Glass Forming Region and Structure of Vitreous RS–Ga$_2$S$_3$ (R = Ca, Sr, Ba)

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Gallium sulfide glasses were prepared in the RS-Ga$_2$S$_3$ (R = Ca, Sr, Ba) systems. Respective glass forming regions are 67.5–70.0 mol% CaS, 63.8–68.8 mol% SrS and 60.0–73.8 mol% BaS. Transmission spectra in the visible region, refractive index and glass transition and onset crystallization temperatures were measured for representative compositions of SrS- and BaS-Ga$_2$S$_3$ transparent glasses. Raman spectroscopy reveals that RS-Ga$_2$S$_3$ glasses consist of the network of GeS$_4$ tetrahedra due to the RS addition. The compositional dependence of molar volume indicates a plateau region at 65–70 mol% RS in SrS- and BaS-Ga$_2$S$_3$ glasses. The morphology of sulfur complex anions in RS-Ga$_2$S$_3$ glass melts is discussed using the sulfur-to-gallium ratio as a variable parameter. The combined results suggest that well-developed glass networks are formed near 66.7 mol% RS (S/Ga = 2.5) in the SrS- and BaS-Ga$_2$S$_3$ systems.

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1. Introduction

Ga$_2$S$_3$ based glasses are recently of interest for passive and active optical materials in the near and mid-infrared. Ga$_2$S$_3$ based glasses have relatively short absorption edges, e.g., 450–500 nm, good thermal- and chemical-stabilities and high rare-earth solubility in comparison with other sulfide glasses. Ga$_2$S$_3$ does not form a glass on its own. The glass forming region reported previously extends to the following binary systems: L$_2$S–Ga$_2$S$_3$ (L = Y, La–Er, except for Eu), Ge$_2$S$_3$–Ga$_2$S$_3$, Na$_2$S–Ga$_2$S$_3$,$^5$ PbS–Ga$_2$S$_3$,$^5$ and BaS–Ga$_2$S$_3$. New glass compositions are still demanded for optical devices in both thin film and fiber forms. There are only a few reports on glass formation and properties in the RS–Ga$_2$S$_3$ (R = Ca, Sr, Ba) systems.

In this study glass forming region is determined by conventional melt-quenching method in the RS–Ga$_2$S$_3$ (R = Ca, Sr, Ba) systems. The optical and thermal properties of the prepared glasses were compared to other sulfide glasses. The structure of RS–Ga$_2$S$_3$ glasses is discussed in terms of Raman spectra and molar volume of glass samples.

2. Experimental procedures

Raw materials of CaS and Ga$_2$S$_3$ and of SrS and BaS with the respective cationic purities of 99.9 and 99.99% were weighed in a N$_2$ gas-filled glove box with < 1 ppm H$_2$O and O$_2$ concentrations. Glass composition was varied with 1.3–2.5 mol% RS intervals. No oxide and sulfate phases were detected by X-ray diffraction analysis in the raw materials. Mixed powders of 0.5 g melts were melted in N$_2$ flow at 1300°C for 30 min in a vitreous carbon crucible which is placed into a quartz tube. The melting temperature was determined due to the phase diagrams$^6$ and melting point$^7$ of the compounds in the CaS– and SrS–Ga$_2$S$_3$ systems. After melting, the crucible with the quartz tube was removed from the furnace and quenched in ice water with an estimated cooling rate of ~10$^5$°C/s. The glass forming region and crystalline phases were determined by X-ray diffraction analysis. The glass samples were annealed for 1 h at the glass transition temperatures and shaped plates with a typical dimension of 6 mm××14 mm and polished for measurements. No chemical damage due to water was confirmed on the surface of samples by the eyes and optical microscopy after polishing.

Transmission spectra were obtained with a U–3500 HITACHI spectrophotometer. Refractive index was determined at 632.8 nm with a Metricon 2010 Prism Coupler Instrument. The glass transition temperature $T_g$ and the onset crystallization temperature $T_c$ were measured by a Rigaku DTA8121 differential thermal analyzer. Sample density was determined by the Archimedes method with kerosene as an immersion liquid. The molar volume $V_m$ was calculated by the equation $V_m = (M_{RS}·N_{RS} + M_{GaS_3}·N_{GaS_3}) / \rho$, where $M_{RS}$ and $M_{GaS_3}$ are the molecular weights of RS and Ga$_2$S$_3$, respectively, $N_{RS}$ and $N_{GaS_3}$ are the molar fractions of RS and Ga$_2$S$_3$, respectively and $\rho$ is the measured density. Raman spectra were measured with a JASCO NRS–2000 micro-Raman spectrophotometer. The light source was an Ar$^+$ ion laser with a wavelength of 514.5 nm and a power of 1 mW.

