FULL PAPER

Glass formation and properties of glasses based on $\text{Ga}_2\text{S}_3\text{--Sb}_2\text{S}_3$ systems incorporated with CsX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) and AgCl Tomoyo ASHIDA¹, Arifumi OKADA², Takashi WAKASUGI² and Kohei KADONO^{2,†}¹Graduate School of Science and Technology, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606–8585, Japan²Faculty of Materials Science and Engineering, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606–8585, Japan

Glass formation was investigated for the $\text{Ga}_2\text{S}_3\text{--Sb}_2\text{S}_3\text{--CsX}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) and $\text{Ga}_2\text{S}_3\text{--Sb}_2\text{S}_3\text{--AgCl}$ systems. Glasses were obtained for the compositional regions that contain the parts of the lines from the eutectic point of the $\text{Ga}_2\text{S}_3\text{--Sb}_2\text{S}_3$ system ($20\text{GaS}_{3/2}\cdot 80\text{SbS}_{3/2}$) to the midpoint of the $\text{GaS}_{3/2}\text{--CsX}$ system ($50\text{GaS}_{3/2}\cdot 50\text{CsX}$), extending to both sides of the lines. The glass transition temperatures were in the range of 210 to 280°C and tended to decrease with increases of the Sb_2S_3 and CsX contents. Some glasses in these systems had a temperature difference between crystallization and a glass transition of more than 200 K. The infrared transmission limits were located at approximately 14 μm , and the transmission range covered the atmospheric windows. These facts indicate that the glasses are suitable for use as optical materials in infrared optics. Furthermore, the absorption edges at the short wavelength side were blue-shifted, reaching the visible region with the incorporation of CsX . However, glasses in some compositional domains showed inhomogeneous structures in their matrices. Particularly, a unique morphology was observed the inhomogeneous CsCl -incorporated glasses, in which many voids of several micrometers in size were formed. The crystallization behaviors at the borders of the glass forming regions are discussed.

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1. Introduction

Because of the increasing priority of the social security and safety, infrared surveillance systems have received increased attention in recent years. These systems typically use wavelength ranges of 3–5 and 8–13 μm , called “atmospheric windows”. The range of 8–13 μm is particularly important in the mid-infrared region because black body radiation of body temperature, at approximately 310 K, is at maximal intensity over this range. Since crystal materials, such as germanium and zinc selenide, have a superior transparency covering the infrared regions, these crystals have mainly been used for infrared optics, such as lenses and windows, to date. However, they suffer from low cost-performance and are not mass-produced because of the high cost of their raw materials and poor formability. As a substitute for these crystals, infrared transmitting glass materials have become increasingly important in recent years because of their good mold-formability.^{1),2)} The high productivity of the mold-shaping process is expected to contribute to the cost performance of infrared optics and devices, resulting in a further expansion of their market.

Chalcogenide-based glasses have excellent transmission in the infrared region and have been the most promising candidates for applications in infrared optics, including optical fibers, for a long time.^{3),4)} Among them, selenide-based glasses, such as Ge--Se and Ge--As--Se glasses, have been well-developed for commercial applications.^{5),6)} These systems have a high glass-forming ability and formability, and are transparent until 16 μm , covering the atmospheric windows. Glass formation for systems based on telluride have been explored extensively in the literature.^{7)–13)} However, there are still only a few systems based on telluride that have enough glass-forming ability and stability against crystallization. On the other hand, there are some sulfide systems that have a good glass-forming ability and mold-formability, and also exhibit high chemical durability. Among them, the Ge--Sb--S system has been studied, as it produces As and Se-free glasses.^{14),15)} The drawback of glasses based on this system, however, is that the transmission range cannot sufficiently cover the atmospheric windows because of the impurity absorption assigned to the Ge--O vibration located at approximately 13 μm . Theoretically, the absorption could be eliminated by thorough purification of the raw materials including the removal of surface oxides. In the case of the sulfide glass, furthermore, since the Ge--O absorption might be located on the tail of

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the intrinsic absorption of the glass, the effect on the optical window is more serious. Another sulfide system, a glass-forming system based on Ga–S, has been studied.^{16)–19)} Particularly, Ga–La–S glasses and their derivatives were extensively studied as host media for rare-earth ions.

Recently, new glass-forming systems based on Ga₂S₃–Sb₂S₃–A (A = CsCl, SnS) have been reported.²⁰⁾ The infrared absorption edges of these glasses are located at approximately 14 μm, shifted to the long wavelength side by 1.5 to 2 μm, compared to the Ge–Sb–S based glasses. The transmission ranges of these glasses cover the atmospheric windows. Some glasses in these systems have high thermal stability and are expected to have high mold-formability despite the lack of Ge, Se, and As. Furthermore, glass formation and optical properties of the glasses including optical nonlinearity based on Ga₂S₃–Sb₂S₃–CsCl and CsI systems have been reported recently.^{21),22)}

Such halide-incorporated sulfide glass is one of the chalcogenide glass systems, which have been recognized as a new family of non-oxide glasses. Some advantages are achieved by the incorporation of halides into chalcogenide systems.^{23)–28)} First, the glass-forming regions are expected to expand, leading to the discovery of new glass-forming systems with superior properties. Second, the tunable composition ranges can be expanded for various properties, such as the thermal expansion coefficient and refractive index and dispersion, because the properties of the glasses vary drastically with the incorporation of halides into chalcogenide systems. Therefore, there is more flexibility for choosing materials and designing optics. In addition, it is often observed that the absorption edges at the short wavelength side are blue-shifted and reach the visible region.^{29)–33)} Thus, chalcogenide glasses can be applied as visible to infrared transmitting materials, and multispectral imaging systems with a simpler optics design can be constructed.

