | 5.31 | [14] |
| 30 GaS\(_{3/2}\) | 50 BiS\(_{3/2}\) | 30 SbS\(_{3/2}\) | 20 SnS | 263 | 44 | 5.17 | [14] |
| 40 GaS\(_{3/2}\) | 30 BiS\(_{3/2}\) | 10 SbS\(_{3/2}\) | 20 SnS | 286 | 110 | 4.82 | [14] |
| 40 GaS\(_{3/2}\) | 30 BiS\(_{3/2}\) | 10 SbS\(_{3/2}\) | 20 SnS | 280 | 122 | 4.30 | [14] |
| 35 GaS\(_{3/2}\) | 20 BiS\(_{3/2}\) | 25 SbS\(_{3/2}\) | 20 SnS | 276 | 89 | 4.55 | [14] |
| 40 GaS\(_{3/2}\) | 20 BiS\(_{3/2}\) | 20 SbS\(_{3/2}\) | 20 SnS | 276 | 122 | 4.04 | [14] |
| 30 GaS\(_{3/2}\) | 20 BiS\(_{3/2}\) | 20 SbS\(_{3/2}\) | 20 SnS | 260 | - | 4.13 | [14] |

*This glass contains GeS\(_2\) instead of GaS\(_{3/2}\).*
The refractive indices of the Ga$_2$S$_3$-Sb$_2$S$_3$-SnS-based and the GeS$_2$-Sb$_2$S$_3$-SnS-based glasses are within the range between 2.6 and 2.8 [7,14]. This is due to the higher molar refractivity or polarizability of Bi$^{3+}$ than that of Sb$^{3+}$; for example, $1.508 \times 10^{-3}$ nm$^3$ and $1.111 \times 10^{-3}$ nm$^3$ are presented for the polarizability values, respectively [30]. In addition, the wavelength at which the refractive index was measured is near to the absorption edge of the Ga$_2$S$_3$-Bi$_2$S$_3$-SnS-based glasses.

Figure 3 shows the XRD patterns of the vitrified and devitrified samples as just quenched in air along with the Bi$_2$S$_3$ crystal. Most of the diffraction lines in the patterns for 20GaS$_{3/2}$· 60BiS$_{3/2}$· 20SnS and 50GaS$_{3/2}$· 30BiS$_{3/2}$· 20SnS are assigned to Bi$_2$S$_3$, the diffraction lines of which are also shown [30].
that of Bi$_2$S$_3$ crystal for comparison. The vitrified samples showed a typical halo pattern, while several diffraction lines were observed in the XRD pattern of the devitrified samples. In the XRD patterns of all the devitrified samples, the diffraction lines assigned to Bi$_2$S$_3$ crystal were observed [31]. In addition, for the samples of the compositions at the side larger than 40 mol% of GaS$_{3/2}$, the diffraction lines of Ga$_2$S$_3$ crystal were observed, while for the samples of the compositions of the side larger than 30 mol% of SnS, the diffraction lines of SnS crystal were observed [31].

Figure 4 shows the transmission spectra in the visible and near-infrared regions for the Ga$_2$S$_3$-Bi$_2$S$_3$-SnS-based glass with those of the GeS$_2$-Sb$_2$S$_3$-SnS and Ga$_2$S$_3$-Sb$_2$S$_3$-SnS-based glasses for comparison. The absorption edge at the short wavelength side fairly shifted to the long-wavelength direction compared with those of the GeS$_2$-Sb$_2$S$_3$-SnS-based and Ga$_2$S$_3$-Sb$_2$S$_3$-SnS-based glasses which have absorption edges within or just near the visible region. The absorption edge of the glass containing both Bi$_2$S$_3$ and Sb$_2$S$_3$, Ga$_2$S$_3$-Bi$_2$S$_3$-Sb$_2$S$_3$-SnS-based glass, was located between those of the Ga$_2$S$_3$-Sb$_2$S$_3$-SnS-based and the Ga$_2$S$_3$-Bi$_2$S$_3$-SnS-based glasses. The electronic structures of the top of the valence band and the bottom of the conduction band are approximately determined by the orbitals of Sb and Sn for the Ge-Sb-Sn-S and Ga-Sb-Sn-S glasses, while those are determined by the orbitals of Bi for the Ga-Bi-Sn-S glass. Then, the variation of the absorption edge is reasonable.

