Coordination Structure of Bi atoms in Li₂O–Bi₂O₃–B₂O₃ Glasses by X-ray Diffraction

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The coordination structure around Bi atoms has been studied in Li₂O–Bi₂O₃–B₂O₃ glasses by X-ray diffraction method. It was found that Bi atoms were coordinated by five or six oxygen atoms. The number of Bi atoms around a Bi atom through Bi–O–Bi bonds increased with an increase in Bi/O ratio. It was inferred that BiO₅ polyhedra were clumped in the glasses, although BiO₆ polyhedra were more clumped in Li₂O–Bi₂O₃–B₂O₃ glasses than in Bi₂O₃–B₂O₃ glasses.

Key-words : Glass structure, Li₂O–Bi₂O₃–B₂O₃, Bi atoms, X-ray diffraction

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1. Introduction

Bismuth oxide is an conditional glass former from the viewpoint of glass-forming ability¹¹ and therefore bismuth containing systems have wide glass forming regions.²,³ Since bismuth oxide is a component of high refractive index and low deformation temperature, the addition of bismuth oxide to glass-forming systems increases the refractive index and reduces glass deformation temperature.⁵,⁶ Therefore, bismuth containing borate and phosphate glasses are utilized for the precision molding.⁵,⁷ However, bismuth containing glass exhibits yellow color due to Bi³⁺ ions, depending on composition.⁵–⁸ Therefore, it is important to study the coordination structure of Bi atoms in bismuth containing glasses for understanding the correlation between the structure and color of glass.¹¹ Although the structure of bismuth containing glasses has been studied extensively by Raman scattering and Infrared absorption spectroscopies, the coordination structure around Bi atoms, especially, the middle range structure around Bi atoms, has not been well-understood.¹¹,¹² On the other hand, some researchers have studied the structure of bismuth containing glass by X-ray or neutron diffraction method, which gives direct information on the coordination structure around Bi atoms. Miyaji et al. have shown that Bi atoms form BiO₅ and/or BiO₆ polyhedra and that they are three- and four-coordinated oxygen atoms are present in Bi₂O₃–Ga₂O₃ glasses.¹³ Stone et al. and Nanba et al. have mainly reported the structure of boron atoms in the diffraction study on Bi₂O₃–B₂O₃ glasses.¹⁴,¹⁵ In the Li₂O–Bi₂O₃ glasses, it has been shown that the structure of glass can be expressed by Bi₂O₄ crystal model with atomic defects.¹⁶ In addition, Nanba et al. have shown that BiO₆ polyhedra form layered structure in Bi₂O₃–SiO₂ glass.¹¹ This study suggests that the diffraction method is suitable to elucidate the middle range structure in bismuth containing glasses. The structure of Li₂O–Bi₂O₃–B₂O₃ glass has not been studied by diffraction method, although Li₂O–Bi₂O₃–B₂O₃ system has a wide glass formation region. In the present study, the coordination structure around Bi atoms has been studied by X-ray diffraction method in Li₂O–Bi₂O₃–B₂O₃ glasses, and since the X-ray scattering factor of Bi atom is much greater than those of Li, B and O atoms.

2. Experimental procedure

Li₂O–Bi₂O₃–B₂O₃ and Bi₂O₃–B₂O₃ glasses shown in Table 1 were prepared by a conventional melting method. Appropriate mixtures of Li₂CO₃ (Kojundo Chemical Lab., 99.9%), Bi₂O₃ (Wako Pure Chemical Ind., 99.9%) and B₂O₃ (Kanto Chemical, 95%) were melted in a platinum crucible at 900–1000°C for 1 h. The melts were poured onto a carbon mold and were annealed around glass transition temperature to form glass plates with a thickness of about 2 mm.