In this paper, we extensively explored glass formation based on new glass systems containing CsX (X = Cl, Br, I) and AgCl. The thermal and optical properties of the obtained glasses were systematically investigated and compared with the type of halide. We also studied the behaviors of the induced inhomogeneity observed for some compositional regions in cesium halide-incorporated glasses.

2. Experimental procedures

Glass formation was examined for the compositions in which CsX (X = Cl, Br, and I) or AgCl were substituted for Ga₂S₃ or Sb₂S₃ in the pseudo-two-component Ga₂S₃–Sb₂S₃ glass system. The glasses were prepared with the conventional melting-cooling method for chalcogenide glasses. Reagent grade Ga (7N), Sb (5N), S (5N), CsX (3N) (X = Cl, Br or I), and AgCl (3N) were used as the starting materials. Sulfur was purified by distillation under vacuum at 120–140°C to remove water impurities. The halides were dried under vacuum at 120–130°C before use. These raw materials were weighed into a silica glass tube with an 8-mm inner diameter to obtain a sample that weighed 4 g with the appropriate composition in a glove

box filled with Ar gas. The silica tube was then sealed in a vacuum using an H₂–O₂ flame burner. The sealed silica tube was heated to 950°C for more than 70 h in a rocking furnace and then quenched in air. Glass formation was examined by naked-eye observation and with X-ray diffraction (XRD) (Rigaku, RINT2500) measurements. The glass transition (*T_g*) and crystallization temperatures (*T_c*) were measured by differential thermal analyses (DTA) (Shimadzu, DTG-60) with a heating rate of 10 K/min. The obtained glasses were annealed for 8 h near their *T_g*s to remove the strain. The glasses were cut into an adequate size, and both sides were optically polished to 1.18 or 1.50 ± 0.05 mm in thickness. The densities were measured by Archimedes' method, using kerosene as the immersion liquid. The refractive indices of the glasses at 1544 nm were measured by the prism coupling method (Metricon Model2010). For some glasses, the indices at 633 and 980 nm were also measured. The transmission spectra were acquired with a visible-near infrared spectrometer (Hitachi, U-3000) and fourier transform infrared spectrometer (JEOL, JIP-WINSPEC50). Observations with optical and laser (KEYENCE, VK-X200) microscopes were performed to investigate the inhomogeneity of the glasses for some compositions.

3. Results

3.1 Glass formation based on the Ga₂S₃–Sb₂S₃–CsX (X = Cl, Br, I) and Ga₂S₃–Sb₂S₃–AgCl systems

Figure 1 shows glass formation for pseudo-three-component systems based on Ga₂S₃–Sb₂S₃–CsX (X = Cl, Br, I). The melts of the compositions marked with circles were vitrified. However, the samples quenched from the melts marked with closed and open triangles were opaque and did not have a glassy appearance or a smooth and lustrous surface by naked eye observation. However, as shown in **Fig. 2**, 20GaS_{3/2}·60SbS_{3/2}·20CsCl (hereafter, this composition is referred to as 20-60-20CsCl), 20-70-10CsCl, and 10-80-10CsCl showed typical halo patterns in the XRD without any diffraction lines. Furthermore, the glass transitions were found in DTA measurements, indicating that they were in a glassy state [see Fig. S7(c) in the Supplemental Materials]. Therefore, we determined that the melts marked with the triangles were vitrified. The opaque and non-glassy appearances are due to the microscopic inhomogeneity of these samples, as described in detail in section 3.3. The difference between the closed and open triangles is also described in section 3.3. Melts of the compositions marked with small letters were partly or completely devitrified after quenching; the small letters represent the precipitated crystals, as shown in Fig. 1. The compositions marked with and are described below in detail. The XRD patterns for the various as-quenched samples are presented in Figs. S1 to S4 in the Supplemental Materials.

For the pseudo-two-component Ga₂S₃–Sb₂S₃ system, glasses were obtained in the range from 10 to 30 mol % of

Fig. 1. Glass formation in the pseudo-three-component Ga_2S_3 – Sb_2S_3 – CsX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) systems. The melts of the compositions marked with circles, closed and open triangles were vitrified, though the as-quenched samples marked with the triangles were opaque and did not have a glassy appearance or a smooth and lustrous surface. The melts of the compositions marked with a–f, were devitrified with the precipitation of the crystals; a, α - Ga_2S_3 ; b, α - $\text{Ga}_2\text{S}_3 + \text{Sb}_2\text{S}_3$; c, Sb_2S_3 ; d, γ - Ga_2S_3 ; e, CsX ; f, $\text{CsCl} + \text{Sb}_2\text{S}_3$; g, $\text{CsI} + \text{unidentified}$. However, the melt, $\square$ was almost vitrified with only a weak diffraction line and the as-quenched samples of $\square$ were transparent, though the precipitation of CsX crystallites were observed. The XRD patterns of these samples are presented in Figs. S1 to S4 in the Supplemental Materials.

