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Structural analysis of sodium silicate glasses containing TiO_2 by pulsed neutron scattering

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By the use of the time-of-flight pulsed neutron total-scattering spectrometer HIT at the Japanese National Laboratory for High Energy Physics, measurement of structure factors $S(Q)$ for glasses of type $10Na_2O \cdot (90 - x)SiO_2 \cdot xTiO_2$ ($x = 0$, 5 and 20 mol%) was made over a wide range of scattering vectors up to Q ($=4\pi \sin \theta/\lambda$) $\sim$ 500 nm^{-1}. High-resolution real-space information was obtained from the Fourier transform of $S(Q)$. The influence of TiO_2 on the nearest-neighbour Si–O bond length of the silicate anions existing in the glass samples studied is different from that of alkali oxides such as Na_2O. It is concluded that most of the Ti^{4+} ions predominantly substitute for Si^{4+} ions in their tetrahedrally coordinated sites, leading to the formation of TiO_6 octahedra.

1. Introduction

It is well known that silicate glasses containing TiO_2 exhibit several interesting physical or chemical properties, and that they have an extremely wide glass-forming composition range. Some of these glasses have a low thermal expansion coefficient. TiO_2 is also considered to be an amphoteric component, that is it behaves as an acidic or basic component in the silicate glass according to the composition.

Recently, many investigators have been studying such anomalous behaviour by spectroscopic and diffraction techniques. X-ray fluorescence spectra of Si$K\beta$ and Ti$K\beta$ for alkali silicate glasses containing TiO_2 were measured and the chemical shifts of the observed bands were discussed [1, 2]. Raman and infrared emission spectroscopic studies [3–5] recorded the characteristic bands caused by the addition of TiO_2, but detailed analyses were left for the future. Wong and co-workers [6, 7] investigated titania-doped silica glasses by techniques for extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES). This revealed the structural details of these glasses. On the other hand, investigations by X-ray [8] and neutron diffraction methods [9], from which direct information on

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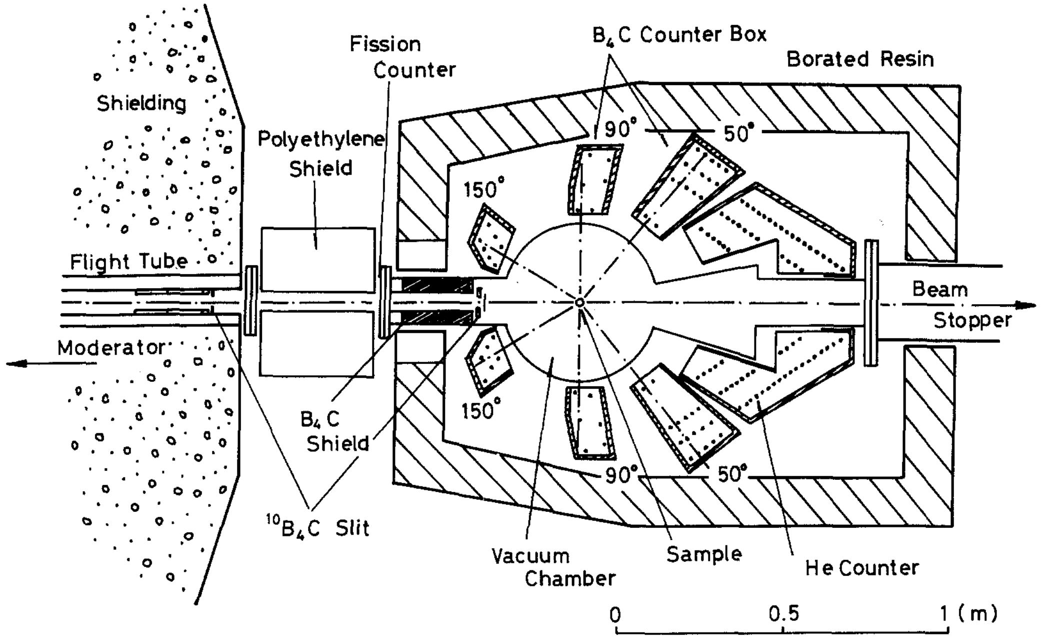

Figure 1 Schematic diagram of the time-of-flight pulsed neutron total-scattering spectrometer HIT (High Intensity Total Scattering Spectrometer) at the National Laboratory for High Energy Physics.

the structure can be obtained, have been attempted to elucidate the structure of silicate glasses containing TiO_2. Unfortunately, detailed structural analyses were not made.