3. Results

3.1 Glass forming region

Figure 1 shows the glass forming regions in the RS–Ga$_2$S$_3$ systems. The regions are located near 66.7 mol% RS and extends to the order of CaS< SrS< BaS. Transparent glasses were obtained in SrS- and BaS–Ga$_2$S$_3$ systems.

3.2 Optical and thermal properties

Figure 2 shows the transmission spectra of SrS- and BaS–Ga$_2$S$_3$ glasses in the range of 300–800 nm. The data of GeS–S and La$_2$S$_3$–Ga$_2$S$_3$ glasses is also shown for comparison. The absorption edge of 65BaS–35Ga$_2$S$_3$ glass is located at ~440 nm, which is comparable to that of Ge$_2$S$_3$–S$_2$S glass. The 65SrS–35Ga$_2$S$_3$ glass has the shortest absorption edge of ~390 nm in the sulfide glasses. Table 1 shows the refrac-
tive indexes at 633 nm, glass transition temperature $T_x$ and onset crystallization temperature $T_c$. All sulfide glasses have high refractive indexes over 2.1. The thermal characteristic temperatures, $T_x$ and $T_c$, of 65SrS–35Ga$_2$S$_3$ and 65BaS–35Ga$_2$S$_3$ glasses are in the same order as those of 30La$_2$S$_3$–70Ga$_2$S$_3$ glass.

3.3 Density and molar volume

Figure 3 shows the variations of density and molar volume with RS concentration for SrS– and BaS–Ga$_2$S$_3$ glasses. The densities of SrS– and BaS–Ga$_2$S$_3$ glasses are in the range of 3.55–3.65 g/cm$^3$ and 3.81–4.13 g/cm$^3$, respectively. The molar volume of the RS–Ga$_2$S$_3$ glasses decreases with increasing RS concentration and shows plateaus in the range of 65–70 mol% RS.

3.4 Raman spectra

Figure 4 shows the Raman spectra of $\alpha$-Ga$_2$S$_3$, SrGa$_2$S$_4$ and BaGa$_2$S$_4$ reference crystals and the RS–Ga$_2$S$_3$ glasses. The symbol $x$ means RS concentration (mol%RS) and (i)–(vi) are the assigned Raman bands. The assignments of the Raman bands are listed in Table 2. The $\alpha$-Ga$_2$S$_3$ crystal belongs to the class of wurtzite structure.$^{[10]–[12]}$ The peak (i) is attributed to the stretching vibration of Ga$_2$S$_4$ tetrahedra, $v_1$ ($A_1$) mode.$^{[11]}$ SrGa$_2$S$_4$ crystal consists of Ga$_2$S$_4$ structural units connected by corners and edges with three dimensional framework.$^{[13]–[15]}$ The peak (ii) in SrGa$_2$S$_4$ is associated with the bonding vibration of two Ga$_2$S$_4$ tetra-

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Table 1. Refractive Indexes at 633 nm and Thermal Properties of SrS–, BaS–Ga$_2$S$_3$, Ge–S and La$_2$S$_3$–Ga$_2$S$_3$ Glasses

<table>
<thead>
<tr>
<th>Glass composition</th>
<th>Refractive index at 633 nm</th>
<th>$T_x$</th>
<th>$T_c$</th>
<th>$T_\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>65SrS–35Ga$_2$S$_3$</td>
<td>2.169</td>
<td>538</td>
<td>564</td>
<td>116</td>
</tr>
<tr>
<td>65BaS–35Ga$_2$S$_3$</td>
<td>2.194</td>
<td>553</td>
<td>673</td>
<td>120</td>
</tr>
<tr>
<td>Ge$<em>{50}$S$</em>{50}$</td>
<td>2.137</td>
<td>473</td>
<td>573</td>
<td>100</td>
</tr>
<tr>
<td>30La$_2$S$_3$–70Ga$_2$S$_3$</td>
<td>2.471</td>
<td>556</td>
<td>681</td>
<td>125</td>
</tr>
</tbody>
</table>
Table 2. Raman Shifts and Their Assignments of α-Ga₅S₃, SrGa₅S₇ and Ba₆Ga₅S₁₂ Crystals and RS-Ga₅S₃ Glasses