Fig. 2. XRD patterns of samples of the CsCl -incorporated system marked with the closed triangles in Fig. 1.

$\text{GaS}_{3/2}$. This range is consistent with that reported in the literature.^{17),19)} Glasses were obtained for compositions in which Sb_2S_3 is a predominant component because the eutectic point is located at 80 mol % of Sb_2S_3 (20 mol % of Ga_2S_3).¹⁷⁾ In the pseudo-three-component Ga_2S_3 – GeS_2 – CsCl system, glasses were obtained for compositions in which CsCl is incorporated until approximately 40 mol %. It has also been reported that glasses have been obtained in the pseudo-two-component Ga_2S_3 – CsCl system, although the glass-forming range is narrow, with an approximate range from 55 to 70 mol % of CsCl .^{34)–37)} In our experiment, the melt of $60\text{GaS}_{3/2}\cdot40\text{CsCl}$ (60-0-40CsCl), marked with $\square$, was almost vitrified by air quenching, and only a weak diffraction line was observed in the XRD pattern, as shown in Fig. S2. It is worth noting that the glass-forming region contains the line connecting the eutectic point of the Ga_2S_3 – Sb_2S_3 system ($20\text{GaS}_{3/2}\cdot80\text{SbS}_{3/2}$) to the midpoint of the $\text{GaS}_{3/2}$ – CsX system ($50\text{GaS}_{3/2}\cdot50\text{CsX}$) and extends to both sides. For the CsBr and CsI systems, glasses were

obtained in similar compositional regions to that of the CsCl system, although the amount of incorporated CsX was limited to less than approximately 30 mol %. For the samples, $30\text{-}40\text{-}30\text{CsX}$ ($\text{X} = \text{Br}, \text{I}$) marked with $\square$ in Fig. 1, weak diffraction lines were observed in the XRD patterns, indicating that cesium halide crystallites were precipitated, even though the samples were still transparent from the visible to infrared regions. The XRD patterns and transmission spectra for the $30\text{-}40\text{-}30\text{CsX}$ ($\text{X} = \text{Br}, \text{I}$) samples are presented in Figs. S3, S4, and S5 in the Supplemental Materials.

Table 1 shows the glass transition and crystallization temperatures, density, and refractive index at 1544 nm for some of the glasses, including glasses incorporated with AgCl instead of CsX . All the data, including the glass transition temperature, density, and refractive index, are presented in Figs. S6(a) to S6(c) in the Supplemental Materials. Some typical DTA curves are shown in Fig. S7 in the Supplemental Materials. In **Table 2**, the glass transition and dilatometric softening temperatures as well as thermal expansion coefficient measured by a dilatometer (Shimadzu, TMA-60) are listed for the four glass compositions. As shown in Table 1 and Fig. S6(a), T_g s decreased with the CsX content, while it increased with the Ga_2S_3 content. The decrease with the CsX content occurred because the networks were terminated by CsX , whereas the increase with the Ga_2S_3 content is attributed to the high melting point of Ga_2S_3 (Ga_2S_3 ; 1255°C, Sb_2S_3 ; 550°C). The thermal stability indices increased with the introduction of CsX to the Ga_2S_3 – Sb_2S_3 system, and some glass compositions showed a ΔT beyond 200 K. Since glasses having ΔT higher than a hundred and several tens degrees are considered to be stable against crystallization for mold-shaping and fiber-drawing processes,^{10),38)} the present systems are expected to provide moldable glasses appli-

Table 1. Glass transition (T_g) and crystallization (T_c) temperatures, thermal stability ($\Delta T = T_c - T_g$), density, and refractive index of $\text{Ga}_2\text{S}_3\text{-Sb}_2\text{S}_3\text{-A}$ ($\text{A} = \text{CsCl}, \text{CsBr}, \text{CsI}, \text{and AgCl}$) glasses

MX	Composition			T_g (°C)	T_c (°C)	ΔT (K)	Density ^{a)} (g/cm ³)	Refractive index at 1544 nm ^{b)}
	$\text{GaS}_{3/2}$	$\text{SbS}_{3/2}$	MX					
	30	70		259	358	99	3.98	2.67
CsCl	10	80	10	235	349	114	3.94	— ^{c)}
	30	60	10	251	342	91	3.81	2.44
	30	50	20	248	462	214	3/66	2.23
	30	40	30	233	473	240	3.55	2.06
CsBr	10	80	10	229	369	140	4.03	2.54
	30	60	10	247	411	164	3.86	2.42
	30	50	20	239	451	212	3.78	2.23
CsI	10	80	10	227	368	141	4.07	2.57
	30	60	10	247	353	106	3.93	2.45
	30	50	20	234	391	157	3.89	2.29
AgCl	10	80	10	213	337	124	4.23	2.70
	30	60	10	241	410	171	4.04	2.56

a) The experimental error is less than ± 0.02 g/cm³. b) The experimental error is less than ± 0.01 . c) The glass is opaque at 1544 nm because of the induced inhomogeneity.

