Structure of Sodium Gallotitanate Glass in Relation to Glass Formation

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The structure of 40NaO0.520GaO1.540TiO2 glass has been investigated by X-ray radial distribution analysis. Nearly all the Ga3+ and Ti4+ ions are four coordinated, constructing highly cross-linked three-dimensional glass networks, and that the number of non-bridging oxygens is very small. The degree of medium-range order in this glass is much lower than in the Na2O2TiO2 glass studied in a previous paper, possibly due to the almost complete absence of TiO6 octahedra in the former glass. The higher glass-forming ability of the Na2O-Ga2O3-TiO2 ternary system compared with the Na2O-TiO2 binary system is ascribed mainly to the higher fraction of four-coordinated Ti4+ ions in the former system. It is suggested that in oxide systems glass-forming ability increases with increasing fraction of four-coordinated Ti4+ ions.

Key-words: Sodium gallotitanate glass, Structure, Glass formation, X-ray diffraction

1. Introduction

Ga2O3 or TiO2 does not form a glass by itself, but each oxide forms a binary glass when it is combined with certain alkali oxides.1)-4) Kokubo et al. found that combination of alkali oxide, Ga2O3 and TiO2 gives pretty wide glass-forming regions, producing ternary alkali gallotitanate glasses.4) The authors studied the structure5) and electrical properties6) of these glasses. Raman spectra of the glasses showed that most Ga3+ and Ti4+ ions are four coordinated and the Ga-O and Ti-O bond strength changes with glass composition.5) However, precise interatomic distances and coordination number of the cations in the glasses have not been given yet. In the present work, we aim at obtaining quantitative structural parameters and correlating the glass structure with glass formation in the system.

From the viewpoint of glass formation, the alkali gallotitanate system can be regarded as the modification of the alkali gallate or alkali titanate systems. The authors already performed the X-ray radial distribution analyses on cesium gallate,7) and sodium8) and potassium9) titanate glasses. Therefore, it is possible to compare the structure of alkali gallotitanate glasses with those of alkali gallate or alkali titanate glasses.

In the present work, we chose 40NaO0.520GaO1.540TiO2 glass as the target composition. First, this composition is chemically quite stable, suitable for long-time X-ray measurements. Second, the X-ray radial distribution analysis on Na2O2TiO2 glass, which is a base composition of 40NaO0.520GaO1.540TiO2 glass, was carried out in the previous work. It was found that Na2O2TiO2 glass contains a certain fraction of TiO6 octahedra in addition to predominant TiO4 tetrahedra.8) In this study, the effect of addition of Ga2O3 on the structure around Ti4+ ions in the Na2O2TiO2 glass will be examined and glass formation in these systems will be discussed based on the structural information obtained.

2. Experimental

2.1 Sample preparation

Glass of molar composition 40NaO0.520GaO1.540TiO2 was prepared by ordinary melt quenching method. A 10 g glass batch consisting of reagent-grade Na2CO3, Ga2O3 and TiO2 was melted in a platinum crucible in an electric furnace at 1550°C for 30 min. The melt was poured onto a brass plate and quickly pressed by another plate. A clear glass about 0.5 mm thick was obtained.

2.2 X-ray radial distribution analysis

The X-ray scattering intensities were measured on fine glass powders prepared by pulverizing the thin glass sheets. A Rigaku Denki (Tokyo, Japan) model RINT 1200-8 horizontal goniometer type X-ray diffractometer was employed. Mo Ka (λ = 0.709Å) radiation was used as X-ray source. A Kevek (Stanford, CA) model P/N 7257-0000 Peltier cooled type Si(Li) solid state detector (SSD) was used as a photon detector.

The effect of Compton shift, Δλ = h(1 - cos 2θ)/mc, cannot be neglected at higher scattering angle, since a part of inelastic Compton scattering is out of window set by a pair of ordinary Zr-Y balanced filters at higher scattering angle. On the contrary, the SSD used in the present measurements can distinguish between elastic and inelastic scattering in-
tensities, because energy window can be arbitrarily set. Especially, the SSD can be effective for the present glass consisting of relatively lighter elements such as oxygen, sodium, titanium and gallium, since the lower the atomic number, the larger the ratio of inelastic intensity to elastic intensity, making the collection of net intensities difficult.

