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X-ray Diffraction Studies on Amorphous Materials (Report 1)[†]

Nobuya IWAMOTO* and Norimasa UMESAKI**

Abstract

Radial distribution functions for Na₂O–SiO₂ and GeO₂ glasses were determined with X-ray diffraction procedure. The analytical means attempted to reduce termination effect and normalization error arising from the uncorrected Compton scattering. The structure of Na₂O–SiO₂ and GeO₂ glasses was composed of tetrahedral SiO₄ (GeO₄), and also the correlation among tetrahedral SiO₄ in Na₂O–SiO₂ glasses depended on Na₂O content. From the above mentioned point of view, it can be anticipated that radial distribution function is useful method for obtaining the structural information of an amorphous material.

1. Introduction

It has been known that an amorphous material such as glass has no repeated structure, that is, long range regularity which is common characteristics in atomic arrangement of crystalline substances. To resolve the question what is a vitreous state, we should make not only the studies concerning physicochemical properties, but also the studies to get basic informations of the atomic arrangement in an amorphous material.

When an incident beam as X-ray, neutron or electron is directed upon a material, diffraction phenomenon occurs. However, we can get only a few halo patterns in the case of an amorphous material. It gives us many useful informations about to what degree atomic regularity are held.

If a suitable experimental conditions are chosen to find another atoms with an equal probability in all space when an atom is chosen as origin, the structure is expressed by a time- and space-average radial distribution function (RDF), $4\pi r^2 \rho(r)$. From the calculation, average number of atoms surrounding an atom as center can be obtained. Although the calculation of RDF gives only a limited knowledge, we can obtain structural information without any a priori assumptions.

The modern theoretical basis of diffraction was established by Zernicke and Prins¹⁾, and they applied the Fourier integral theorem to obtain RDF.

The first quantitative application of this method was carried out by Debye and Menke²⁾ to solve the structure of mercury. Since then, many investigators are continu-

ously making their efforts to obtain direct and reliable information on liquid structure.

Besides, Warren and his co-workers^{3)–6)} presented an approximation method applicable to vitreous systems composed from many sorts of atoms and studied widely on glasses. The essential conclusion of their works can be endured for the criticisms even in today.

In this report, the results of RDF about the glasses, Na₂O–SiO₂ and GeO₂ are presented. Furthermore, the authors discussed the various problems regarding the analytical means.

Depending on the precise study on vitreous SiO₂ as basis, it is quite well established that the glass is composed of the linkage of tetrahedral SiO₄ in which definite Si-O and O-O interatomic distances are held.^{6)–8)}

Warren and Biscoe performed first X-ray diffraction study of Na₂O–SiO₂ glass⁵⁾. Recently, Waseda carried out X-ray and neutron diffraction studies about the glassy and molten states in this system.⁹⁾

On the other hand, it is known that GeO₂ takes crystalline polymorphs similar to SiO₂ structure in addition to rutile form with octahedral coordination of oxygen around a germanium atom. Liquid GeO₂ can be readily supercooled, and takes glassy state easily. Limited studies with X-ray and neutron diffraction on GeO₂ glass have been made until now.^{10)–14)} Warren performed X-ray diffraction study of glassy GeO₂, but he did not to apply Fourier analysis¹⁰⁾. Afterwards, Zarzycki¹¹⁾ carried out X-ray diffraction study of glassy GeO₂, and concluded.

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that it is composed of tetrahedral GeO_4 as well as SiO_2 glass. Neutron diffraction studies about this glass were reported by Lorch¹²⁾ and Ferguson and Hass¹³⁾ respectively. Their results were nearly agreed with the result by Zarzycki¹¹⁾. Recently, Leadbetter and Wright¹⁴⁾ have done X-ray diffraction study with good experimental precision on GeO_2 glass and compared their result with quasi-crystalline model based on the assumption to take various crystalline polymorphs. From this, they postulated that the average structure of the glass closely resembled to that of the quartz modification.

2. Experimental Procedures

Diffraction data were obtained with a θ - θ diffractometer having Bragg-Brentano focusing system designed expressly for the study of liquids and glasses.