The glass plates were polished so that the absorption coefficient of glass plates for X-rays was less than about
unity. The density was measured by the Archimedes method. The error of density measurement was within 0.003 g cm$^{-3}$. X-ray diffraction measurement was carried out in the region of $Q$ from 0.16 to 25.00 Å$^{-1}$ ($Q = 4\pi\sin\theta/\lambda$, $\lambda$: X-ray wavelength and $2\theta$: diffraction angle) by the transmission mode using a monochromatized X-rays with an energy of 61.7 eV as an incident X-ray at SPring-8 BL04B2 high-energy X-ray diffraction facility. The X-ray diffraction intensity was reduced to total interference function, multiplied by $Q$ and Loach function, and Fourier-transformed into differential correlation function, $D(r)$, by the conventional method. Measurement and analytical methods have been described elsewhere in detail.$^{17,18}$

The reverse Monte Carlo simulation was carried out for the interference function curve in the region of $Q$ from 0.2 to 16.3 Å$^{-1}$ using RMC_POT$^{19}$ under the following constraints: $r_B-B > 2.3$ Å, $r_{B-Bi} > 2.8$ Å, $r_{B-Li} > 2.5$ Å, $r_{B-O} > 1.25$ Å, $r_{Bi-Bi} > 3.38$ Å, $r_{Bi-Li} > 2.8$ Å, $r_{Bi-O} > 2.0$ Å, $r_{Li-Li} > 3.1$ Å, $r_{Li-O} > 1.8$ Å, $r_{O-O} > 2.2$ Å, $n^B_O \geq 3$, $n^B_B \leq 2$ and $n^B_{Li} = 4$, where $n$ represent the coordination number of atomic pairs. The subscripts subsequent to $r$ represent the atomic pairs and the superscripts and subscripts subsequent to $r$ represent the central atoms and the co-ordinating atoms, respectively. These constraints were determined by reference to the crystal structures.$^{20-23}$ The cell size and the number of Bi atoms in a cell were 33 Å and 80 Bi atoms at the minimum, respectively, for simulation. The coordination number of Bi atoms, the number of Bi-O-Bi linkages, Pielou’s index of non-randomness$^{29-31}$ for Bi atoms were calculated from the atomic position obtained by reverse Monte Carlo simulation.

### 3. Results

All the glasses used in the present study were transparent and were colorless or yellow. The density of glasses is shown in Table 1. **Figures 1 and 2** depict the interference function curves and $D(r)$ curves of the glasses obtained experimentally. Small angle scattering was clearly observed in the ternary glasses, as shown in Fig. 1. The difference between the interference function curves obtained by Reverse Monte Carlo simulation and those obtained experimentally are displayed in Fig. 1. It can be seen that both the curves agree well with each other.

### 4. Discussion

The assignment of peaks in the $D(r)$ curves of the glasses was carried out from the comparison with the partial pair correlation function curves, $g(r)$, obtained from the simulation, taking into account the atomic scattering factor. A peak at about 1.4 Å was assigned to the nearest neighboring B–O pair in 7005, 7010, 7030 and 6020 glasses. A peak and a shoulder at about 2.2 Å was assigned to Bi–O pair in all the glasses. A peak around 2.35 Å was

### Table 1. Composition, density $CN_{Bi-O}$, $BV_{g}$, and $N_{Bi-O-Bi}$ of glasses

| Sample No. | Composition mol % | Composition ratio | Density $g/cm^3$ | $CN_{Bi-O}$ | $BV_{g}$ | $N_{Bi-O-Bi}$ |
|------------|-------------------|------------------|----------------|-------------|--------|--------------|
| Li$_2$O   | Bi$_2$O$_3$ | B$_2$O$_3$ | Li:B:Bi:B | Li:Bi:O:B |
| 7005 | 25 | 5 | 70 | 0.040 | 2.865 | 5.0 | 3.0 | 0.7 |
| 7010 | 20 | 10 | 70 | 0.077 | 3.433 | 5.3 | 3.0 | 1.8 |
| 7030 | 0 | 30 | 70 | 0.200 | 5.342 | 5.5 | 3.2 | 5.5 |
| 6020 | 20 | 20 | 60 | 0.154 | 4.661 | 5.5 | 3.2 | 3.5 |
| 4040 | 20 | 40 | 40 | 0.308 | 6.341 | 5.9 | 3.2 | 5.5 |
| 3050 | 20 | 50 | 30 | 0.385 | 6.964 | 5.5 | 3.2 | 6.3 |
| 4060 | 0 | 60 | 40 | 0.400 | 7.449 | 6.3 | 3.4 | 7.8 |

