

Local order in Ge₁₀Sb₃₀S₆₀ glass

Fujio KAKINUMA*

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The atomic structures of Ge₁₀Sb₃₀S₆₀ ternary glass have been investigated by using the neutron diffraction method. The structure factor, $S(q)$, of this glass has a first sharp diffraction peak (FSDP) at 1.14 Å⁻¹. The oscillation in $S(q)$ persisted up over 25 Å⁻¹ indicates that the chemical short range order is presented in these glasses. The results of structural analysis show that the short-range orders of tetrahedral GeS₄ and pyramidal SbS₃ units seem to exist in the Ge₁₀Sb₃₀S₆₀ glasses.

Keywords: glass, neutron diffraction, chemical short-range order

1. Introduction

The physical and chemical properties of the Ge-X-M ternary glasses (X: chalcogen, M: metal) have been widely investigated [1-3]. The chalcogenide glasses are of considerable interest in a practical point of view. The Ge-S-Ag glasses are super ionic conductors and have attracted a great deal of attention from application to optical device [4]. The Ge-Sb-S and Ge-Sb-Se ternary glasses have characteristic behaviour in the IR-transmission that makes them useful for optical application [5-9].

The physical properties of chalcogenide glasses depend on their structure associated with the bonding nature. The Ge-S and Ge-Se binary systems form typical covalent network glasses. According to the structural studies for Ge-S and Ge-Se glass systems [10-12], these glasses have GeX₄ tetrahedral units that were connected with corner sharing or edge-sharing. On the other hand, the Sb-S and Sb-Se systems have a chemical order of pyramidal SbX₃ as a structural unit [5-7]. The binary Ge-S(Se) alloys are good glass former over a wide concentration range. The Sb₂S₃ alloy has low glass-forming ability. Then high cooling rate is required for its preparation. The substitution of Ge for Sb in the Sb₂S₃ alloy improves the glass forming ability. As is analogized from the structure of binary Ge-S and Sb-S systems, it seems that the ternary Ge_xSb_{40-x}S₆₀ glasses have two kinds of structural unit. In the Ge_xSb_{40-x}Se₆₀ glasses, the structural phase transition has been discussed by using the average

* Department of Information and Electronic Engineering, Professor

coordination number [9]. On the basis of the X-ray diffraction data, the existence of the topological phase transition was suggested for the $\text{Ge}_x\text{Sb}_{40-x}\text{S}_{60}$ glasses [8].

To investigate the intrinsic chemical ordering in chalcogenide materials is important for understanding their physical and optical properties. The neutron diffraction technique is useful method to investigate the local structure of disordered materials. In this paper, we report the results of the neutron diffraction measurements and discuss the local structure of the $\text{Ge}_{10}\text{Sb}_{30}\text{S}_{60}$ glass.

2. Experimental

The glass samples were prepared by melt quenching. The purities of starting materials were 99.999%. The weighed elements were placed in a quartz ampoule of 3 mm inner diameter and 0.5 mm wall thickness. The ampoules were evacuated to a pressure of 6×10^{-6} Torr and sealed. The ampoule containing 7.5 g of weighed was heated up to 1223 K at a heating rate of 1.7 K/min. In order to avoid the increase of sulphur vapour pressure, the ampoule was kept at 673 K for four hours, at 973 K for twelve hours and at 1223 K for five hours in the heating process. The sample capsule was often shaken to insure the homogeneity of the melt. The melt was maintained at 1173 K for four hours and then quenched into ice water with 10 wt.% NaCl. An X-ray powder diffract meter was used to verify the amorphous state of the samples.

Pulsed neutron scattering experiments were carried out at room temperature using the high intensity total scattering spectrometer (HIT II) installed at High Energy Accelerator Research Organization (KEK) at Tsukuba, Japan. The glass sample was coarsely powdered and held in a vanadium cell of inner diameter 8.0 mm with 0.025 mm wall thickness. The structure factors, $S(q)$, where $q = 4\pi\sin\theta/\lambda$, 2θ is the diffraction angle and λ is the neutron wavelength, were obtained from the scattering intensity after making the usual corrections, such as the subtraction of the cell intensity, inelasticity, multiple scattering, absorption and normalization with a vanadium rod.

The pair correlation function, $g(r)$, can be derived from the Fourier transformation of $S(q)$ as follows;

$$g(r) = 1 + \frac{1}{2\pi^2 r \rho_0} \int_0^\infty q(S(q) - 1) \sin(qr) dq \quad (1)$$

where ρ is the average number density of atoms, which was measured by Archimedes method with toluene. The radial distribution function, $rdf(r)$, is defined as

$$rdf(r) = 4\pi r \rho_0 g(r). \quad (2)$$

The average coordination number, n , can be calculated as

$$n = \int_{x_1}^{x_2} r df(r) dr \quad , \quad (3)$$

where x_1 and x_2 are radius in a spherical shell around any given atom.