The X-ray source and detector of this diffractometer rotate around a sample in a vertical plane at same angular rate and in opposite directions; these conditions are schematically shown in Fig. 1. The sample was placed on the sample stage in an enclosed chamber with a beryllium window for passage of X-ray beam. The pressure in the chamber can be evacuated till 10^{-6} mHg and various sorts of gases can be flown.

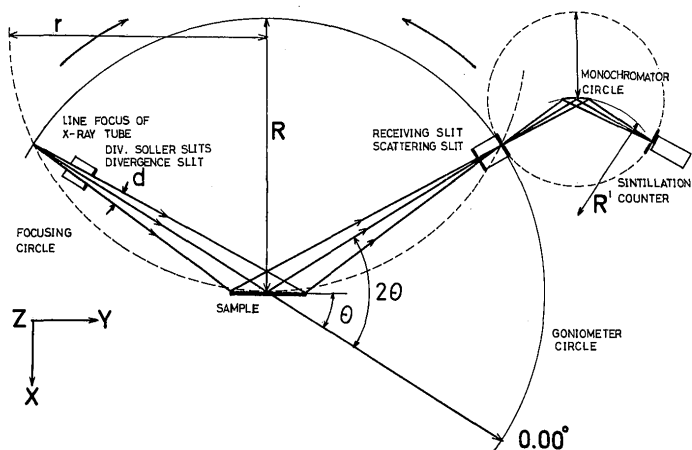


Fig. 1 X-ray optical geometry.

Monochromatic $\text{MoK}\alpha$ radiation was obtained through the use of a bent graphite monochromator on the diffraction site. A scintillation counter with pulse-height analyzer was used as a detector.

A final check on the adjustment of the apparatus was made by scanning with silicon powder sample.

Fixed count method was used to study the diffraction of glasses of the Na_2O - SiO_2 system. The accumulated counts per 0.5° steps in 2θ between 4° and 100° were changed from 10,000 cps in the small angle region to 20,000 cps in the high angle region.

In the other hand, the diffracted intensities of GeO_2 glass were also registered continuously in 2θ between 4° and 100° with recording.

The samples used for the experiments in every cases were prepared from reagent grade Na_2CO_3 , SiO_2 and GeO_2 powders by melting in air with platinum crucible, and then cooling to room temperature. Flat pieces ($20 \times 20 \times 3\text{mm}$) were cut from the clear region of glass blocks. The sample plates were optically polished before the measurement. Density of each samples was determined by Archimedean method.

The characteristics of the samples studied are given in Table 1.

Table 1. Characteristics of the samples studied.

| Sample | Chemical composition (mole %) | | Melting ($^\circ\text{C}$) | Density (g/cm^3) |
|--|-------------------------------|----------------|------------------------------|------------------------------------|
| | Na_2O | SiO_2 | | |
| Na_2O - SiO_2 glass | 20 | 80 | 1400x5hr | 2.381 |
| | 40 | 60 | 1300x5hr | 2.530 |
| GeO_2 glass | | | 1500x27hr | 3.662 |

3. Analytical Means

The observed intensities $I^{\text{obs}}(S)$ in arbitrary units were corrected for the background, for the polarization of beam at the sample and the monochromator used $[(1 + \cos^2 2\theta \cos^2 2\theta_m)/(1 + \cos^2 2\theta_m)]$, where θ_m is the Bragg angle for the monochromator.

Absorption correction was not necessary for Bragg-Brentano focusing system.

The corrected intensities $I^{\text{cor}}(S)$ were normalized to a scale of electron units per one stoichiometric unit of the sample by the expression,

$$I_{\text{eu}}^{\text{cor}}(S) = K I^{\text{cor}}(S) \quad (1)$$

, where $S = (4\pi/\lambda) \sin\theta$, and K is a normalization constant.

The normalization constant was calculated from the High-Angle region method¹⁵⁾ and the Krogh-Moe-Norman method¹⁵⁾. The corrected intensity can be related to the coherently scattering in electron units $I_{\text{eu}}^{\text{coh}}(S)$, and the Compton scattering intensity $I_{\text{eu}}^{\text{inc}}(S)$ from the following equation

$$I_{\text{eu}}^{\text{cor}}(S) = I_{\text{eu}}^{\text{coh}}(S) + I_{\text{eu}}^{\text{inc}}(S). \quad (2)$$

The High-Angle method is based on the assumption that the coherent intensity converges the mean square dispersion corrected atomic scattering factor, i.e.,

$$\langle f^2 \rangle = \sum_i x_i f_i(S)^2 \quad (3)$$

at the high value of S , where

\sum_i is the summation over a stoichiometric unit of the sample

x_i is atomic fraction of an element i

$f_i(S)$ is scattering factor of element i .