<table>
<thead>
<tr>
<th>Material</th>
<th>Frequency shift / cm⁻¹</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Ga₅S₃</td>
<td>(i) 233</td>
<td>ν₃(Ga₅S₃)(A₃)</td>
</tr>
<tr>
<td>SrGa₅S₇</td>
<td>(ii) 280</td>
<td>ν₁(edge-shared GaS₃)</td>
</tr>
<tr>
<td>(iii) 357</td>
<td>ν₃(Ga-S-Ga)</td>
<td></td>
</tr>
<tr>
<td>Ba₆Ga₅S₁₂</td>
<td>(iv) 303</td>
<td>νₓ(Ga₅S₃)(Fₓ)</td>
</tr>
<tr>
<td>RS-Ga₅S₃ glasses</td>
<td>(v) 318</td>
<td>νₓ(Ga₅Sₓ(Fₓ), νₓ(edge-shared GaSₓ)</td>
</tr>
<tr>
<td></td>
<td>(vi) 358–378</td>
<td>νₓ(Ga-S-Ga)</td>
</tr>
</tbody>
</table>

hedra connected by edges νₓ(Ga₅Sₓ) (edge-shared). The peak (iii) in SrGa₅S₇ is attributed to the vibration of corner-shared GaS₃ tetrahedra ν₁(Ga-S-Ga). Ba₆Ga₅S₁₂ crystal consists of GaS₃ tetrahedra connected by corners with three-dimensional framework. The peak (iv) is attributed to the deformation mode made by the vibration of the GaS₃ tetrahedral units. The band (v) corresponds to the peak (iv) of the reference crystal. The broad band (v) may also be attributed a stretching mode of edge-shared GaS₃ tetrahedra νₓ(edge-shared GaSₓ) which was observed in Na₃S–Ga₂S₃ glasses. It is confirmed that the band (vi) in the RS-Ga₅S₃ glasses correspond to the peak (iii) of the reference crystal. Therefore, RS–Ga₅S₃ glasses are mainly composed of GaS₃ tetrahedral units connected by corners with the possibility of edge-shared GaS₃ tetrahedra. The frequency of the band (vi) remains constant at <65.0 mol% RS and shifts slightly toward the lower frequency side with increasing SrS and BaS concentrations at >65.0 mol% RS. Relative intensities of the bands (v) and (vi) depend on RS concentration. The relative intensity of the band (vi) is weaker than that of band (v) at <66.7 mol% BaS but it becomes stronger at ≥66.7 mol% BaS (S/Ga ≥2.5). No S–S bonds, which were observed in the S-rich Ge–S glasses, were detected in the RS–Ga₅S₃ glasses. CaO–Al₂O₃ glasses with >50 mol% CaO are known to form O–O bonds due to the incorporation of oxygen from melting atmosphere. Glass samples in this study were melted in N₂ atmosphere without sulfur using stoichiometric compounds as raw materials. Consequently, no S–S bonds may be formed in the RS–Ga₅S₃ glasses prepared by our method.

4. Discussion

The glass forming region in the RS–Ga₅S₃ (R=Ca, Sr, Ba) systems extends to near 66.7 mol% RS in the order of CaS < SrS < BaS, as shown in Fig. 1. These regions are located around eutectic compositions according to the phase diagrams of the CaS– and SrS–Ga₅S₃ systems. The melt quenching method forms glass near eutectic compositions in the binary RO–Fe₂O₃, Al₂O₃, and –Ga₂O₃ systems as well as the RS–Ga₅S₃ systems. The Raman spectral assignment (Table 2) concludes that RS–Ga₅S₃ glass is composed of GaS₃ tetrahedral units. Amphoteric oxides Fe₂O₃, Al₂O₃ and Ga₂O₃ are known to form the glass networks of FeO₄, AlO₄, and GaO₄ tetrahedra due to the oxygen-ion-donors of alkaline earth oxides (RO). These correspondences suggest that GaS₃ behaves in the same as amphoteric oxides for glass formation.

