TECHNICAL NOTE

Structural Investigation of Glass System Na_2O-Ga_2O_3-SiO_2 †

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Previous investigations on Na_2O-Al_2O_3-SiO_2 glasses revealed that many of their physical properties change abnormally at or near the composition of Al/Na ratio of 1. From the electrical conduction measurement, Isard[1] interpreted this anomalous behaviour in terms of the change in coordination number of Al^{3+} ions in the glasses; all of the Al^{3+} ions are tetrahedrally coordinated when the Al/Na ratio is equal to or less than 1, while they are octahedrally coordinated when the ratio is larger than 1. On the other hand, on the basis of the viscosity data of Na_2O-Al_2O_3-SiO_2 melt, Riebling[2] concluded that all of the Al^{3+} ions are fourfold coordination when $Al/Na \leq 1$, but that one-fourth of the Al^{3+} ions become sixfold coordination when $Al/Na > 1$. However, Al $K\alpha$ X-ray emission measurement[3] and X-ray diffraction study[4] indicated that the coordination number of the Al^{3+} ions remains 4 even when the Al/Na ratio exceeds 1. Recent infrared emission measurement[5] recognized that the most of the Al^{3+} ions take the form of the tetrahedrally coordinated oxygens in molten and glassy Na_2O-Al_2O_3-SiO_2. In addition, Lacy[6] argued from the viewpoint of crystal geometry and energy that no Al^{3+} ions have the coordination number larger than 4 even though the Al/Na ratio exceeds 1. In view of similarity between of aluminum and gallium ions, it is expected that the physical properties of Na_2O-Ga_2O_3-SiO_2 glasses show similar anomalous changes to those of Na_2O-Al_2O_3-SiO_2 glasses. In order to make the structural interpretation of the cause of these anomalies, the short range distribution of interatomic distances in four Na_2O-Ga_2O_3-SiO_2 glasses has been determined by X-ray structural analysis.

The reagent grade SiO_2, Na_2CO_3 and β-Ga_2O_3 were used as the starting materials to the following two series of glasses: A series; $xGa_2O_3 \cdot (100\text{-}x)(Na_2O\cdot 2SiO_2)/3$, B series; $xGa_2O_3 \cdot (100\text{-}x)(Na_2O\cdot SiO_2)/2$, where x is the mole percent of Ga_2O_3. The X-ray diffraction experiment was carried out with the use of a ϑ-ϑ diffractometer with parafocusing reflection geometry and Mo $K\alpha$ radiation monochromatized by a curved graphite monochromator mounted in the path of the diffracted beam. After the X-ray measurement, they were corrected for background, polarization and Compton scattering, and then were scaled by means of both the high angle region method and the Krogh-Moe, Norman's method. The radial distribution function D (r) was obtained by Fourier transformation of the observed reduced intensity function S·i (S).

Fig. 1 shows the D(r) curves observed for A-25, B-10, B-30 and B-45 glasses. As shown this figure, the first peaks at 1.77 ~ 1.83 Å are due to the nearest neighbour ionic pairs Si-O and Ga-O. These peaks have a good symmetry and cannot deconvoluted into two peaks of Si-O and Ga-O. Therefore, they were analyzed as the mixed T-O

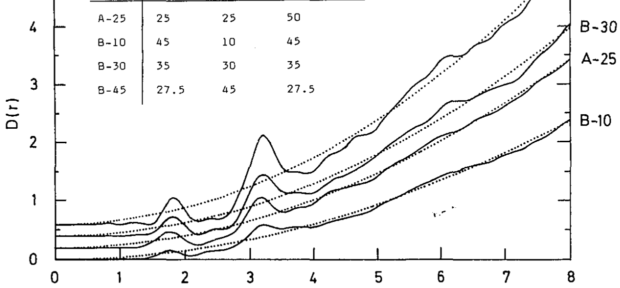

Fig. 1 Radial distribution function D(r) for the glasses in the system Na_2O-Ga_2O_3-SiO_2.

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(T=Si, Ga) ionic pair. Using the effective electron number of T calculated from the molar fraction of Si and Ga, the coordination number of T ($N_{T/O}$) was obtained by the numerical integration of the area for the first peak. The second peaks at 2.34 ~ 2.41 Å are due to the nearest neighbour Na-O ionic pair. The third peaks at 3.14 ~ 3.33 Å are due to the T-T ionic pair. The short range parameters for the nearest neighbours are summarized in **Table 1**. It is well known that in silicate glasses all of the Si ions are fourfold coordination[7]. The coordination

Table 1 Short range parameters of the ionic pairs in Na_2O-Ga_2O_3-SiO_2 glasses.