Therefore, the following equation is obtained

$$K I^{\text{cor}}(S) = \langle f^2 \rangle + I_{\text{eu}}^{\text{inc}}(S). \quad (4)$$

The High-Angle constant K_{HA} is given from the equation

$$K_{\text{HA}} = \int_{S_{\text{min}}}^{S_{\text{max}}} [\langle f^2 \rangle + I_{\text{eu}}^{\text{inc}}(S)] dS / \int_{S_{\text{min}}}^{S_{\text{max}}} I^{\text{cor}}(S) dS \quad (5)$$

where S_{min} is the minimum value of S beyond which $I^{\text{cor}}(S)$ shows only small oscillations, and S_{max} is the maximum value accessible in scattering experiments.

The normalization constant K_{KMN} is obtained by using the Krogh-Moe-Norman method can be derived as follows:

$$K_{\text{KMN}} = \frac{\int_0^{S_{\text{max}}} S^2 \{ [\langle f^2 \rangle + I_{\text{eu}}^{\text{inc}}(S)] / \langle f^2 \rangle \} \exp(-\alpha S^2) dS - 2\pi^2 \rho_0}{\int_0^{S_{\text{max}}} S^2 [I^{\text{cor}}(S) / \langle f^2 \rangle] \exp(-\alpha S^2) dS} \quad (6)$$

, where $\exp(-\alpha S^2)$ is a convergence factor, ρ_0 the average atomic density of the sample, and $\langle f^2 \rangle$ the square of the mean dispersion corrected atomic scattering factor, i.e.,

$$\langle f^2 \rangle = \left(\sum_i x_i f_i(S) \right)^2 \quad (7)$$

The normalization constants were calculated by using the following parameters: $S_{\text{min}}=10.0 \text{ \AA}^{-1}$, $S_{\text{max}}=13.5 \text{ \AA}^{-1}$, $\alpha=0.0$ & 0.008 , and the uses of atomic scattering factors given by Cromer and Waber¹⁶, the values of anomalous dispersion correction by Cromer¹⁷ and Compton scattering factors calculated by Cromer and Mann¹⁸.

The normalized intensity $I_{\text{eu}}^{\text{cor}}(S)$ was extrapolated to zero scattering angle from the observed values in the lower angle parts.

The reduced intensity $i(S)$, defined as

$$i(S) = (I_{\text{eu}}^{\text{cor}}(S) - \langle f^2 \rangle) / \langle f^2 \rangle \quad (8)$$

is the structure sensitive part of scattering intensity. The reduced intensity $i(S)$ is directly related to the radial pair distribution, $4\pi r^2 \rho_{ij}(r) = D_{ij}(r)$ of distinct pair of atoms of kind i and j from the expression

$$S_i(S) = \sum_i \sum_j x_i x_j f_i(S) f_j(S) / \langle f^2 \rangle \int_0^\infty 4\pi r^2 [\rho_{ij}(r) - \rho_0] \sin(Sr) dr \quad (9)$$

, where the summation over both i and j are over a stoichiometric unit.

Fourier transform of eq.(10) gives a radial distribution function $D(r)=4\pi r^2 \rho(r)$, i.e.,

$$D(r) = \sum_i \sum_j D_{ij}(r) = 4\pi r^2 \rho_0 + (2r/\pi) \int_0^\infty S_i(S) \sin(Sr) dS \quad (11)$$

Eq. (11) requires data from $S=0$ to $S=\infty$, but the reduced intensity $i(S)$ is only known with the use of maximum value S_{max} accessible in scattering experiments.

Therefore, Eq (11) has to be replaced by

$$D(r) = 4\pi r^2 \rho_0 + (2r/\pi) \int_0^{S_{\text{max}}} S_i(S) \sin(Sr) dS. \quad (12)$$

The reduced radial density function is obtained as

$$H(r) = (2r/\pi) \int_0^{S_{\text{max}}} S_i(S) \sin(Sr) dS. \quad (13)$$

The pair correlation function which is an alternate form of $D(r)$ is expressed by

$$G(r) = \rho(r) / \rho_0 = 1 + (2\pi^2 r \rho_0)^{-1} \int_0^{S_{\text{max}}} S_i(S) \sin(Sr) dS. \quad (14)$$

The pair correlation function $G(r)$ shows deviation of radial density from the macroscopic density.