Table 2. Glass transition (T_{dg}) and softening (T_{ds}) temperatures, expansion coefficient (α) measured using dilatometry, and refractive indices at 633, 980, and 1544 nm

X	Composition			T_{dg} (°C)	T_{ds} (°C)	α (10^{-6} K^{-1})	Refractive indices			A ^{a)}	B ^{a)} (10^4)	C ^{a)} (10^9)
	$\text{GaS}_{3/2}$	$\text{SbS}_{3/2}$	CsX				633	980	1544			
	20	80		261	282	14.8			2.73			
Cl	30	50	20	256	287	24.5	2.37	2.26	2.23	2.21	4.24	7.95
Br	30	50	20	242	274	23.5	2.36	2.26	2.23	2.21	4.11	7.51
I	30	50	20	237	272	22.8	2.43	2.32	2.29	2.26	4.69	9.29

a) Parameters of Cauchy's equation; $n = A + (B/\lambda^2) + (C/\lambda^4)$.

Fig. 3. Transmission spectra in the visible to infrared regions for the pseudo-two-component $\text{Ga}_2\text{S}_3\text{-Sb}_2\text{S}_3$ glasses and the $20\text{GeS}_2\cdot 80\text{SbS}_{3/2}$ glass for comparison; 10-90 means $10\text{GaS}_{3/2}\cdot 90\text{SbS}_{3/2}$.

cable for infrared optics. The densities decreased with the CsX content and increased in the order of CsCl, CsBr, and CsI compared to glasses with the same composition but different halides. The refractive indices also decreased with the CsX contents and were higher in the order of CsCl, CsBr, and CsI. For the 30-50-20CsX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) glasses, the indices were also measured at 980 and 633 nm, and the fitting parameters for Cauchy's equation are presented in Table 2. The fitting parameters show that the dispersion for this wavelength range decreased in the order of CsI, CsCl, and CsBr. This order is consistent with the

position of the absorption edge at the short wavelength side as shown in the next section.

3.2 Optical transmission

Figure 3 shows the transmission spectra in the visible to infrared regions for the pseudo-two-component $\text{Ga}_2\text{S}_3\text{-Sb}_2\text{S}_3$ glasses and $20\text{GeS}_2\cdot 80\text{SbS}_{3/2}$ glass for comparison.¹⁴⁾ For the long wavelength side, strong absorption at approximately $13 \mu\text{m}$ was observed for the $\text{GeS}_2\text{-Sb}_2\text{S}_3$ glass.¹⁴⁾ This absorption is assigned to the impurity Ge-O stretching vibration and determines the transmission limit

for the GeS_2 – Sb_2S_3 glass at the long wavelength side.^{39,40)} On the other hand, the transmission limits for the Ga_2S_3 – Sb_2S_3 glasses are determined by the Ga–O stretching vibration. This is consistent with the limits for the Ga_2S_3 – Sb_2S_3 glasses shifting slightly to the longer wavelength side with the decrease in the Ga_2S_3 content. The sharp peaks at 3.04 and 4.06 μm are assigned to the impurity O–H and S–H, respectively. The transmission limits for the Ga_2S_3 – Sb_2S_3 glasses were located at approximately 13 to 14 μm , which were shifted by 1.5 to 2 μm compared with those of the GeS_2 – Sb_2S_3 glasses because the glasses are free of the Ge–O impurity. Concerning the short wavelength side, as shown in Fig. 3, the absorption edges of the Ga_2S_3 – Sb_2S_3 glasses were blue-shifted with the decrease in the Sb_2S_3 content. The absorption edges of the Ga_2S_3 – Sb_2S_3 glasses tended to be located at a longer wavelength compared with that of the GeS_2 – Sb_2S_3 glass.

Figure 4 shows the transmission spectra in the visible region for the Ga_2S_3 – Sb_2S_3 – CsCl glasses with various compositions containing 20 to 30 mol % of CsCl . Compared with the absorption edges of the glasses without CsCl , as seen in Fig. 3, they were blue-shifted by the

Fig. 4. Transmission spectra in the visible region for the Ga_2S_3 – Sb_2S_3 – CsCl glasses; 30-50-20CsCl means 30 $\text{GaS}_{3/2}$ ·50 $\text{SbS}_{3/2}$ ·20CsCl.

incorporation of CsCl into the Ga_2S_3 – Sb_2S_3 glass. In the comparison of Ga_2S_3 – Sb_2S_3 – CsCl glasses with the same CsCl content, the glasses with lower contents of Sb_2S_3 had a shorter wavelength absorption edge. This was the same tendency observed for the pseudo-two-component Ga_2S_3 – Sb_2S_3 glasses, as seen in Fig. 3.