The intensities were measured from 4 to 140° in 2θ, corresponding to 0.6 to 16.6 Å⁻¹ in S (= 4π sin θ/λ). The measurements were carried out by 400 s fixed-time counting method with step scanning at intervals of 0.5° in 2θ and repeated until the accumulative intensities exceeded 5 × 10⁵ counts at each point. The input power was set to 50 kV–40 mA. The average intensities at each angle was taken as the scattered X-ray intensity.

The intensity curve was normalized after being corrected for air scattering and polarization. The experimental amplitude function Si(S) was calculated from the normalized intensity. Then the Si(S) was transformed into the radial distribution function, RDF.

3. Results

The density of the glass measured by Archimedian method was 3.49 g·cm⁻³.

Figures 1 and 2 show the normalized X-ray intensity and the modified experimental amplitude function Si(S) curves, respectively. The oscillations in the curves continue up to 16.6 Å⁻¹. Figure 3 shows the RDF curve obtained by the Fourier transformation of Si(S), in which peaks are observed at 1.90 and 3.55 Å. Figure 4 shows the differential RDF curve. Clear peaks appear at 1.88, 3.28 and 4.58 Å in the curve. The first peak overlaps with the large second peak.

The first peak at 1.88 Å in the differential RDF curve can be interpreted as the nearly complete overlapping of the two peaks due to GaO₄ and TiO₄⁻.⁷⁻⁹
The peak corresponding to six-coordinated Ga\textsuperscript{3+} and Ti\textsuperscript{4+} ions is located at more remote distance than 1.95 Å.\textsuperscript{7,8} However, this is not the case.

Fig. 5. Pair-function fitting curves for 40NaO\textsubscript{0.5}20GaO\textsubscript{1.5}40TiO\textsubscript{2} glass.

Table 1. Optimized Parameters of Pair-Function Fitting for 40NaO\textsubscript{0.5}20GaO\textsubscript{1.5}40TiO\textsubscript{2} Glass

<table>
<thead>
<tr>
<th>Pair</th>
<th>Coordination number</th>
<th>Interatomic distance Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti\textsuperscript{-}O</td>
<td>4</td>
<td>1.86</td>
</tr>
<tr>
<td>Ga\textsuperscript{-}O</td>
<td>4</td>
<td>1.86</td>
</tr>
<tr>
<td>Na\textsuperscript{-}O</td>
<td>6</td>
<td>2.24</td>
</tr>
</tbody>
</table>

The above assignments was examined by pair-function fitting to the first peak. The optimized result of the fitting is shown in Fig. 5. The parameters obtained in the calculation are listed in Table 1. The calculated curve well fits to the observed curve. This result indicates that most of the Ga\textsuperscript{3+} and Ti\textsuperscript{4+} ions are predominantly four coordinated and the fraction of six-coordinated Ga\textsuperscript{3+} and Ti\textsuperscript{4+} ions should be small, if any.

4. Discussion

4.1 Glass structure

Table 2 compares the present glass with several alkali gallate and titanate glasses with respect to the coordination states of Ga\textsuperscript{3+} and Ti\textsuperscript{4+} ions. The coordination state around Ga\textsuperscript{3+} ions in the present glass is almost the same, that is, four, as those in other Ga\textsubscript{2}O\textsubscript{3}-containing glasses. This implies that the local structure around Ga\textsuperscript{3+} ions in Ga\textsubscript{2}O\textsubscript{3}-containing glasses is less affected by other oxide components.

On the other hand, the coordination state of Ti\textsuperscript{4+} ions significantly changes with glass composition. In fact, a fair fraction of Ti\textsuperscript{4+} ions is present in the form of TiO\textsubscript{6} in Na\textsubscript{2}O·2TiO\textsubscript{2} glass,\textsuperscript{8} while nearly all the Ti\textsuperscript{4+} ions are four coordinated in K\textsubscript{2}O·2TiO\textsubscript{2} glass.\textsuperscript{9} In the present glass, the addition of Ga\textsubscript{2}O\textsubscript{3} to Na\textsubscript{2}O·2TiO\textsubscript{2} composition results in a substantial change in the structure, that is, six-coordinated Ti\textsuperscript{4+} ions are no longer present.