All the computations were carried out with computer (NEAC2200).

4. Results and Discussions

4.1 $\text{Na}_2\text{O}-\text{SiO}_2$ Glasses

The correction intensities $I_{\text{eu}}^{\text{cor}}(S)$ calculated are shown in Fig. 2. It will be seen that with increasing Na_2O content a strong peak at about $S=1.6 \text{ \AA}^{-1}$ and a shoulder at about $S=5.0 \text{ \AA}^{-1}$ each diminish, also a new peak at about $S=2.3 \text{ \AA}^{-1}$ appears.

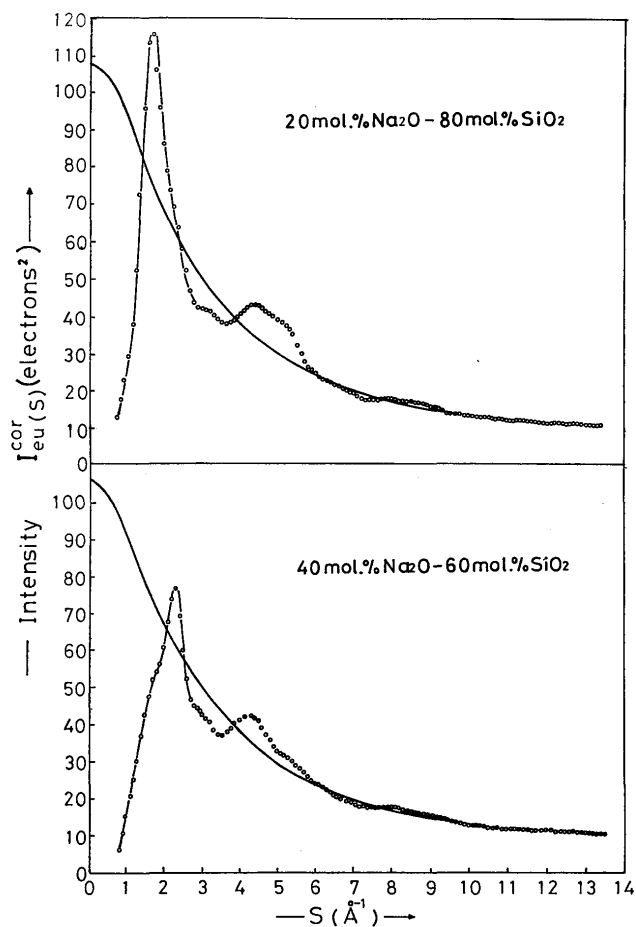


Fig. 2 Corrected intensities $I_{\text{eu}}^{\text{cor}}(S)$ for $\text{Na}_2\text{O}-\text{SiO}_2$ glasses in electron units.

It does not seem that the difference of the corrected intensity $I_{eu}^{cor}(S)$ between 20mole%Na₂O—SiO₂ and 40mole%Na₂O—SiO₂ glasses will be recognized at higher values of S . Thus it can be considered that extreme short range correlation on the structure such as well-defined tetrahedral SiO₄ does not change with the change of Na₂O content in glass, as estimated from the property of Fourier transform. On the other hand, it will be realized that from the clear change of the corrected intensities $I_{eu}^{cor}(S)$ at smaller values of S , the distribution among tetrahedral SiO₄ alters when the amount of Na₂O increases. The results coincides with those found by Warren and Biscoe.⁵⁾

4.1.1 Reliability of the RDF

The RDF calculated from Eq. (12) are shown in Fig. 3.

We must carefully examine whether the obtained RDF have a fully physical meaning or not, because they will usually include some false phenomena originating from experimental errors and unsuitable treatments of experimental data. Some problems arising from the errors were examined.