Some authors have performed time-of-flight (TOF) pulsed neutron diffraction measurements with short wavelengths, using neutrons produced by a LINAC in order to reveal the structures of various amorphous materials [10–14]. This method is a very powerful technique to obtain high-resolution real-space information concerning the short-range structure of amorphous materials, because the structure factor $S(Q)$ can be easily measured up to a very high scattering vector Q ($=4\pi \sin\theta/\lambda$, where 2θ = scattering angle and λ = neutron wavelength) such as 300 to 500 nm^{-1}. In this study, TOF pulsed neutron diffraction measurements were made in order to elucidate the structure of sodium silicate glasses containing TiO_2, and the role of the titanium component in these glasses is discussed.

2. Experimental procedure

Analytical-reagent grade powders of Na_2CO_3, SiO_2 and TiO_2 were used as the starting materials to obtain three glass samples with composition $10Na_2O \cdot (90 - x)SiO_2 \cdot xTiO_2$ (where $x = 0, 5$ and 20 mol %). Mixtures of about 10 g were melted in a platinum crucible by the use of an SiC electric furnace. The melting temperature and time were 1600° C and 2 h. The melts were quenched by dipping the platinum crucible partially in cold water. The densities of the glasses obtained were measured by the Archimedes method with water as the reference liquid.

The measurement of $S(Q)$ was made by using the TOF pulsed neutron total-scattering spectrometer HIT (High Intensity Total Scattering Spectrometer) at the National Laboratory for High Energy Physics[†]. Fig. 1 shows a schematic view of this spectrometer. The neutron source is installed at the 500 MeV proton booster synchrotron. The glass sample was kept in a vacuum chamber to protect it from hygroscopic reactions and also to eliminate the background due to air scattering. The detailed data procedures for converting observed TOF spectra to $S(Q)$ have been described in previous papers [11, 12].

3. Results

Fig. 2 shows $S(Q)$ curves obtained for the three glass samples. As shown in this figure, the

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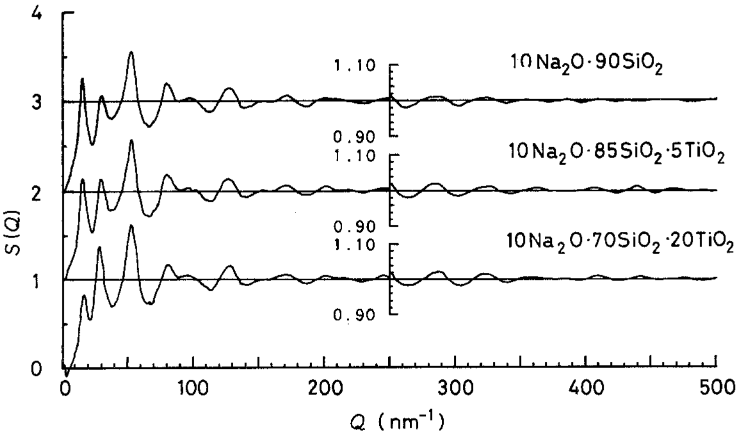

Figure 2 Structure factors $S(Q)$ of glasses of type $10Na_2O \cdot (90 - x)SiO_2 \cdot xTiO_2$ ($x = 0$, 5 and 20 mol %).