In **Fig. 5**, the transmission spectra in the visible to infrared regions for the 30-50-20CsX glasses are shown in comparison to that of the 30-60-10AgCl glass to observe the dependence on the type of halide. The transmission limits at the long wavelength side were almost identical, regardless of the halide. Thus, the absorption due to Ga–O stretching is not strongly affected by the type of halide. For the short wavelength side, the absorption edge was located at the shortest wavelength side for the CsBr-incorporated glass. The transmission spectra for the 30-40-30CsX glasses are shown in Fig. S5 in the Supplemental Materials. The 30-40-30CsBr and 30-40-30CsI glasses contained a small amount of CsBr or CsI crystals, as indicated by the XRD patterns (see Fig. S3 and S4) and as mentioned in the previous section. However, the glasses were still transparent, even in the visible region, and the absorption edges were located at the shorter wavelength in the order of CsI, CsCl, and CsBr. Since the 30-50-20AgCl glass composition could not be obtained, the spectrum of the 30-60-10AgCl glass is shown in Fig. 5 for comparison. The transmission limit at the long wavelength side was the same with those of the CsX-incorporated glasses, although the absorption edge at the short wavelength side did not blue-shift like those of the CsX-incorporated glasses. The relatively broad band peaking at 9.51 μm , which is often observed in the spectra for glasses containing halides, is assigned to an impurity oxide although it has been yet vague. It is considered that, as a possible assignment, the band originates from an impurity Si–O.³¹⁾

The transmission ranges of the Ga_2S_3 – Sb_2S_3 – CsX glasses cover the atmospheric windows, while those of the Ge–S based glasses hardly cover them due to the Ge–O impurity absorption, as seen in Fig. 3. This fact is of importance for the Ga_2S_3 – Sb_2S_3 – CsX glass to be practically applied as an infrared transmitting material.

Fig. 5. Transmission spectra in the visible to infrared regions for the Ga_2S_3 – Sb_2S_3 – CsX and Ga_2S_3 – Sb_2S_3 – AgCl glasses.

Fig. 6. (a) Transmission spectra of CsCl-incorporated glasses marked with the closed triangles in Fig. 1; The spectrum of 5-85-10CsCl was not shown because the sample was completely opaque in the whole spectral range. (b) Transmission spectra of CsX-incorporated glasses (X = Br, I) marked with the open triangles in Fig. 1. Spectra for CsX-incorporated and CsCl-incorporated glasses with similar compositions to those of the respective glasses were also shown for comparison. In addition to the peaks assigned to O–H (2.80 μm) and S–H (4.00 μm) vibrations, the peak at 6.25 μm is assigned to the bending vibration of impurity or adsorbed H₂O.

3.3 Inhomogeneity or phase separation in the pseudo-three-component glasses

As mentioned in Fig. 1, the glasses marked with closed and open triangles were opaque and did not have a glassy appearance even though they showed the typical halo patterns in the XRD, as shown in Fig. 2, and Figs. S3 and S4 in the Supplemental Materials. **Figure 6(a)** shows the transmission spectra of these glasses based on the CsCl-incorporated system, 20-60-20CsCl, 20-70-10CsCl, 10-80-10CsCl glasses, with those of the 10-80-10CsBr and 10-80-10CsI glasses for comparison. The spectrum of the 10-80-10CsCl glass was very different from those of the 10-80-10CsX (X = Br, I) glasses, though their compositions are similar and only differ in the type of halide. Furthermore, for the spectra of the CsCl-incorporated glasses, the absorption edge shifted to the longer wavelength side and the transmittance in the infrared region decreased with increasing Sb₂S₃. The 20-60-20CsCl and 20-70-10CsCl glasses were transparent in the range of 2–14 and 6–14 μm, respectively, while the 10-80-10CsCl glass was barely transparent in the entire infrared region.

The spectra of the 40-40-20CsBr and 40-40-20CsI glasses marked with open triangles of the CsBr- and CsI-incorporated systems were also different from that of the 40-40-20CsCl glass, as shown in Fig. 6(b); the transmittance of the former glasses decreased gradually with wavelength shortening from 12 μm, while that of the latter glass remained transparent from 600 nm to 14 μm.

These decreases in transmittance in the short wavelength side are attributed to the scattering caused by the induced inhomogeneity in the glass matrices. Thus, we performed a microscopic observation of these glasses. **Figure 7** shows pictures of the (a) 20-70-10CsCl, (b) 10-80-10CsCl, and (c) 5-85-10CsCl glasses observed by laser microscopy. The observations were conducted for the freshly broken surfaces. In Fig. 7(a), a number of dots that were 0.2–0.4 μm in size were distributed throughout the glass matrix. The images presented in Figs. 7(b) and 7(c) show several voids of 0.8–1.2 and 1.4–2.0 μm diameters, respectively, in the glass matrices. The voids look like trails, as observed in Fig. 7(c). Figures 7(d)–7(f) show the depth profiles along the lines illustrated in Figs. 7(a)–7(c),

Fig. 7. Pictures and line profiles for the CsCl -incorporated glasses marked with the closed triangles in Fig. 1 obtained by laser microscopy observation; (a) (d) 20-70-10 CsCl , (b) (e) 10-80-10 CsCl , (c) (f) 5-85-10 CsCl glasses. The line profiles were taken along the lines shown in the pictures.

Fig. 8. Optical microscope images for the CsX -incorporated glasses ($\text{X} = \text{Br}, \text{I}$) marked with the open triangles in Fig. 1; (a) 40-40-20 CsBr , (b) 40-40-20 CsI . Inhomogeneous phases indicated by the white arrows were observed.

respectively. These profiles indicate that the dots or voids seen in the pictures are holes with (d) 0.4 μm to (e) (f) 0.6 μm depths. More specifically, the bottoms of the holes shown in Fig. 7(e) and 7(f) are slightly swollen by approximately 0.1 to 0.2 μm . Additionally, small red particles were also observed in the holes under an optical microscope.