The heaviest Ga–Ga pairs make a greatest contribution to the large second peak observed at about 3.3 Å in Fig. 4. In fact, it has been reported that the peak at about 3.3 Å in the RDF curve of 30Cs\textsubscript{2}O·70Ga\textsubscript{2}O\textsubscript{3} glass corresponds to Ga–Ga pairs.\textsuperscript{7} Considering that the Ga–O and Ti–O distances in oxygen tetrahedra are almost the same, the nearest Ti–Ti distance is assumed to equal the nearest Ga–Ga distance. Therefore, Ti–Ti pairs are also responsible for the peak. It should be mentioned here that in the case of Na\textsubscript{2}O·2TiO\textsubscript{2} glass, the second peak at about 3.2 Å overlaps with a clear shoulder at about 3.7 Å, indicating the coexistence of two kinds of structural units, TiO\textsubscript{4} and TiO\textsubscript{6}.

The peak at 4.58 Å is much smaller than the corresponding peak at 4.68 Å in Na\textsubscript{2}O·2TiO\textsubscript{2} glass.\textsuperscript{8} This peak mainly reflects the M–O (M=Ti or Ga) next nearest pairs. The diminished peak in the present glass suggests that the MO\textsubscript{4} tetrahedra are more randomly linked to each other and the distribution of M–O–M angles are widespread compared with Na\textsubscript{2}O·2TiO\textsubscript{2} glass. In addition, no clear peaks appear in the RDF curve in the region longer than 5 Å which reflects medium-range order. This result is different from that for Na\textsubscript{2}O·2TiO\textsubscript{2} glass in which the RDF curve shows a distinct peak at 5.48 Å.\textsuperscript{8} The lack of medium-range order in 40NaO\textsubscript{0.5}20GaO\textsubscript{1.5}40TiO\textsubscript{2} glass in contrast with Na\textsubscript{2}O·2TiO\textsubscript{2} glass is attributed to the almost complete absence of TiO\textsubscript{6} octahedra in the former glass. This is also the case for the comparison of K\textsubscript{2}O·2TiO\textsubscript{2} glass with Na\textsubscript{2}O·2TiO\textsubscript{2} glass.\textsuperscript{8,9} Na\textsubscript{2}O·2TiO\textsubscript{2} glass containing a fair concentration of TiO\textsubscript{6} octahedra retains a higher medium-range order than K\textsubscript{2}O·2TiO\textsubscript{2} glass consisting only of TiO\textsubscript{4} tetrahedra.

The most remarkable difference in environments of Ga\textsuperscript{3+} and Ti\textsuperscript{4+} ions consists in a way of charge compensation of GaO\textsubscript{4} and TiO\textsubscript{4} tetrahedra. Even if all the oxygens in a GaO\textsubscript{4} tetrahedron are bridging, excess negative charge is produced around the tetrahedron. This requires that at least one Na\textsuperscript{+} ion is lo-
cated near one GaO₄ tetrahedron in order to compensate the excess negative charge. In contrast, the charge balance of a TiO₄ tetrahedron is retained if all the oxygens in the tetrahedron are bridging. It is only when a TiO₄ tetrahedron has a non-bridging oxygen that an Na⁺ ion is forced to be adjacent to it. It is assumed that a part of GaO₄ tetrahedra contain non-bridging oxygens in Na₂O-Ga₂O₃-TiO₂ glasses; the strong stretching vibration of GaO₄ tetrahedra containing non-bridging oxygens is observed in the Raman spectra of the glasses. These indicate that non-bridging oxygens may be present in both GaO₄ and TiO₄ tetrahedra in the present glass. The total fraction of non-bridging oxygen calculated from the glass composition is, however, as low as 7.7%, indicating that the present glass consists of highly cross-linked three-dimensional glass network. A simple structural model proposed for the present 40NaO₀.₅₂₀GaO₁.₅₄₀TiO₂ glass is shown in Fig. 6.