	A-25	B-10	B-30	B-45
r_{T-O} (Å)	1.78	1.77	1.82	1.83
r_{Na-O} (Å)	–	2.37	2.41	2.35
$N_{T/O}$ (atoms)	3.7	3.6	3.7	3.8
$N_{Na/O}$ (atoms)	–	4.0	5.1	4.5
$\angle$T-O-T (deg.)	127	132	124	123

number $N_{T/O}$ is near four, which indicates that the coordination number of Ga ions is also four. The Na-O distance (r_{Na-O}) and the coordination number of Na ions ($N_{Na/O}$) for B series glasses show the maxima at the Ga/Na ratio 1. Imaoka[8] has reported from the analysis of RDF that the basic structures for $Na_2O{\cdot}2SiO_2$ and $Na_2O{\cdot}SiO_2$ glasses are the layer and chain structure, respectively, and that the coordination number $N_{Na/O}$ is three for $Na_2O{\cdot}2SiO_2$ glass and four for $Na_2O{\cdot}SiO_2$ glass. Taylor et al.[4] has suggested that $Na_2O{\cdot}Al_2O_3{\cdot}2SiO_2$ glass has the six-menbered ring structure and $N_{Na/O}$ is six. In view of their suggestions, it may be considered that the layer or chain structure of sodium silicate glass changes into the three dimensional network structure containing six-menbered ring with the addition of Ga_2O_3 to sodium silicate glasses. Thus, a structural model based on the three dimensional six-menbered rings was constructed and examined using the following Debye scattering equation[9] for A-25 glass, which has the same composition with the carnegiete-type crystal.

$$S{\cdot}i(S) \sum_i x_i f_i^2 = \sum_i \Sigma_j N_{ij} f_i f_j \exp(-b_{ij}S^2) \sin(Sr_{ij})/r_{ij} \quad (1),$$

where f_i and f_j are the independent atomic scattering factors of atoms i and j, r_{ij} the distance between atoms i and j and b_{ij} the disorder term that is one-half of the mean square variation in r_{ij}. The value of b_{ij} is calculated from the following equation[4].

$$b_{ij} = (B_i + B_j)/(8\pi^2) + (r_{ij}/kr_c) \quad (2),$$

where B_i and B_j are the X-ray isotropic thermal parameters of atoms i and j, k the constant nearly equal to 4 for most glass and r_c the finite size of the selected structural model. In **Fig. 2**, S·i(S) for this carnegiete-like structural model is shown and compared with the observed D(r) curve for A-25 glass. The calculation was performed, permitting about 20% of random vacancies at the distance more than about 4 Å. A reasonable agreement between the observed and calculated D(r) curves can be seen. The disagreement around 2.5 Å is due to the ignorance of the contribution from 0-0 pair in SiO_4 tetrahedra; 0-0 bond length of SiO_4 tetrahedra is about 2.65 Å, while that of TO tetrahedra is about 2.9 Å. As given Table 1, $N_{Na/O}$ for B-45 glass is smaller than that for B-30 glass. This seems to indicate that the three dimensional network structure break down when the amount of Ga_2O_3 becomes more than the Ga/Na ratio 1. From the obtained result of X-ray structural analysis, it is concluded that the nonbridging oxygens existing in sodium silicate glass change bridging oxygens with the addition of Ga_2O_3 by forming $GaO_4^-Na^+$ units when the Ga/Na ratio is less than 1, but they appeared again along with the formation of Ga-O-Ga bond with further addition of Ga_2O_3 over the Ga/Na ratio of 1.

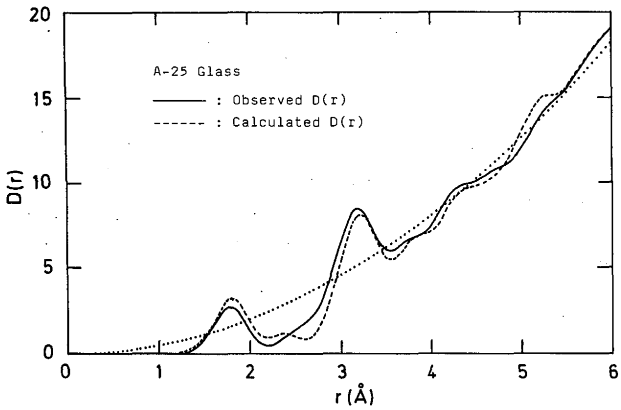

Fig. 2 Comparison between the calculated D(r) and observed D(r) for A-25 glass.

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