Figure 8 shows optical microscope images obtained in the transmission mode for the 40-40-20 CsX ($\text{X} = \text{Br}, \text{I}$) glasses, in which some particles of approximately 10 μm in diameter were observed instead of the voids seen in the 10-80-10 CsCl and 5-85-10 CsCl glasses. Since the heat-treated 40-40-20 CsX ($\text{X} = \text{Br}, \text{I}$) glasses showed the diffraction lines of γ - Ga_2S_3 crystallites, as mentioned in the next section, the particles are probably the glassy phases with a high content of Ga_2S_3 separated from the matrix.

3.4 Crystallization

Figure 1 shows the crystal phases precipitated from the melts of compositions that are located outside of the glass-forming region. For the pseudo-two-component Ga_2S_3 – Sb_2S_3 system, both α - Ga_2S_3 and Sb_2S_3 crystals, or only α - Ga_2S_3 , were precipitated from the melts depending on their compositions. This is consistent with the fact that no complex salts between Ga_2S_3 and Sb_2S_3 have been reported in

the phase diagram.¹⁷⁾ From the melts of the compositions on the line of $\text{SbS}_{3/2}$ and CsCl , both Sb_2S_3 and CsCl crystals were precipitated. On the other hand, it is worth noting that only γ - Ga_2S_3 was precipitated from melts that were composed of the Ga_2S_3 side for the glass-forming regions while only CsX was precipitated from the melts of the CsX side. Furthermore, with heat treatments at temperatures of $T_g + 40 \text{ K}$ for 6 h for the 40-40-20 CsX ($\text{X} = \text{Br}, \text{I}$) glasses, only the γ - Ga_2S_3 crystal was precipitated in the 40-40-20 CsBr glass; no crystallite phases were precipitated in the 40-40-20 CsI glass. Interestingly, the Ga_2S_3 crystals precipitated in the three-component system, including CsX , were always of the γ -type, which essentially has the cubic zinc blende structure, while those precipitated in the two-component Ga_2S_3 – Sb_2S_3 system were the α -type, with the hexagonal wurtzite structure. One of the possible reasons for this phenomenon is that the γ - Ga_2S_3 crystals were precipitated on CsX nuclei that had cubic structures in the three-component system.

Precipitation of the Sb_2S_3 crystal was not observed from melts that were not vitrified, whereas crystal was precipitated by heat treatment of glasses that had a high content of Sb_2S_3 , such as the 10-80-10 CsX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) glasses, as seen in Fig. S8 in the Supplemental Materials. Noticeably, the CsCl -incorporated glasses in this compositional region showed an inhomogeneous structure with voids, as previously mentioned.

4. Discussion

4.1 Glass formation

Glasses based on the pseudo-three-component Ga_2S_3 – Sb_2S_3 – CsCX systems were obtained in the compositional regions containing the parts of the lines from the eutectic point of the Ga_2S_3 – Sb_2S_3 system (20 $\text{GaS}_{3/2}$ ·80 $\text{SbS}_{3/2}$) to the midpoint of the $\text{GaS}_{3/2}$ – CsX system (50 $\text{GaS}_{3/2}$ ·50 CsX) and extending to both sides of the lines. It is interesting that these regions are similar to those of the Ga_2S_3 – GeS_2 – CsCl system, in which glasses are obtained

Table 3. Partial molar volume, v , and molecular refractivity, ρ , calculated by least squares fit using Eqs. (1) and (2)

A	v (cm ³)				Δ^2 (g/cm ³)	ρ (cm ³)				Δ
	GaS _{3/2}	SbS _{3/2}	A	rms ¹⁾		GaS _{3/2}	SbS _{3/2}	A	rms	
CsCl	36.6	39.8	55.3	0.13	0.02	20.78	28.26	16.81	0.10	0.02
CsBr	35.8	40.1	61.3	0.17	0.03	19.87	28.53	21.88	0.11	0.02
CsI	35.3	40.3	67.9	0.16	0.04	19.51	28.62	28.81	0.13	0.03
GeS ₂ ³⁾	34.7	40.4	49.8	0.30	0.05	20.63	28.46	25.82	0.23	0.06

1) Root mean square of the deviation between the observed and calculated values.

2) Maximal deviation between the measured and calculated densities and refractive indices.

3) The values calculated from the data presented in Ref. 14.