measurements were made with fair accuracy to high values of Q, and also the oscillatory behaviour of these $S(Q)$ curves was observed up to a value of Q close to 500 nm^{-1}. Thus, compared with X-ray diffraction methods, high-resolution observation of short-range structure such as the bond lengths of nearest-neighbour atomic pairs Si–O, O–O and Ti–O can be performed by this TOF pulsed neutron scattering method. The coherent neutron scattering amplitudes used for atoms of sodium, silicon, titanium and oxygen were 0.36, 0.42, -0.34 and 0.58×10^{-14}m, respectively [15]. The radial distribution function (RDF) $D(r)$ was calculated from experimental values of $S(Q)$ with the following equation:

$$D(r) = 4\pi r^2 \varrho_0 + \frac{2r}{\pi} \int_0^{Q_{\max}} [Q\,S(Q) - 1] \sin(rQ)\, \mathrm{d}Q \qquad (1)$$

where ϱ_0 is the average atomic number density of the glass sample, and $Q_{\max}$ the maximum value of Q reached in this work. The RDF curves obtained are represented in Fig. 3. The peaks near 0.16 nm are due to the nearest-neighbour Si–O pair. The second peaks with negative sign observed near 0.19 nm in the curves for glasses $10Na_2O \cdot 85SiO_2 \cdot 5TiO_2$ and $10Na_2O \cdot 70SiO_2 \cdot 20TiO_2$ are due to the nearest-neighbour Ti–O pair, because the scattering amplitude of the titanium nucleus is negative ($b_{Ti} = -0.34 \times 10^{-14}$m). The peaks near 0.26 nm are due to the nearest neighbour O–O pair.

Fig. 4 shows the effect of truncating the $S(Q)$ RDF Fourier transformation on the resolution of the nearest-neighbour Si–O peak position, in the RDF curve of a $10Na_2O \cdot 70SiO_2 \cdot 20TiO_2$ glass. As shown in this figure, the value of bond length $l_{Si\text{–}O}$ is almost unchanged at value $Q_{\max} = 300$ nm^{-1}. The value $Q_{\max} = 500$ nm^{-1} was therefore used in this work. The coordination numbers of oxygen atoms around a silicon atom ($N_{Si\text{–}O}$), and of silicon and oxygen atoms around an oxygen atom ($N_{Si\text{–}O}$ and $N_{O\text{–}O}$) are calculated from the peak areas using the

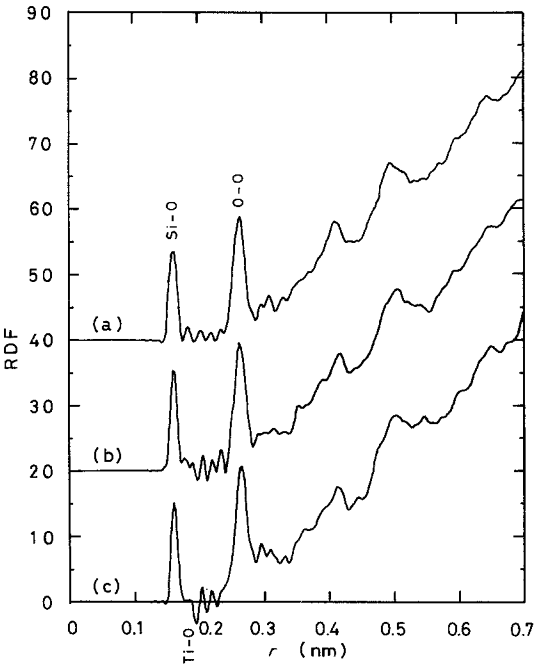

Figure 3 Radial distribution functions $D(r)$ (RDF) of glasses of type $10Na_2O \cdot (90 - x)SiO_2 \cdot xTiO_2$ ($x = 0$, 5 and 20 mol %); (a) $10Na_2O \cdot 90SiO_2$, (b) $10Na_2O \cdot 85SiO_2 \cdot 5TiO_2$, (c) $10Na_2O \cdot 70SiO_2 \cdot 20TiO_2$. Fourier transformation of $S(Q)$ to obtain the RDF is truncated at $Q_{\max} = 500$ nm^{-1}.