When the RS fully dissociates in the glass melt, the parameter S/Ga gives the number of sulfur atom per gallium atom. On the analogy of amphoteric oxides, the morphology of complex anions depends on an anion-to-cation ratio, S/Ga. In the case of Ga₅S₃ behaving as a basic sulfide in pure Ga₅S₃ melts, Ga₅S₃ dissociates according to the following reaction.

\[
\text{Ga}_5\text{S}_3 \rightarrow [\text{Ga}_5\text{S}_3]^{1-} + 5\mathrm{S}^{2-}
\]

Besides the ionic radius of Ga⁺ is smaller, the basicity of Ga⁺ is lower than those of Ca²⁺, Sr²⁺ and Ba²⁺. Therefore, Ga₅S₃ is regarded as an acidic sulfide with basic components of alkaline-earth sulfide RS. In the case of Ga₅S₃ behaving as an acidic sulfide in the melts, Ga₅S₃ dissociates and forms sulfur complex anions by the following general reaction formula.

\[
\text{Ga}_5\text{S}_3 + 5\mathrm{S}^{2-} \rightarrow [\text{Ga}_5\text{S}_3]^{13(3x+6)-} \quad (1 \leq x \leq 5)
\]

The RS has an essential S²⁻-providing role in the formation of sulfur complex anions. The anions \([\text{Ga}_5\text{S}_{12}-]\) and \([\text{Ga}_5\text{S}_{7-}]\) at \(x = 1\) (S/Ga = 2), \([\text{Ga}_5\text{S}_{10-}]\) at \(x = 2\) (S/Ga = 2.5) and \([\text{Ga}_5\text{S}_{15-}]\) at \(x = 3\) (S/Ga = 3), are thought as the complex ones being related to glass formation. The presumable morphology of the complex anions corresponds to the atomic structures of Ba₆Ga₅S₁₂ crystals reported by Eisenmann. The schematic variation of these complex anions with BaS concentration is shown in Fig. 5. It is thought that these coexisting complex anions form glass networks due to melt quenching over critical cooling rates for crystallization. The numerical condition is S/Ga = 2 (50 mol% RS) when all Ga⁺ ions contribute to form the three dimensional networks of Ga₅S₃ tetrahedra connected fully by the corners with no non-bridging sulfur. Nevertheless, no glass is formed at S/Ga = 2 under the experimental condition in this study. Figure 1 indicated that the glass forming region extends to higher RS concentration near S/Ga = 2.5 (66.7 mol% RS) in the order of CaS < SrS < BaS. The width of glass forming region corresponds to the basicity order of CaS < SrS < BaS on the analogy of alkaline oxides.

Fig. 5. Variations of structure with BaS concentration in the BaS–Ga₅S₃ system.

<table>
<thead>
<tr>
<th>[Ga₅S₃]²⁻</th>
<th>S/Ga = 2 (50 mol% BaS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ga₅S₃]⁷⁻</td>
<td>S/Ga = 2.5 (66.7 mol% BaS)</td>
</tr>
</tbody>
</table>

The anions \([\text{Ga}_5\text{S}_{12}-]\) (Fig. 5(b)) at S/Ga = 2.5 are transformed into well-developed glass networks because
this complex anion is composed of a network of a GaS₄ tetrahedron with a terminal sulfur atom. The situation leads that the number of bridging sulfur per GaS₄ tetrahedron is the largest in the GaS₄ complex anions. The variation of molar volume with RS concentration (Fig. 3(b)) exhibits a plateau region at which the glass-network due to the anions [Ga₂S₄]⁻ (Fig. 5(b)) is well-developed.

Figure 6 shows the compositional dependence of relative intensity ratio of the Raman bands (vi) and (v). Each relative intensity is derived by the deconvolution of Raman spectra based on Gaussian fitting. ν₁(GaS₄)(F₂) mode appears intensively because of the large fraction of bridging sulfur and the low degree of freedom of GaS₄ tetrahedral arrangement at <66.7 mol% RS (S/Ga = 2.5). The band (vi) (ν₂(Ga-S-Ga) mode) is relatively more intense than the band (v) (ν₂(Ga₂S₄)(F₂) mode) at ≥66.7 mol% BaS (S/Ga = 2.5) because the degree of the freedom is heightened due to the de-polymerization of the glass-network with the increase of the number of non-bridging sulfur. The above discussion of Raman spectra suggests that the stable glass formation region extends to around S/Ga = 2.5 (66.7 mol% RS) with the moderate degree of the freedom of GaS₄ tetrahedra displacement in the SrS- and BaS-GaS₂ systems.

5. Conclusions

New GaS₄-based glass forming systems are presented. Representative transparent glasses with the compositions of 65SrS-35GaS₂ and 65BaS-35GaS₂ have high refractive indexes of >2.1 and show good thermal stability with moderate differences over 100°C between glass transition and on-set crystallization temperatures. The 65SrS-35GaS₂ glass has the shortest absorption edge of ~390 nm in the sulfide glasses. Raman spectroscopy reveals that RS–Ga₃S₄ glasses consist of the network of GaS₄ tetrahedra due to the RS addition.

References