in the domain that includes the line from the GeS₂ corner to the midpoint of the GaS_{3/2}–CsCl line (50GaS_{3/2}·50CsCl). In the two-component Ga₂S₃–CsCl system, it has been reported that glasses are obtained around the composition 50GaS_{3/2}·50CsCl (or 33Ga₂S₃·67CsCl) and that the glass network principally consists of GaS_{4–n}Cl_n tetrahedra that share the sulfide ions.^{41)–43)} On the other hand, the network of the Ga₂S₃–Sb₂S₃ glasses consists of GaS₄ tetrahedra and SbS₃ tripyramids that share sulfide ions.¹⁴⁾ Although sulfide ions usually have a two-fold coordination in sulfide-based glasses, such as GeS₂ and As₂S₃ glasses, some of the sulfide ions in the Ga₂S₃–Sb₂S₃ glass network are expected to be three-fold and are likely four-fold coordinated to balance the charge of the trivalent Ga³⁺ cations. In fact, Ga₂S₃ crystals essentially have zinc blende or wurtzite structures, in which both Ga³⁺ and S^{2–} ions are in the tetrahedral sites.⁴⁴⁾ With the increase in the Ga₂S₃ content in the Ga₂S₃–Sb₂S₃ glasses, the fraction of the three (and four)-fold coordinated sulfide ions increases, and then, the flexibility of the network is lost, resulting in a decrease in the glass-forming ability. When introducing CsX into the Ga₂S₃–Sb₂S₃ glasses, some parts of the halide ions are bonded to Ga³⁺, forming GaS₃X tetrahedra. Then, the glass network is terminated by the halide ions. Even if the three sulfide ions of a GaS₃X tetrahedron are coordinated by two cations, the formal charge of the GaS₃X tetrahedron is –1, which can be compensated by a counter ion, Cs⁺. This means that the introduction of CsX decreases the fraction of sulfide ions coordinated by more than two cations and, as a result, increases the flexibility of the glass network and glass formability.

4.2 Additivity of density and refractive index

The density and refractive index of glasses are often estimated by summing the contributions from the individual components; the contribution allocated to each component is independent of the compositions of the glasses. This is known as an additivity concept. It has been reported that additivity holds for the density and refractive index of the stoichiometric sulfide glass system based on Ga₂S₃–GeS₂–Sb₂S₃.¹⁴⁾ To confirm the additivity for these properties in the Ga₂S₃–Sb₂S₃–CsX systems, Eqs. (1) and (2) are used:

$$\frac{W_M}{d} = V_M$$

$$= x_{\text{GaS}_{3/2}} v_{\text{GaS}_{3/2}} + x_{\text{SbS}_{3/2}} v_{\text{SbS}_{3/2}} + x_{\text{CsX}} v_{\text{CsX}} \quad (1)$$

$$\frac{n^2 - 1}{n^2 + 2} V_M = R_M$$

$$= x_{\text{GaS}_{3/2}} \rho_{\text{GaS}_{3/2}} + x_{\text{SbS}_{3/2}} \rho_{\text{SbS}_{3/2}} + x_{\text{CsX}} \rho_{\text{CsX}} \quad (2)$$

where d and n are the density and refractive index, respectively; W_M , V_M , and R_M are the molar weight, molar volume, and molar refractivity of the glass, respectively. V_M is written as the mole fraction x and partial molar volume v of each component as Eq. (1). Equation (2) represents the Lorentz-Lorentz relationship for refractivity, and R_M is assumed to be the sum of the molecular or ionic refractivity ρ of each component or ion. Additivity means that the partial molar volume and molecular refractivity are assumed to be independent of the composition. We estimated these values by the least squares fit using Eqs. (1) and (2) to the experimental data presented in Figs. S9(a) and S9(b) for the molar volume and molecular refractivity, respectively, in the Supplemental Materials. The results are summarized in **Table 3** together with the result for the Ga₂S₃–GeS₂–Sb₂S₃ glass system.¹⁴⁾ The root mean squares for the molar volume and molar refractivity were small. The maximal deviations between the measured and calculated data for the density were 0.02, 0.03, and 0.04 g/cm³ in the CsCl, CsBr, and CsI-incorporated systems, respectively, and were 0.02, 0.02, and 0.03 for the refractive index. Therefore, the additivities for both the density or molar volumes and refractive index or molar refractive index hold for these glass systems. This suggests that the structural units composing the glass networks and nearest neighbor coordination environments of ions are not drastically varied with the compositions. The v and ρ of GaS_{3/2} and SbS_{3/2} were almost identical regardless of the type of halide. Furthermore, the values of the Ga₂S₃–GeS₂–Sb₂S₃ glass system are similar to those of the CsX-incorporated systems, as shown in Table 3. This means that the contribution to the density and refractive index from each component is not changed very much in the different glass systems, at least those consisting of stoichiometric compounds.

4.3 Absorption edge at the short wavelength side

Here, we discuss the compositional dependence of the absorption edge at the short wavelength side, which is determined by the band gap energy. In the pseudo-two-component system, Ga₂S₃–Sb₂S₃, it is believed that the lone pair orbitals of S^{2–} (3p) and Sb³⁺ (5s) contribute to

the top of the valence band, and the latter is probably more important in determining the highest energy level of the valence band. On the other hand, the lowest level of the conduction band is determined by the antibonding orbitals of the bonds between the cations and S^{2-} , and/or the 5p vacant orbitals of Sb^{3+} . Therefore, the decrease in the Sb_2S_3 content leads to a decrease in the energy of the valence band and increase in the energy of the conduction band, resulting in a blue shift of the absorption edge.

The introduction of halides into the $\text{Ga}_2\text{S}_3\text{--Sb}_2\text{S}_3$ glass shifted the absorption edges to the shorter wavelength direction. The incorporated halides play the role of a glass modifier and terminate the glass network, as mentioned in section 4.1. As a result, the continuous band structures become discrete, leading to a widened band gap. In addition, the difference in the electronegativity of sulfur and halogen, particularly, chlorine and bromine, should be considered. The incorporated halide ions bound to Sb^{3+} attract electrons more strongly from Sb^{3+} than sulfide because of the larger electronegativity of the halogen. This leads to a lowering of the energy of the valence bands.