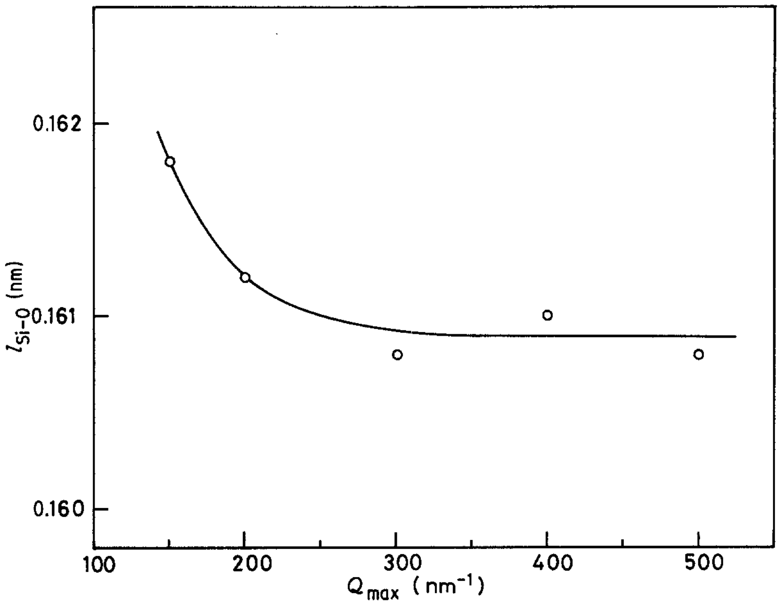

Figure 4 Q_{max} dependence of the Si–O bond length (l_{Si-O}) in $10Na_2O \cdot 70SiO_2 \cdot 20TiO_2$.

following equations:

$$N_{Si-O} = A_{Si-O} \frac{\langle b \rangle^2}{b_{Si} b_O} \frac{1}{2X_{Si}} \quad (2)$$

$$N_{O-Si} = A_{O-Si} \frac{\langle b \rangle^2}{b_O b_{Si}} \frac{1}{2X_O} \quad (3)$$

$$N_{O-O} = A_{O-O} \frac{\langle b \rangle^2}{b_O^2} \frac{1}{X_O} \quad (4)$$

where A_{i-j} is the peak area of the i–j pair, b_i and X_i are the neutron scattering amplitude and atomic fraction of atom i, and

$$\langle b \rangle = \sum_i X_i b_i \quad (5)$$

Table I lists the distances and the coordination numbers of the nearest neighbour pairs Si–O and O–O, and the mean bond angle at the silicon atom (O–Si–O) for the three samples of glass. As shown in this table, values obtained for N_{Si-O} are near to four. The distance ratios l_{O-O}/l_{Si-O} ($=0.2636/0.1611$) are nearly equal to the value of $(8/3)^{\frac{1}{2}}$ obtained from the geometry of a tetrahedron. It can be deduced from these experimental data that the fundamental structural unit in these glass samples is an SiO_4 tetrahedron. It is found that the distance l_{Si-O} decreases slightly with increasing TiO_2 content.

4. Discussion

It is known that the average distance of all the nearest-neighbour Si–O bond lengths tends to increase with the degree of depolymerization of silicate anions, due to the creation of $Si-O^-$ non-bridging bonds when an alkali oxide such as Na_2O is introduced into an SiO_2 glass and/or crystal. Suzuki and co-workers have reported that the distance l_{Si-O} is 0.1613 nm for SiO_2 glass [11], 0.1631 nm for $Na_2O \cdot 2SiO_2$ glass [11] and 0.164 nm for $Na_2O \cdot SiO_2$ glass [14] by the same TOF pulsed neutron diffraction method. In the case of silicate crystals [16–18], the average distance l_{Si-O} for $Na_2O \cdot SiO_2$ crystals (0.164 nm) is

TABLE I Interatomic distances l and coordination number N for Si–O and O–O pairs. O–Si–O is the mean bond angle at the Si atom

Sample	Si–O			O–O (nearest neighbour)		O–O (second-nearest neighbour)	O–Si–O (deg)
	l(nm)	N_{Si-O}	N_{O-Si}	l(nm)	N_{O-O}	l(nm)	
$10Na_2O \cdot 90SiO_2$	0.1611	3.71	1.76	0.2636	5.17	0.410	109.82
$10Na_2O \cdot 85SiO_2 \cdot 5TiO_2$	0.1610	3.50	1.48	0.2628	5.39	0.417	109.38
$10Na_2O \cdot 70SiO_2 \cdot 20TiO_2$	0.1607	3.53	1.30	0.2640	4.78	0.414	110.49