3. Results

Figure 1 shows the structure factors, $S(q)$, for $\text{Ge}_{10}\text{Sb}_{30}\text{S}_{60}$ glass. The observed characteristics behaviour in $S(q)$ are as follows; (i) The oscillation in $S(q)$ is persisting up to high q values. (ii) A first sharp diffraction peak (FSDP) exists at 1.14 \AA^{-1} . Figure 2 shows the pair correlation function, $g(r)$, for $\text{Ge}_{10}\text{Sb}_{30}\text{S}_{60}$ glass. The ripple in $g(r)$ at $q < 2 \text{ \AA}^{-1}$ is the Fourier transform termination errors. Three peaks are found in the range of $r < 5 \text{ \AA}$.

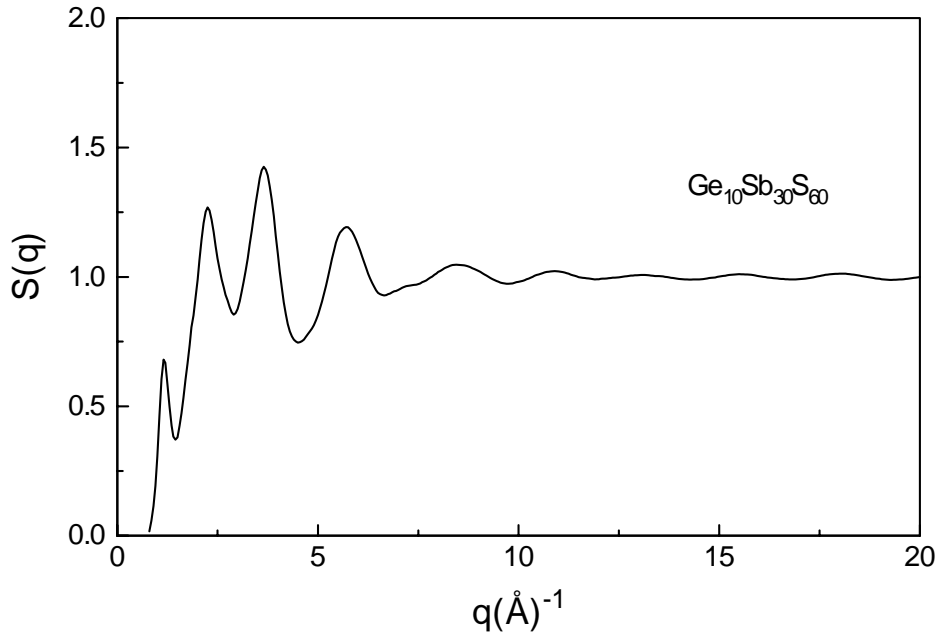


Fig. 1 Structure factor, $S(q)$, for $\text{Ge}_{10}\text{Sb}_{30}\text{S}_{60}$ glass.

4. Discussion

It has been known that the glassy Sb_2S_3 , GeS_2 , and Ge-Sb-S films have covalently bonded pyramidal unit, SbS_3 , and tetrahedral unit, GeS_4 , as structural units [5, 6]. As seen in Fig. 1, the characteristic features of the structure factors indicate the existence

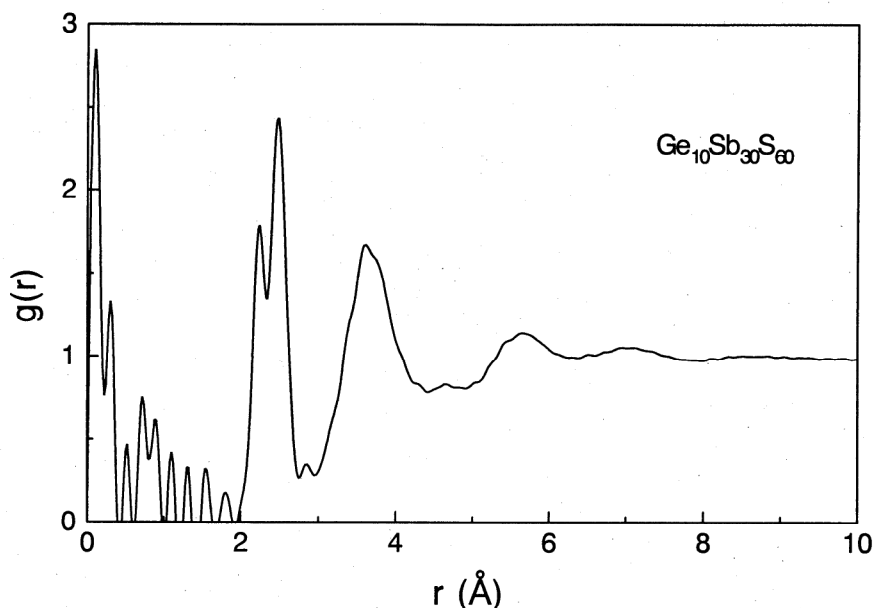


Fig. 2 Pair correlation function, $g(r)$, for $\text{Ge}_{10}\text{Sb}_{30}\text{S}_{60}$ glass