The transmission spectra in the infrared regions are presented in Figure 5, showing that all the Ge-free glasses had almost the same transmission limit, which is located at 13 μm in wavelength and shifted by more than 1 μm to a long wavelength direction, from that of the GeS$_2$-Sb$_2$S$_3$-SnS-based glass. The transmission limit of the GeS$_2$-Sb$_2$S$_3$-SnS-based glass is determined by the absorption band assigned to the impurity Ge-O.
vibration around 13 μm as mentioned above. The absorption band has a clear peak for this sample, though the peak would completely disappear if the sample were thicker. On the other hand, the transmission limits for the GaS₂-based glasses are determined by the absorption due to the stretching vibration of impurity Ga-O located around 14.7 μm, as shown in the inset of Figure 5 [32,33].

4. Discussion

The gallium sulfide-containing glass systems reported to date are classified into two groups [21]; one is a group represented by the Ga-Ge-S glass system [22,24] and the other is a group represented by the Ga-La-S glass system [18,19]. The former is characterized by a glass composition, in which a sulfide other than GaS₂ is a main component that forms the glass network predominantly, and GaS₂ is incorporated into the network. In these systems, glasses are obtained for the compositions containing less than approximately 50 cation at% of Ga. However, GaS₂ plays a role helping the glass formation in these systems. Other than the Ga-Ge-S system, the Ga-Sb-S and the Ga-Ge-Sb-S glass systems are included in this group [7,11–17]. For example, in the pseudo-two-component GeS₂-GaS₂ system, the glass-forming region is below 30 mol% of GaS₂ [22,24]. On the other hand, the latter group represented by the Ga-La-S glass system is characterized by a glass composition in which GaS₂ plays a role of a network former as a main component and the other components work as a network modifier. These systems contain Ga more than 50 cation at%. Other than the Ga-La-S system, the Ga-Na-S and Ga-M-S (M = Sr, Ba) systems are included in this group [20,25,27,28]. Although GaS₂ is not vitrified singly, these glasses based on GaS₂ can be obtained with the incorporation of other sulfides working as a glass modifier. It is believed that the glass network of these glasses consists of Ga₄ tetrahedra sharing edges and corners [34]. The glass-forming region in the GaS₂-La₃S₃ system is 85 to 50 mol% of GaS₂. This range corresponds to 1.7 or 3 of the S/Ga atomic ratio. In the GaS₂-La₃S₃-Na₃S system, the glasses were obtained for the compositional region for which the S/Ga ratio is in the range of 1.7 to 2 [25]. Takebe et al. proposed a well understandable picture, in which the glass network consisting of the Ga₄ tetrahedra is developed by sharing S²⁻ ions [27]. They discussed the model on the basis that the S/Ga atomic ratio is in the range from 2 to 2.5 in the glass-forming region [27]. On these S/Ga atomic ratios, the glass network has both shared S²⁻ and terminated S²⁻ ions and therefore has moderate flexibility. On the other hand, for the first group, in which a sulfide other than GaS₂ is contained as a glass-forming component, the content of Ga is typically less than 50 cation at%, and the S/Ga atomic ratio is larger than approximately 5. Thus, Ga₄ tetrahedra may be isolated in the network constructed by the glass-forming component other than GaS₂.

Here, it is interesting to compare the glass-forming region of the Ga₃S₃-Bi₂S₃-SnS system with that of the Ga₂S₃-Sb₂S₃-SnS system [14]. Both regions expand from the Ga₂S₃-M₂S₃ (M = Bi, Sb) lines to 30 mol% of SnS. On the pseudo two-component Ga₂S₃-M₂S₃ (M = Bi, Sb) lines, however, the former system is partially vitrified only in the range from 40 to 50 mol% of Ga₃S₃/2, while the latter is completely vitrified in the compositions containing less than 30 mol% of Ga₃S₃/2, although GaS₂ is indispensable for the glass formation. The S/Ga atomic ratio for the Ga₂S₃-Sb₂S₃-SnS glass system is larger than 4.7 (30GaS₃/2 · 50SbS₃/2 · 20SnS) [14]. These facts mean that the glass network for the Ga₂S₃-Sb₂S₃-SnS system is constructed with Sn₂S₃ that plays a role as a glass former. On the other hand, the S/Ga atomic ratio of the Ga₂S₃-Bi₂S₃-SnS glass system is in the range from 2.5 (60GaS₃/2 · 40BiS₃/2) to 4.7 (30GaS₃/2 · 50BiS₃/2 · 20SnS). This is between the values for the first and second groups, which are larger than 5 and smaller than 3, respectively. This probably means that since the effect of Bi₂S₃ as a network former is weak compared with that of Sn₂S₃, the linkage of Ga₄ tetrahedra is necessary for the Ga₂S₃-Bi₂S₃-SnS system to construct a stable glass network.