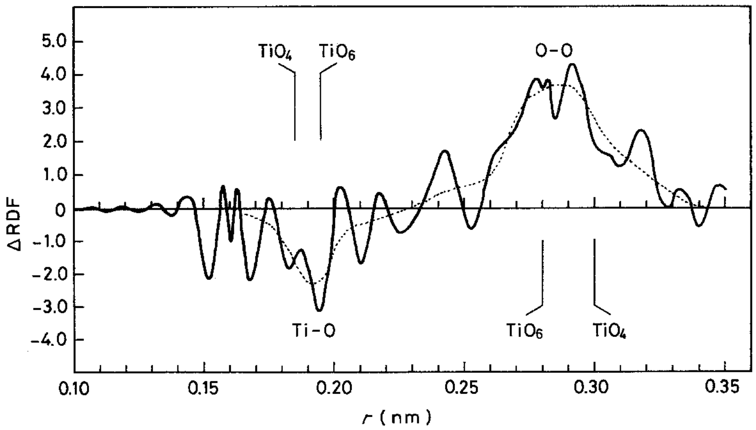

Figure 5 Difference function ΔRDF between $10Na_2O \cdot 90SiO_2$ and $10Na_2O \cdot 70SiO_2 \cdot 20TiO_2$ glasses.

larger than that for crystals of α-$Na_2O \cdot 2SiO_2$ (0.162 nm) and β-$Na_2O \cdot 2SiO_2$ (0.163 nm). From Si$K\beta$ X-ray fluorescence measurement of glasses of type Na_2O–SiO_2–TiO_2 and K_2O–SiO_2–TiO_2, Sakka and Hotta [1] suggested that TiO_2 has the role of a modifier component which is similar to Na_2O. However, as shown in Table I, the calculated distance l_{Si-O} remains almost unchanged as the TiO_2 content increases. It is therefore considered that the influence of TiO_2 on the silicate anions existing in the glass samples studied is different from that of Na_2O.

As shown in Table I, the average coordination number N_{O-O} of the nearest-neighbour O–O pairs decreases with increasing TiO_2 content. This result is interpreted in the following manner: (a) Ti^{4+} ions substitute for Si^{4+} ions in silicate anions, and consequently form tetrahedral TiO_4 in the glasses studied; and (b) Ti^{4+} ions occupy interstitial sites such as the octahedral hole. If solution of TiO_2 in silicate glass results in the formation of TiO_6 octahedra, each oxygen from TiO_2 breaks a bridging oxygen bond of the original silicate network structure by the same mechanism as that for alkali oxides. The influence of TiO_2 on the silicate glasses studied is, however, different from that of the alkali oxides already mentioned. Moreover, the value obtained for the mean bond angle O–Si–O increases with increasing TiO_2 content, and this implies distortion of the SiO_4 tetrahedra. It is therefore concluded that most of the Ti^{4+} ions predominantly substitute for Si^{4+} ions in their tetrahedrally coordinated sites, leading to the formation of TiO_6 octahedra.

From Raman spectroscopy, Furukawa and White [3] and Mysen *et al.* [4] noted that titanium has four-fold coordination in alkali silicate glasses. The peak near 0.41 nm in RDF curves is due to the second-nearest neighbour O–O pair. Fig. 3 shows that the interatomic distance for this pair also increases with increasing TiO_2 content. This seems to be caused by a variation of the mean bond angle Si–O–Si, which indicates a three-dimensional configuration of linked SiO_4 units [19]. Greegor *et al.* [7] reported from EXAFS measurement of TiO_2–SiO_2 glasses that the value of the angle Si–O–Si in this glassy system is slightly greater than in SiO_2 glass, owing to the formation of Ti–O–Si bonds between tetrahedral TiO_4 and SiO_4. In the case of Na_2O–TiO_2–SiO_2 glasses, it is apparent that substitutional Ti^{4+} ions are accommodated within the silicate anions by forcing a change in bond angles.