If one assumes that GaO₄ tetrahedra in the present glass should form clusters as in PbO-Ga₂O₃ and Bi₂O₃-Ga₂O₃ glasses, Na⁺ ions would be concentrated around the Ga-O network because at least one Na⁺ ion is located near one GaO₄ tetrahedron as stated in the above. However, such aggregation of Na⁺ ions may be unfavorable for glass formation, since the ionic field strength for the Ga-O network by Na⁺ ions is assumed to increase. It is rather favorable for glass formation that GaO₄ and TiO₄ tetrahedra are linked more randomly as shown in Fig. 6 in order to disperse the Na⁺ ions. In this sense, similar coordination states of Ga³⁺ and Ti⁴⁺ ions, which will be discussed later, can be advantageous for random linkage of GaO₄ and TiO₄ tetrahedra.

In the PbO-Bi₂O₃-Ga₂O₃ glasses, it was found that a large fraction of oxygens bonded to Ga³⁺ ions are three coordinated because of the serious shortage of oxygens for Ga³⁺ ions to form GaO₄ tetrahedra. On the other hand, in RO₀.₅-GaO₁.₅ (R=alkali metal) binary glasses three-coordinated oxygens are present at only the compositional region RO₀.₅/GaO₁.₅<1.₅. Taking into account the fact that NaO₀.₅/GaO₁.₅ ratio is 2 in the present glass, the fraction of three-coordinated oxygens should be low in the glass, if any. That is, in the present glass the three-coordinated oxygens are not needed, since sufficient number of oxygens for Ga³⁺ ions are present.

4.2 Glass formation
It has been reported that in the binary alkali titanate systems the higher the fraction of four-coordinated Ti⁴⁺ ions, the larger the glass-forming tendency. That is, glass-forming ability increases in the order Na₂O-TiO₂<K₂O-TiO₂<Cs₂O-TiO₂, which is parallel to the order of fraction of four-coordinated Ti⁴⁺ ions. This criterion can be extended to the ternary titanate systems. While the Na₂O-TiO₂ binary system does not form a glass by ordinary melt quenching with metal plate, the Na₂O-Ga₂O₃-TiO₂ ternary system forms a glass in the considerably wide composition region by that technique. As indicated in the Section 4.1, the fraction of TiO₆ octahedra in the present glass is very low, although small vibration peaks due to TiO₆ octahedra were found in the Raman spectra of alkali gallotitanate glasses. Considering that the glass-forming ability increases in the order Na₂O-Ga₂O₃-TiO₂<K₂O-Ga₂O₃-TiO₂<Cs₂O-Ga₂O₃-TiO₂ glasses, nearly all the Ti⁴⁺ ions in K₂O-Ga₂O₃-TiO₂ and Cs₂O-Ga₂O₃-TiO₂ glasses are expected to take also four coordination as in the present glass. Consequently, it can be said that in oxide systems the variation in glass-forming tendency is parallel to fraction of four-coordinated Ti⁴⁺ ions.

In the R₂O-Ga₂O₃-TiO₂ (R=Na, K, Cs) ternary systems the glass-forming regions symmetrically spread around the central line corresponding to Ga/Ti=1 in the triangular composition diagram. This fact suggests that both Ga³⁺ and Ti⁴⁺ ions equally contribute to glass formation, participating in the construction of glass network in these glasses. This may be ascribed to the similarity of local structure around Ga³⁺ and Ti⁴⁺ ions. That is, the Ga-O and Ti-O interatomic distances are the same at about 1.85Å and the oxygen coordination numbers are nearly four for both ions. It is well understood that the short-range structures of both ions are similar, because both ions have a resemblance to each other in several physicochemical properties; valence (Ga : +3, Ti : +4), ionic radius (Ga : 0.47Å, Ti : 0.42Å) and electronegativity (Ga : 1.5, Ti : 1.6). Kokubo et al. examined the glass-forming regions in the R₂O-Ga₂O₃-Nb₂O₅ and R₂O-Ga₂O₃-Ta₂O₅ systems. The glass-forming regions are apparently narrower in these systems than in the R₂O-Ga₂O₃-TiO₂ system and spread to the Ga/(Nb, Ta) > 1 composition. Nb⁵⁺ and Ta⁵⁺ ions are assumed to take six