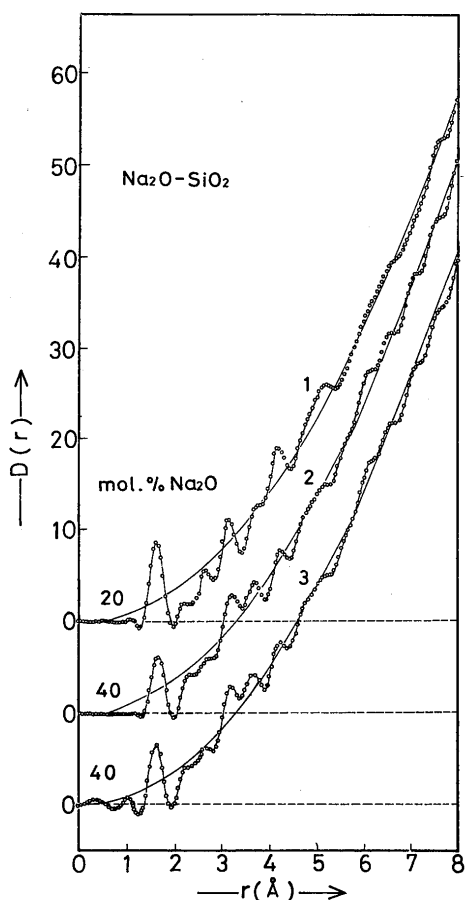


Fig. 3 Radial distribution functions for Na₂O—SiO₂ glasses. 1, 2: corrected $D(r)$ 3: uncorrected $D(r)$.

A. Ghosts in the Region below the First Peak of the RDF

The theoretical $\rho(r)$ must be zero in the region below the first peak in the RDF, because the atoms can not approach one another inside of the atomic diameter.

However, general shift to positive or negative density in this region is originated due to the errors in background subtraction, fluorescent correction, absorption correction, bulk density value,¹⁹⁾ atomic scattering factors or normalization.^{20),21)} The spurious oscillations are clearly recognized in the region below the first peak in the uncorrected RDF of 40mole%Na₂O—SiO₂ glass as shown in Fig.3. Background subtraction, fluorescent and absorption correction can regard negligible in this study. And then, the measured bulk densities showed good coincidence with the previous studies.^{22), 23)}

It can be assumed that the effect of the wrong normalization constant by the use of incorrect Compton scattering might cause the oscillations. Especially in the case of amorphous materials composed of low atomic number, Compton scattering becomes remarkably than coherent scattering at larger values of S , while the difference of the wavelength between Compton scattering and selected value from the monochromator correction increases. For these reasons, Compton scattering falls above a scattering angle by using the monochromator. In order to eliminate the normalization error and also obtain the accurate reduced intensity $Si(S)$, the correction of Compton scattering should be performed.

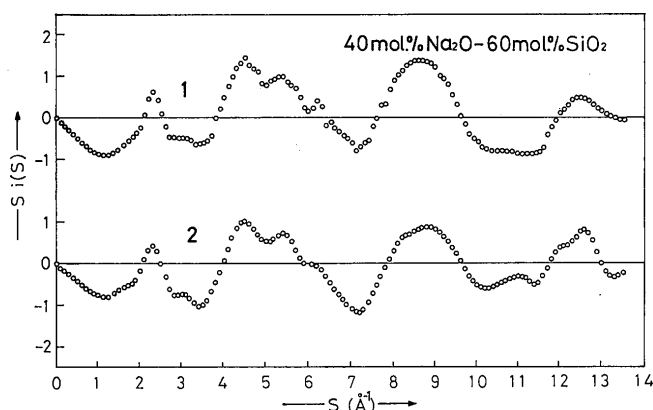


Fig. 4 Reduced intensities $Si(S)$ for 40mole%Na₂O—SiO₂ glass. 1: uncorrected $Si(S)$, 2: corrected $Si(S)$.

Since the spurious oscillations occur only at small values of r , they can be removed by repeated Fourier transform.^{20),24)} Figure. 4 shows the uncorrected and corrected reduced intensity $Si(S)$ of 40mole%Na₂O—SiO₂ glass. Furthermore, the corrected RDF shown in Fig. 3 is recalculated with the use of the corrected reduced

intensity $S_i(S)$. The difference between the uncorrected and corrected RDF can not be recognized except in the lower region than first peak.