As shown in Fig. 3, a negative peak for the nearest-neighbour Ti–O pair appears near 0.19 nm in the RDF curve because of the negative nuclear scattering amplitude of titanium. The radial distribution difference function (ΔRDF) can be obtained by subtracting the RDF curve of $10Na_2O \cdot 90SiO_2$ from that of $10Na_2O \cdot 70SiO_2 \cdot 20TiO_2$. This ΔRDF curve is shown in Fig. 5. The negative peak near 0.19 nm is considered to consist of two peaks: one near 0.185 nm due to the Ti–O pair of TiO_4 tetrahedra, and another near 0.195 nm due to the Ti–O pair of TiO_6 octahedra. Needless to say the proportion of TiO_6 octahedra is relatively less than that of TiO_4 tetrahedra, as shown in this figure.

The geometries of tetrahedral TiO_4 and octahedral TiO_6 are shown in Fig. 6. The edge-distance l_{O-O} of a TiO_4 tetrahedron l_{O-O} is 0.3 nm when the distance l_{Ti-O} is 0.185 nm, while the distance l_{O-O} of a TiO_6 octahedron with

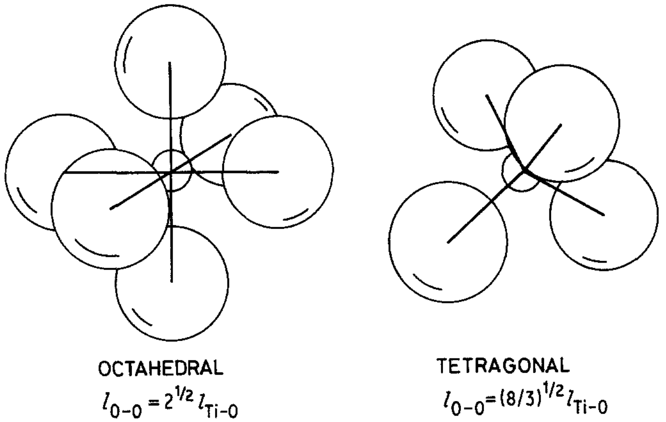

Figure 6 The geometries of tetrahedral TiO_4 and octahedral TiO_6.

l_{Ti-O} = 0.195 nm is 0.28 nm. It can therefore be estimated that the broad positive band from 0.25 nm to 0.34 nm in the ΔRDF curve is due to the convolution of these two O–O peaks. If all of the Ti^{4+} ions are in six-fold coordination in alkali silicate glasses, as reported by Kusabiraki and Shiraishi [5] from infrared emission measurements, the distance l_{O-O} of octahedral TiO_6 with l_{Ti-O} = 0.19 nm, which is at a negative maximum in the ΔRDF curve, is anticipated to be 0.27 nm. With this consideration, it is difficult to explain the right-hand side of this positive band from 0.25 nm to 0.34 nm in the RDF curve. It is, therefore, concluded that most of the Ti^{4+} ions predominantly substitute for Si^{4+} ions in their tetrahedrally coordinated sites, while the fraction of Ti^{4+} ions in octahedral coordination is small relative to that of tetrahedral TiO_4. This result is in agreement with EXAFS/XANES investigations on TiO_2–SiO_2 glasses [6, 7].

5. Conclusions

TOF pulsed neutron diffraction measurements have been made in order to elucidate the structure of sodium silicate glasses containing titania, and high-resolution real-space information concerning short-range structure has been obtained. The interpretation of these results has led to the following conclusions: (a) the influence of TiO_2 on silicate anions in the glass samples studied is different from that of alkali oxides such as Na_2O; (b) most of the Ti^{4+} ions predominantly substitute for Si^{4+} ions in their tetrahedrally coordinated sites, leading to the formation of TiO_6 octahedra; and (c) Ti^{4+} ions in octahedral coordination coexist with tetrahedral TiO_4 in these glasses, but the proportion is small relative to that of tetrahedral TiO_4.

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