$CN_{Bi-O}$: coordination number of Bi atom, $BV_g$: average of sum of bond valence of Bi atoms, $N_{Bi-O-Bi}$: the number of Bi atoms around a Bi atom linked through Bi–O–Bi linkages.

![Fig. 1. Interference function curves of Li$_2$O–Bi$_2$O$_3$–B$_2$O$_3$ and Bi$_2$O$_3$–B$_2$O$_3$ glasses.](image1.png)

![Fig. 2. Differential correlation function curves, $D(r)$, of Li$_2$O–Bi$_2$O$_3$–B$_2$O$_3$ and Bi$_2$O$_3$–B$_2$O$_3$ glasses.](image2.png)

**Figure 3** shows partial pair correlation function of Bi–Bi pair, $g(r)_{Bi-Bi}$ obtained by the simulation.
assigned to O–O pair in BO3 triangles and BO4 tetrahedra in 7005 and 7010 glasses. Peaks at about 2.9, 4.3 and 4.7 Å were assigned to O–O and B–O pairs in 7005 glass. A small shoulder at about 2.9 Å was assigned to Bi–O pair in the glasses other than 7005 and 7010 glasses. A peak at about 3.7 Å was assigned to B–O pair in 7005 glass and to Bi–Bi pair in the other glasses. Peaks and shoulders at about 6.5, 7.5, 8.5, 10.0, 10.5, 13.2 and 16.5 Å were assigned to Bi–Bi pairs in all the glasses.

The oxygen coordination number for Bi atoms obtained by RMC simulation ranged from 5 to 6, assuming that Bi–O bond length was not longer than 3 Å, as shown in Table 1. The average of the sum of bond valence, $BV_{av}$, of Bi atoms was calculated by dividing the summation of bond valence of all the Bi–O bonds by the number of Bi atoms. $BV_{av}$ was near the formal valence of Bi ions, namely three, in all the glasses, indicating the adequacy of the above-mentioned assumption.

The average number of Bi atoms around a Bi atom linked through the Bi–O–Bi linkages, $N_{Bi-O-Bi}$, in Li2O–Bi2O3–B2O3 glasses was calculated by dividing the summation of bond valence of Bi atoms, namely three, by $BV_{av}$.

Fig. 3. Pair correlation function curves of Bi–Bi pair, $g(r)_{Bi-Bi}$, in Li2O–Bi2O3–B2O3 and Bi2O3–B2O3 glasses.

Fig. 4. Average number of Bi atoms around a Bi atom linked through the Bi–O–Bi linkages, $N_{Bi-O-Bi}$, in Li2O–Bi2O3–B2O3 and Bi2O3–B2O3 glasses.

The Pielou’s index of non-randomness, $P_j$, was calculated for the distribution of Bi atoms in the glasses from Eq. (1),

$$P_j = \frac{4\pi \rho_{av}}{3} \sum_{i=1}^{n} l_{ij}^3$$

where $l_{ij}$, $n$ and $\rho_{av}$ represent the distance between randomly selected $i$th reference point and its $j$th-nearest neighboring Bi atoms, the number of reference points and the average atomic density of Bi, respectively. $P_1$ and $P_5$ were calculated to detect the non-randomness at the smallest scales, as well as at larger scales. Roughly speaking, $P_1$ and $P_5$ implies the average volume of the smallest spheres centered at reference points which include one and five atoms, respectively, normalized to the inverse of atomic density. The index was also estimated for the random distribution of Bi atoms under the constraint $r_{Bi-Bi} > 3.38$ Å by a Monte Carlo technique, for comparison. Figure 5 depicts $P_1$ and $P_5$ of the glasses, along with those of random distribution. Since $P_1$ and $P_5$ of the glasses were greater than those of random distribution beyond the 99% confidence limits, it was found that Bi atoms were clumped in the glasses. That is, BiO6 polyhedra gathered together through the formation of Bi–O–Bi linkages in these glasses.