B. Termination Effect

The error originating from the termination effect, which means the cutting-effect of integration until S_{max} as shown in Eq. (12), is a case of the serious ghosts appearing in RDF. The termination error introduces the extraneous oscillations in RDF, primarily in the vicinity of the first peak.²⁰⁾ Kaplow, Rowe and Averbach²⁵⁾ suggested that the reduced intensity $S_i(S)$ must be extended to a value of $S=2S_{max}$ in order to eliminate the termination error in RDF. The influence of the termination effect is shown in Figs.5 and 6, in which the RDF and reduced radial density functions are shown for a series of S_{max} , and also the result computed with Kaplow's method ($2S_{max}=27.0\text{\AA}^{-1}$) is shown. As is evident from the figures, it is understood that the structural resolution of RDF is also governed by S_{max} .

However, in order to reduce the spurious oscillations due to termination effect, the application of convergence factor has often been tried.²⁶⁾ A convergence factor of the form $\exp(-\alpha S^2)^{26)}$ is most commonly applied to $S_i(S)$ before the use of Fourier transform by Eq.(12). On the other hand, by Lorch¹²⁾ and Leadbetter and Wright¹⁴⁾ a convergence factor of the form $\sin(\pi S/S_{max})/(\pi S/S_{max})$

has been used. Comparison of the reduced radial density functions when used various convergence factors are shown in Fig.7. It will be realized that the use of the convergence factors broadens the individual peaks of RDF. Therefore, the correction with convergence factors does not bring any essential improvement to the result. On the contrary, Kaplow's method seems to be superior.

4.1.2 Results of $\text{Na}_2\text{-SiO}_2$ Glasses

In the various crystalline silicates, each silicon atom is tetrahedrally surrounded by four oxygen atoms with a Si-O distance of about $1.54\sim 1.62\text{\AA}$, an O-O distance of about $2.52\sim 2.63\text{\AA}$, and a Si-Si distance of about $3.08\sim 3.10\text{\AA}$.^{27),28)} With this information, first peak at the RDF of Fig.3, occurring at $r=1.62\text{\AA}$, can be identified as a Si-O peak within the experimental error. The third peak at $r=2.62\text{\AA}$ can be identified as an O-O peak. From the geometry of tetrahedron, the ratio of the these values becomes to be $2.62/1.62\approx\sqrt{8/3}$. The area under the first peak of the RDF represents the coordination number connected to oxygen and silicon atoms. By means of the method reported in a previous paper²⁹⁾, the average coordination number of nearest neighbor oxygen atoms about a silicon atom becomes about 3.9 at 20mole% $\text{Na}_2\text{O-SiO}_2$ glass, and about 3.5 at 40mole% $\text{Na}_2\text{O-SiO}_2$ glass.

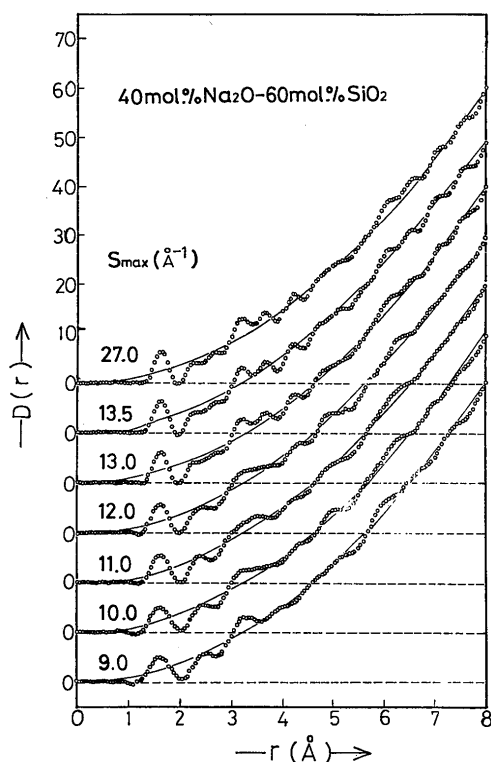


Fig. 5 Termination effect on corrected radial distribution functions for 40mole% $\text{Na}_2\text{O-SiO}_2$ glass.