However, concerning the absorption edges of the CsCl - and CsBr -incorporated glasses, this is opposite to the prediction from the electronegativity. The reason for this difference is unclear. Similar examples have been reported for the $\text{GeS}_2\text{--Sb}_2\text{S}_3\text{--CsX}^{33)}$ and $\text{Ga}_2\text{S}_3\text{--GeS}_2\text{--CsX}^{45)}$ glasses, which were explained by the differences in the ionic diameters and the energy levels of the valence electrons of Cl^- , Br^- , and S^{2-} . For the present glasses, however, the effect of the inhomogeneity for CsCl -incorporated glasses should also be considered. As mentioned previously and in the next section, CsCl -incorporated glasses show a unique inhomogeneous structure for specific compositions, which makes the glasses opaque. Therefore, the absorption edge of the 30-50-20 CsCl glass might have shifted to the longer wavelength from the intrinsic edge due to the scattering induced by the nano-scale inhomogeneity in the glass.

4.4 Inhomogeneity in the $\text{Ga}_2\text{S}_3\text{--Sb}_2\text{S}_3\text{--CsCl}$ glass

One of the characteristic features for the $\text{Ga}_2\text{S}_3\text{--Sb}_2\text{S}_3\text{--CsX}$ glass systems is that the microscopic inhomogeneity is induced in the as-prepared glasses in specific compositional regions. Particularly, a number of voids of approximately $1\text{ }\mu\text{m}$ in diameter were observed in the glasses based on the $\text{Ga}_2\text{S}_3\text{--Sb}_2\text{S}_3\text{--CsCl}$ system. Two significant points should be noted regarding this phenomenon; the voids were formed only in the CsCl -incorporated glasses at the compositional region containing a high content of Sb_2S_3 , and the voids are spherical in shape and contain deposits.

The formation mechanism of these voids is still unclear. Considering the spherical shape of the voids, however, we deduce that they originated from bubbles formed by volatile species in the melts, and the volatile species become the deposits during the cooling process. From the glass compositions in which the voids were observed, Sb_2S_3 and chloride ions play an important role in the mechanism. In

fact, the size of the voids increased with the content of Sb_2S_3 , as shown in Fig. 7. Furthermore, as an additional experiment, we prepared a sample with the composition, $10\text{GaS}_{3/2}\cdot 80\text{SbS}_{3/2}\cdot 10\text{CsCl} + 17\text{Sb}$ (10-80-10 $\text{CsCl} + 17\text{Sb}$), containing an excess amount of Sb compared to the 10-80-10 CsCl glass. The XRD pattern of the prepared sample showed a halo and diffraction lines assigned to the metal Sb. The characteristics of the sample are that several voids of 10–200 μm in diameter were observed in the matrix and the bottoms of the voids swelled, as shown in the photo and depth profile in Figs. S10(a) and S10(b), respectively. The structure of the voids is similar to those shown in Figs. 7(e) and 7(f), although the sizes are different. The additional experiment showed that the excess amount of Sb accelerates the formation of voids. On the other hand, as mentioned in section 3.4, the Sb_2S_3 crystals that precipitated in the 10-80-10 CsCl glass by the heat treatment at 295°C for 6 h included a number of voids. From these experiments, we consider that the volatile species forming the bubbles and deposits inside the voids consist of at least Sb and sulfide, and for the volatile species, chloride also participated to achieve the high vapor pressure of the species. Finally, it should be noted that Ga_2S_3 is also important because we have not yet found such a phenomenon in the system based on $\text{GeS}_2\text{--Sb}_2\text{S}_3\text{--CsCl}$.

5. Conclusions

Glass formation was systematically explored for sulfide halide systems based on $\text{Ga}_2\text{S}_3\text{--Sb}_2\text{S}_3\text{--CsX}$ ($\text{X} = \text{Cl}, \text{Br}$, and I) and $\text{Ga}_2\text{S}_3\text{--Sb}_2\text{S}_3\text{--AgCl}$. Glasses were obtained in a wide range of compositional regions including the parts of the lines from the eutectic point of the $\text{Ga}_2\text{S}_3\text{--Sb}_2\text{S}_3$ system (20 $\text{GaS}_{3/2}\cdot 80\text{SbS}_{3/2}$) to the midpoint of the $\text{GaS}_{3/2}\text{--CsX}$ system (50 $\text{GaS}_{3/2}\cdot 50\text{CsX}$) and extending to the both sides of the lines. Some glasses had good thermal stability against crystallization; the stability index, ΔT , was beyond 200 K. This indicates that the glasses are stable against crystallization for mold-shaping and fiber-drawing processes. The transmission limits in the infrared region were located at approximately $14\text{ }\mu\text{m}$, covering the atmospheric windows. This makes the glasses useful for the infrared transmitting materials compared with glasses based on Ge--S , which have a cutoff at approximately 11 to $12\text{ }\mu\text{m}$. Furthermore, the incorporation of halides shifted the absorption edges at the short wavelength side to the visible region, giving visible transparency to the glasses. The dependences of other properties on the composition and type of halide were also investigated. CsCl -incorporated glasses with specific compositions had an interesting inhomogeneous structure that included a number of voids although their formation mechanism has not yet been clarified.

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