Finally, we estimated the additivity of molar volume of the Ga₂S₃-Bi₂S₃-SnS-based glass presented by the next equation.

\[ \frac{W_M}{d} = V_M = x_{GaS_2}V_{GaS_2} + x_{BiS_2}V_{BiS_2} + x_{SnS}V_{SnS} \]  

where \( d \), \( W_M \), and \( V_M \) are the density, molar weight, and molar volume of the glass, respectively, and \( x \) and \( v \) are the mole fraction and partial molar volume of each component, respectively. A least-squares fit was carried out using molar volumes obtained from measured densities, molar weights, and molar fractions of all glasses. Then, we determined the molar volumes of the individual components as fitting parameters, which are presented in Table 3. The root mean square deviation between the observed and calculated molar volumes was 0.08 cm³/mol (0.2%), indicating that the additivity of the molar volume for this glass system holds. This means that the structural units and the ways of the linkage of these units hardly change in the whole range of the compositions. Table 3 shows the molar volumes of individual components of other glass systems, in which the additivity holds, and those of crystals for comparison. The molar volumes for the components of Ga-La-Na-S glass were calculated from the glass compositions and densities presented in the literature [25]. It is noteworthy that the molar volumes of the glass-forming sulfides, Ga₂S₃, GeS₂,
Table 3. Partial molar volumes of the individual components of glasses estimated from the least-squares fit using Equation (1) and molar volumes at room temperature of the corresponding crystals.

| Glass system | Partial molar volume of component (cm$^3$/mol) | SnS | rms | Reference |
|---------------|-----------------------------------------------|-----|-----|-----------|
| Ga$_2$S$_3$-Bi$_3$S$_5$-SnS | 32.0 | 0.08 | This work |
| Ga$_2$S$_3$-Sb$_2$S$_3$-SnS | 35.3 | 0.14 | [14] |
| Ga$_2$S$_3$-La$_2$S$_3$-Na$_2$S | 33.4 | 0.09 | [25] |
| Ge$_2$-Ga$_2$S$_3$-Sb$_2$S$_3$ | 34.7 | 0.30 | [7] |
| Crystal$^a$ | 32.0 | 29.1 | | |

$^a$The partial molar volumes of this glass system were obtained from the compositions and densities of the glasses presented in the literature [25] by the least-squares fit. The partial molar volumes of La$_2$S$_3$ and Na$_2$S in the glass system were 37.6 and 23.1 cm$^3$/mol, respectively.

$^b$The molar volumes of crystals were calculated from their crystal structures at room temperature. Molar volumes of La$_2$S$_3$ and Na$_2$S crystals are estimated to be 37.5 and 21.0 cm$^3$/mol, respectively.

and Sb$_2$S$_3$, in the Ga$_2$S$_3$-Sb$_2$S$_3$-SnS-based and Ge$_2$-Sb$_2$S$_3$-SnS-based glasses are larger than those of the corresponding crystals by 8 to 10%. However, the molar volume of Ga$_2$S$_3$ in the Ga$_2$S$_3$-Bi$_2$S$_3$-SnS-based glass is the same as that of the crystal. This means that the flexibility of the coordination environment around the gallium sulfide structural unit is restricted, which may result in the difficulty of glass formation in the Ga$_2$S$_3$-Bi$_2$S$_3$-SnS-based system compared with other glass systems based on Ga$_2$S$_3$.

5. Conclusions

Glass formation was investigated in the system based on Ga$_2$S$_3$-Bi$_2$S$_3$-SnS. Although the glasses were hardly obtained for the two-component, Ga$_2$S$_3$-Bi$_2$S$_3$ system, glass formation became easy with the addition of SnS in the range from 10 to 30 mol%. At the maximal $\Delta T = T_c - T_g$, the thermal stability index was 89 K for 40Ga$_2$S$_3$/60Bi$_2$S$_3$ · 20SnS glass in the present study. Refractive indices of the glasses were approximately 2.9, which were higher than those of Ge$_2$-Sb$_2$S$_3$ and Ga$_2$S$_3$-Sb$_2$S$_3$-SnS-based glasses. Since the glasses have no absorption due to impurity germanium oxide, i.e. the Ge-O stretching vibration located around 13 μm, which limits the absorption edge to about 11 μm, the transmission range of the glasses expanded to approximately 13 μm. This absorption limit is 1 or 1.5 μm longer than those of the Ge-based glass. Then, the glasses are transparent in the wavelength range covering the atmospheric window. The glasses are free from selenium and arsenic, and even antimony. Therefore, these glasses may become an excellent potential candidate for infrared transmitting optics for commercial use.

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Disclosure Statement

No potential conflict of interest was reported by the authors.

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