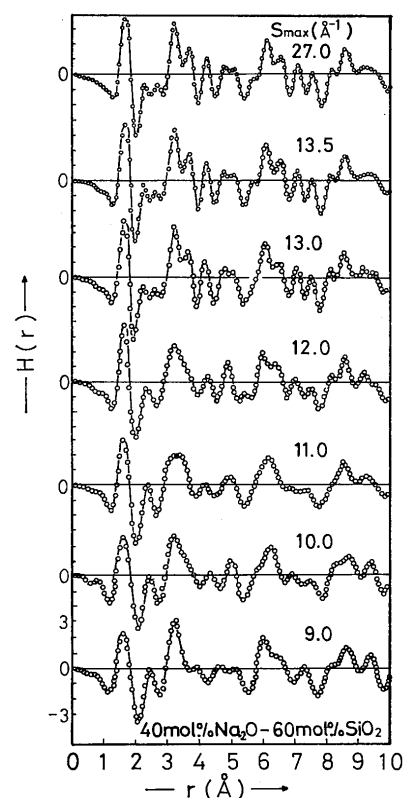


Fig. 6 Termination effect on corrected reduced radial density functions for 40mole% $\text{Na}_2\text{O-SiO}_2$ glass.

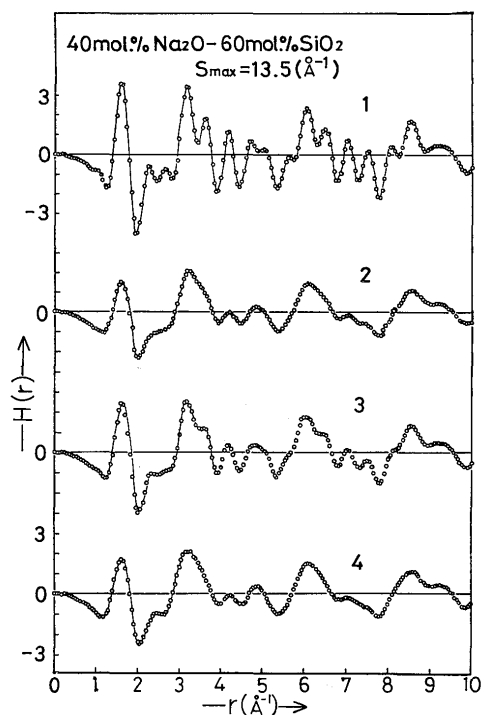
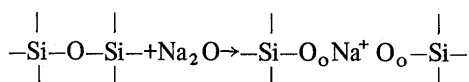


Fig. 7 Corrected reduced radial density functions for 40mole% $\text{Na}_2\text{O}-\text{SiO}_2$ glass employing convergence factor. Form of convergence factor 1: uncorrection, 2, 3: $\exp(-\alpha S^2)$, chosen such that $\exp(-\alpha S_{\text{max}}^2) = 0.1$ and $\alpha^2 S_{\text{max}}^2 = 1.0$, 4: $\sin(\pi S/S_{\text{max}})/(\pi S/S_{\text{max}})$.

However, Warren and Biscoe⁵⁾ have postulated that the introduction of Na_2O leads to the rupture of $\text{Si}-\text{O}$ bonds to accommodate the supplementary oxygen ions according to the scheme:



with the formation of pair of non-bridging O_o ions bearing $-1/2$ charge electrostatically compensated by the Na^+ ions, which are placed in various holes in the irregular silicon-oxygen network. Therefore, the second peak corresponds obviously to $\text{Na}-\text{O}$ contact distance ($r_{\text{Na}^+} + r_{\text{O}^{2-}} = 2.37\text{\AA}$, r_{Na^+} , $r_{\text{O}^{2-}}$: the ionic radii of Na^+ , O^{2-}).

The strong fourth peak at about 3.10\AA in the case of 20mole% $\text{Na}_2\text{O}-\text{SiO}_2$ glass and about 3.15\AA in the case of 40mole% $\text{Na}_2\text{O}-\text{SiO}_2$ glass is attributed to the first $\text{Si}-\text{Si}$ peak, indicating average $\text{Si}-\text{O}-\text{Si}$ angle of about $146^\circ - 153^\circ$. By increasing Na_2O content, the fourth peak due to $\text{Si}-\text{Si}$ pairs shifts slightly to small value of r , which is related to rupture of silicon oxygen network. This agrees qualitatively with the result of Waseda.⁹⁾

Above the value of $r=3.5\text{\AA}$, the difference of the shape of RDF between 20mole% $\text{Na}_2\text{O}-\text{SiO}_2$ and 40mole% $\text{Na}_2\text{O}-\text{SiO}_2$ glasses can be clearly recognized. It is

shown that the distribution of tetrahedral groups and Na^+ in glass depends upon Na_2O content.