The total interference function curves are compared with the partial interference function curves of Bi–Bi pair in Fig. 1. It was deduced, from the similarity between the total and partial interference curves in the region lower than 1 Å$^{-1}$, that the small-angle scattering was due to Bi–Bi pair. In order to elucidate the origin of small angle
scattering, the partial interference function of Bi–Bi pair was obtained from \( g(r)_{\text{Bi–Bi}} \) by the inverse Fourier transformation in the distance region from 0 to \( r_{\text{max}} \) and its average slope between \( Q = 0.2 \) and \( 1 \, \text{Å}^{-1} \), \( S_{\text{av}} \) was calculated according to Eq. (2). The negative value of \( S_{\text{av}} \) implies the occurrence of small angle scattering.

\[
S_{\text{av}} = K_{\text{Bi}}^{\text{eff}} \int_{0}^{r_{\text{max}}} 4\pi r^2 \rho_{\text{av}}[g(r)_{\text{Bi–Bi}} - 1] df(r) dr
\]

where \( K_{\text{Bi}}^{\text{eff}} \) represents the effective electron number. \( r_{\text{max}} \) to be dealt with was less than 15 Å in this discussion, since Debye function\(^{33} \) showed that the interference function curve had high value at \( Q = 0.2 \, \text{Å}^{-1} \) when \( r_{\text{max}} < \text{ca. 15 Å} \). The approximate equation of \( S_{\text{av}} \) for \( 3.3 \leq r_{\text{max}} \leq 15.6 \, \text{Å} \), Eq. (3), was obtained by modifying Eq. (2), since \( g(r)_{\text{Bi–Bi}} \) is zero in the region of \( 0 < r \leq 3.3 \, \text{Å} \) and the numerical calculation showed that \( f(r) \approx 0.3 \, r \) in the region of \( 0 < r \leq 3.3 \, \text{Å} \) and \( f(r) \approx 0.08 \, r - 1.25 \) in the region of \( 3.3 \leq r \leq 15.6 \, \text{Å} \).

\[
S_{\text{av(approx.)}} \approx \frac{0.08 \rho_{\text{av}} \cdot K_{\text{Bi}}^{\text{eff}}}{0.8} \left[ A(B - C) - \frac{1.25}{0.08} C \right] \quad (3),
\]

where \( r_1 = 3.3 \, \text{Å} \) \((1.25/(0.08 + 0.3))\). \( \frac{\pi r_1}{3} \) expresses that \( g(r)_{\text{Bi–Bi}} = 0 \) in the region of \( 0 < r \leq 3.3 \, \text{Å} \). The first term in \( B \) approaches \(-1/\rho_{\text{av}} \) as \( r_{\text{max}} \) approaches infinity, as a matter of course. Since \( B \) is the oscillating function and \( C \) is the average of \( B \), the first term in \( B \) represents the oscillation part of \( S_{\text{av}} \). The oscillation of \( S_{\text{av}} \) is the inverse of that of \( B \) owing to the negative value of \( A \). In addition, the oscillation is attenuated with \( r_{\text{max}} \) until 15.6 Å. On the other hand, the second term in \( B \) represents the base line part of \( S_{\text{av}} \). The positive value of \( C \) implies the shift of \( S_{\text{av}} \) toward negative value owing to the negative multiplicator in the second term.