of the chemical short-range order and the middle-range order in the $\text{Ge}_{10}\text{Sb}_{30}\text{S}_{60}$ glass. Three peaks observed in $g(r)$ suggest the present of the structural unit. The value of the first peak position, $2.24 \pm 0.02 \text{ \AA}$, is comparable to the value of the Ge-S bond length in the GeS_2 glass and glassy Ge-S-Metals [1, 11]. It appears that this peak can be identified as being mainly due to the Ge-S correlations. Furthermore, the third peak in $g(r)$ is located at $3.61 \pm 0.03 \text{ \AA}$. The ratio of third peak position, r_3 , to the first peak one, r_1 , is 1.61 ± 0.03 . This value is compared with a value of $\sqrt{8/3} = 1.63$ for perfect tetrahedra. Although the broad peak at 3.61 \AA may be comprised of secondary partial Ge-Ge, Ge-Sb and Sb-Sb correlations as well as S-S correlation, the ratio of r_3 / r_1 suggests the presence of GeS_4 unit in the $\text{Ge}_{10}\text{Sb}_{30}\text{S}_{60}$ glass. As mentioned previously, the position of the first peak in $g(r)$ is independent of the composition, which can be related to the presence of the GeS_4 units. According to the structural studies [3, 5], the Sb_2S_3 binary glass and glassy Ge-Sb-S films have the pyramidal units with Sb-S bond distance of about $2.45\text{-}2.50 \text{ \AA}$. The second peak in $g(r)$ at 2.48 \AA for $\text{Ge}_{10}\text{Sb}_{30}\text{S}_{60}$ glass can be mainly attributed to the Sb-S contribution.

Assuming that the peaks at 2.24 and 2.48 \AA are due to the Ge-S and Sb-S correlations, the coordination numbers corresponding to these correlations were

obtained by fitting each peak to a Gaussian function for which the area, A_{ij} , was integrated. The partial coordination number of Ge and Sb is given by

$$n_{ij} = \sum_{ij} \frac{\langle b \rangle^2}{c_i b_i b_j} A_{ij} \quad (4)$$

where i denotes Ge and Sb, j means S, $\langle b \rangle = c_{\text{Ge}} b_{\text{Ge}} + c_{\text{Sb}} b_{\text{Sb}} + c_{\text{S}} b_{\text{S}}$, c_i is the atomic fraction, b_i , b_j is the coherent scattering length of Ge (0.81929×10^{-12} cm [12]), Sb (0.5641×10^{-12} cm [12]) and S (0.2847×10^{-12} [12]).

The results are as follows; $n_{\text{Ge-S}} = 3.6 \pm 0.1$, $n_{\text{Sb-S}} = 3.0 \pm 0.1$, $n_{\text{S}} = 2.1 \pm 0.1$. Here $n_{\text{Ge-S}}$ means the average number of S atoms around Ge atom, $n_{\text{Sb-S}}$ means the average number of S atoms around Sb atoms, and n_{S} is the sum of the Ge and Sb atoms bonded with S atom. Rough estimation of the coordination numbers described above suggests that the Sb and Ge atoms in the $\text{Ge}_{10}\text{Sb}_{30}\text{S}_{60}$ glass have three and four coordination numbers, respectively. These results are consistent with the speculation on the basis of the peak position in $g(r)$. If the coordination numbers of constitutional elements are 4, 3 and 2, for Ge, Sb and S, respectively, and the glass is composed of the $\text{Ge}(\text{S}_{1/2})_4$ and $\text{Sb}(\text{S}_{1/2})_3$ chains connected by S-bridge, the $\text{Ge}_{10}\text{Sb}_{30}\text{S}_{60}$ glass has a less stoichiometry of metal atoms. Then the contribution from Ge-Ge, Ge-Sb and Sb-Sb correlations to the first coordination shells cannot be neglect. In the present results of $g(r)$, the peak at 2.06 \AA , which corresponds to the S-S bond length, is not apparently observed.

For the $\text{Ge}_{10}\text{Sb}_{30}\text{S}_{60}$ glass, the $-\text{Ge-S-S-Ge}-$ or $-\text{Sb-S-S-Sb}-$ connectivity does not denied by the model described above. Since the coherent scattering length of S atom is small compared to other constituents, the contribution of the S-S correlation to $rd f(r)$ is much smaller than those of others. Its full width at half maximum (FWHM) of the FSDP, Δq_{FSDP} , obtained by reflecting the low q region on q_{FSDP} , is $0.29(3) \text{ \AA}^{-1}$ which corresponds to a correlation length of $2\pi/q_{\text{FSDP}} = 22(1) \text{ \AA}$ [14]. The origin of FSDP mainly is due to the correlation between Ge-Ge atoms in the binary Ge-S glasses [11]. In the $\text{Ge}_{10}\text{Sb}_{30}\text{S}_{60}$ glass, FSDP seems to be associated with the correlation between chemical units such as GeTe_4 and SbS_3 .

5. Conclusion

We have studied the local structure of $\text{Ge}_{10}\text{Sb}_{30}\text{S}_{60}$ glass. The first sharp diffraction peak (FSDP) has been observed in the structure factor. The results of structural analysis show that the short-range orders of tetrahedral GeS_4 and pyramidal SbS_3 units exist in the $\text{Ge}_{10}\text{Sb}_{30}\text{S}_{60}$ glass. The middle-range order seems to be due to the correlation between those chemical short-range orders in this glass.

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