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Fig. 6. Simplified structural model of 40NaO₀.₅₂₀GaO₁.₅₄₀TiO₂ glass.
coordination in the glasses,\textsuperscript{2,3} which makes glass formation more difficult compared to the R\textsubscript{2}O-Ga\textsubscript{2}O\textsubscript{3}-TiO\textsubscript{2} system. In other words, glass-forming ability of the TiO\textsubscript{2}-containing systems is much larger than that of the Nb\textsubscript{2}O\textsubscript{5}- or Ta\textsubscript{2}O\textsubscript{5}-containing systems because Ti\textsuperscript{4+} ions preferentially take four coordination in the glasses.

Ga\textsubscript{2}O\textsubscript{3} can form a glass when it combined with either typical network modifiers, such as alkali and alkaline earth oxides, or heavy-metal oxides such as PbO or Bi\textsubscript{2}O\textsubscript{3}. On the other hand, TiO\textsubscript{2} forms a glass not with PbO and Bi\textsubscript{2}O\textsubscript{3} but with alkali or alkaline earth oxides, and PbO or Bi\textsubscript{2}O\textsubscript{3} does not form a glass with alkali or alkaline earth oxides. From this point of view, Ga\textsubscript{2}O\textsubscript{3} has a considerably high glass-forming ability among the above mentioned intermediates. This may be first attributed to the amphoteric nature of Ga\textsubscript{2}O\textsubscript{3}; Ga\textsubscript{2}O\textsubscript{3} has an affinity for both acidic and basic oxides and may form a homogeneous glass melt. Second, Ga\textsuperscript{3+} ions preferentially take four coordination in oxide glasses, and this is favorable for glass formation. Third, the oxygens bonded to Ga\textsuperscript{3+} ions have a tendency to take three coordination to accommodate the shortage of oxygens when the number of oxygens in the system are insufficient for Ga\textsuperscript{3+} ions to form GaO\textsubscript{4} tetrahedra.\textsuperscript{11}

5. Conclusion

The structure of 40NaO\textsubscript{0.5}20GaO\textsubscript{1.5}40TiO\textsubscript{2} glass was examined by X-ray radial distribution analysis and the structure and ease of glass formation were discussed by comparing with Na\textsubscript{2}O-2TiO\textsubscript{2} glass.

(1) The present glass can be prepared by ordinary melt-quenching technique. X-ray radial distribution analysis shows that nearly all the Ga\textsuperscript{3+} and Ti\textsuperscript{4+} ions are four coordinated and the medium-range order is low in the present glass.

(2) The lower medium-range order in the present glass than in the Na\textsubscript{2}O-2TiO\textsubscript{2} glass is attributed to the almost complete absence of TiO\textsubscript{6} octahedra in the former glass.

(3) The higher glass-forming ability of the Na\textsubscript{2}O-Ga\textsubscript{2}O\textsubscript{3}-TiO\textsubscript{2} ternary system compared with the Na\textsubscript{2}O-TiO\textsubscript{2} binary system is ascribed to the higher fraction of four-coordinated Ti\textsuperscript{4+} ions in the former system.

(4) Glass-forming ability of the titanate systems increases as fraction of four-coordinated Ti\textsuperscript{4+} ions increases; Na\textsubscript{2}O-TiO\textsubscript{2}<K\textsubscript{2}O-TiO\textsubscript{2}<Cs\textsubscript{2}O-TiO\textsubscript{2} and Na\textsubscript{2}O-Ga\textsubscript{2}O\textsubscript{3}-TiO\textsubscript{2}<K\textsubscript{2}O-Ga\textsubscript{2}O\textsubscript{3}-TiO\textsubscript{2}<Cs\textsubscript{2}O-Ga\textsubscript{2}O\textsubscript{3}-TiO\textsubscript{2}. It is suggested that in oxide systems the variation in glass-forming tendency is parallel to fraction of four-coordinated Ti\textsuperscript{4+} ions.

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