Figure 6 shows the dependence of \( S_{\text{av}} \) on \( r_{\text{max}} \) in the glasses, as well as \( S_{\text{av(approx.)}} \), \( B \), \( C \) and \( \frac{\pi r_1}{3} \), \( B \) and \( C \) implies the \(-1/\rho_{\text{av}} \) for the first term in \( B \). \( S_{\text{av}} \) agreed fairly well with \( S_{\text{av(approx.)}} \), indicating that the approximate Eq. (3) is useful to discuss the change of \( S_{\text{av}} \). The value of \( S_{\text{av}} \) was negative in case of \( r_{\text{max}} > \text{ca. 3.7 Å} \) for 7005, 7010 and 6020 glasses. \( r_{\text{max}} = 3.7 \, \text{Å} \) corresponded to the position of the first peak in \( g(r)_{\text{Bi–Bi}} \) curve and the intensity of the first peak of \( g(r)_{\text{Bi–Bi}} \) curve was higher in 7005, 7010 and 6020 glasses than in the other glasses, as seen in Fig. 3. Furthermore, the curves of \( B \), hence the curves of \( C \), continued to be higher than zero until \( r_{\text{max}} \) reached 15.6 Å in 7005, 7010 and 6020 glasses. These findings indicate that the high intensity of the first peak in \( g(r)_{\text{Bi–Bi}} \) caused the continuous positive deviation of \( C \) until \( r_{\text{max}} = 15.6 \, \text{Å} \) in 7005, 7010 and 6020 glasses, which led to the small angle scattering in case of \( r_{\text{max}} > 3.7 \, \text{Å} \). The value of \( S_{\text{av}} \) became negative and positive alternatively and became negative persistently at \( r_{\text{max}} > 9.5 \) and 12.8 Å for 4040 and 3050 glasses, respectively, owing to the oscillation of \( B \) and the positive value of \( C \). The
positive value of $C$ was probably due to that the curves of $B$ did not approached $\pi r^2 / 3 - 1/\rho_{av}$ within 15 Å. In other words, the Bi atomic density in a sphere with a radius of $r_{max}$ was still larger than $\rho_{av}$ within 15 Å in 4040 and 3050 glasses, as well as 7005, 7010 and 6020 glasses.

On the other hand, the value of $S_m$ became negative and positive alternatively and became positive persistently at $r_{max} > 5.6$ and 11.7 Å for 7030 and 4060 glasses, respectively. The curves of $B$ oscillated about $\pi r^2 / 3 - 1/\rho_{av}$, that is, the first term in $B$ oscillated about $1/\rho_{av}$. Since $\pi r^2 / 3 - 1/\rho_{av}$ was smaller than zero, $S_m$ was larger than zero, resulting in the absence of the small angle scattering in 7030 and 4060 glasses. The detailed observation showed that, although the peak at 4.5 Å in the curve of $B$ was much larger than $\pi r^2 / 3 - 1/\rho_{av}$ in 7030 glass, the curve of $B$ oscillated about $\pi r^2 / 3 - 1/\rho_{av}$ in the region of $r_{max} > 6$ Å, since the peak at 6.5 Å was smaller in $g(r)_{Bi-Bi}$ curve of 7030 glass than in those of 4060, 3050 and 4040 glasses. This observation was consistent with the result of Pielou’s index that Bi atoms were clumped at the smallest scales and less clumped at larger scales in 7030 glass. Therefore, it was inferred that the small angle scattering was caused by the clumping of Bi atoms in the glass, although converses were not always true.

5. Conclusions

The coordination structure around Bi atoms was studied by X-ray diffraction and reverse Monte Carlo simulation methods in Li2O–Bi2O3–B2O3 glasses. It was found that a Bi atom was coordinated by 5–6 oxygen atoms. The number of Bi–O–Bi linkages increased monotonically with an increase in Bi/O ratio. It was inferred from the analysis by Pielou’s index that BiO2 polyhedra were clumped in the glasses, although BiO3 polyhedra were more clumped in Li2O–Bi2O3–B2O3 glasses than in Bi2O3–B2O3 glasses. The clumping of BiO2 polyhedra caused the small angle scattering.

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