4.2 GeO_2 Glass

The pair correlation function $G(r)$ is shown in Fig.8. In Table 2, the interatomic distances and the coordination numbers calculated from the result are tabulated. The result is consistent with tetrahedral coordinated oxygen atoms around a germanium atom with an average $\text{Ge}-\text{O}$ distance of 1.74\AA , indicating an average $\text{Ge}-\text{O}-\text{Ge}$ angle of about 131° . The strong peak in $G(r)$ at about 3.16\AA can be attributed to $\text{Ge}-\text{Ge}$ distance, and it agrees well with the result determined with X-ray studies by Zarzycki¹¹⁾ and Leadbetter and Wright¹⁴⁾. Whereas Lorch¹²⁾ and Ferguson and Hass¹³⁾ presented the value about 3.45\AA with neutron diffraction studies. Leadbetter and Wright¹⁴⁾ denied the $\text{Ge}-\text{Ge}$ distance obtained with neutron diffraction from their X-ray diffraction and calculation with quasi-crystalline model. Since the structure of GeO_2 glass is very similar to SiO_2 glass, it can be estimated that an average $\text{Ge}-\text{O}-\text{Ge}$ angle is analogy to an average $\text{Si}-\text{O}-\text{Si}$ angle. Warren and Mozzi⁶⁾ have reported that the $\text{Si}-\text{O}-\text{Si}$ angle can change with some distribution ranging from 120 to 180° with a maximum possibility at 144° . Therefore, it can be considered that the $\text{Ge}-\text{Ge}$ distance determined with X-ray study is reliable. The radial density $\rho(r)$ converges on the macroscopic density above 9\AA . It can be considered that a small peak at about 2.55\AA in $G(r)$ is mainly originated from the normalization error and termination error. The explanation as to individual peak above 3.5\AA necessitates the more precise experiment.

From the above mentioned point of view, it can be anticipated that RDF is useful method for obtaining the structural information of an amorphous material.

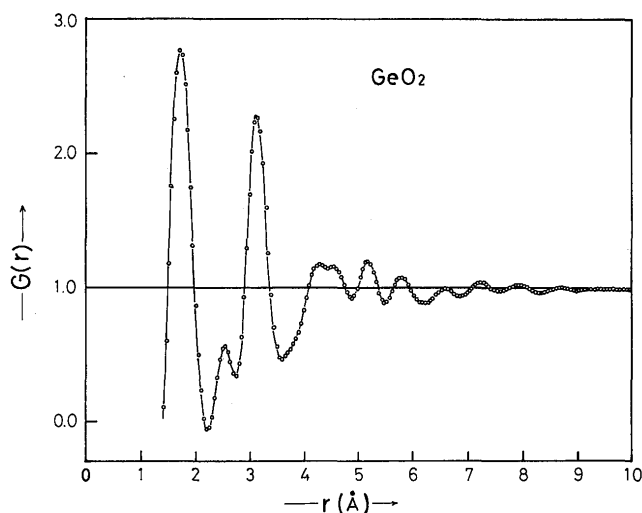


Fig. 8 Pair correlation function for GeO_2 glass.

Table 2. Interatomic distances and coordination numbers for GeO₂ glass.

| Peak Atoms | Interatomic Distance (Å) | | | | | Coordination No. | |
|------------|--------------------------|------------------|-----------------|--------------------------|--------------------------|------------------|----------|
| | Present Work (X-ray) | Zarzycki (X-ray) | Lorch (neutron) | Ferguson et al (neutron) | Leadbetter et al (X-ray) | Expected | Measured |
| | | | | | | | |
| 1 Ge-O | 1.74 | 1.70 | 1.72 | 1.73 | 1.74 | 4 | 3.9 |
| 2 O-O | | | 2.85 | 2.85 | | | |
| 3 Ge-Ge | 3.16 | 3.15 | 2.45 | 3.45 | 3.18 | | |

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