

Local structure of Mg in Na₂O-MgO-B₂O₃ glasses

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Abstract

The local structure around Mg in Na₂O-MgO-B₂O₃ glasses has been investigated by Mg K-edge EXAFS spectroscopy. No striking peaks except first peak can be found in the radial structure function, suggesting that the periodic network structure consists of MgO_n polyhedra is very poor, comparing to crystalline material. The position of first peak in radial structure function, which can be attributed to Mg-O pair, shifted to short-distance side with MgO content, implying that the mean coordination number of MgO_n polyhedra decreases (e.g., from octahedrally coordinated Mg²⁺ to tetrahedrally coordinated one). The tetrahedral unit may contribute to the improvement of mechanical properties of glass, with forming random network structure consist of MgO_n polyhedra.

1. Introduction

A glass material is now widely and commonly used not only in our life but also in industrial field due to the valuable properties. Particularly, the glasses contain boron oxide, which is one of the major components in glass acts as network former, has the utilities such as high chemical durability, low thermal expansion, low chromatic aberration and so on. However, in general, a glass is known as a brittle material and it sometimes triggers serious problems. Hence, the strengthening is long and big challenge in the present fields in terms of the trust, safety and weight saving of glass products. There are some techniques for the strengthening of glass (e.g., chemical, physical, coating etc.). In the previous research, it is reported that MgO is the one of promising component for improvement of brittleness of glass (e.g., [1]), implying that MgO play an important role in the glass structure. From this point of view, it is necessary to investigate the structure of Mg-containing glass for the understanding the origin of mechanically strong glass.

So far, the experimental study on the structure of MgO in glass has been poorly conducted due to the analytical constraints. Moreover, in general, since the composition of glass is often complicating (i.e., multiple components), the method that can analyze certain element selectively can be powerful tool to investigate the glass structure consist of multiple oxides. Nuclear Magnetic Resonance (MNR) is the one of powerful method to analyze the structure selectively. In actual, a challenging experiment with ^{25}Mg 3Q MAS NMR on the structure of Mg silicate glass has been conducted, suggesting the new insight into the coordination configuration of MgO polyhedra in MgSiO_3 glass (i.e., existence of highly distorted MgO_6 polyhedra: [2]). On the other hand, Reverse Monte Carlo analysis based on diffraction techniques proposed the possibility that periodic network of MgO_n polyhedra could be exist in high MgO containing glass such as Mg_2SiO_4 [3]. Generally, MgO is so-called “network modifier” and doesn’t contribute to glass-forming ability in glass composition such like SiO_2 , B_2O_3 etc. Although, if MgO_n polyhedra could form network by itself as proposed in previous study, it can be closely related to the origin of mechanically strong glass. Additionally, it is also important to investigate how the borate network and/or boron coordination are influenced by the addition of MgO component, because the borate groups should mainly dominate the properties of the glass.

In this study, x-ray absorption fine structure (XAFS) technique, which has high elemental selectivity as well as NMR, was adopted. Comparing with NMR spectroscopy, the present technique has the additional advantages as quick measurement, unnecessary of sample enrichment (or small volume of sample) and high freedom of sample state (i.e., bulk, powder and so on). In this report, the investigation on the effect of MgO content on the local structure of Mg^{2+} in $\text{Na}_2\text{O-MgO-B}_2\text{O}_3$ glasses by Mg K-edge EXAFS is presented.

2. Methods

2.1 Sample preparation

In the present study, 5 glass samples were prepared. $10\text{Na}_2\text{O}-10\text{MgO}-80\text{SiO}_2$ was set as the basic composition, then two sample groups, which were specifically $(10+x)\text{Na}_2\text{O}-(10+x)\text{MgO}-(80-20x)\text{SiO}_2$ ($x= 5, 10$) and $(10-x)\text{Na}_2\text{O}-(10+x)\text{MgO}-80\text{SiO}_2$ ($x= -5, 5$), were made. The former and latter samples are for investigation on the effect of the change in network modifiers and in $\text{MgO}/\text{Na}_2\text{O}$, respectively. The glass samples were prepared by melting method. Na_2CO_3 , MgO and B_2O_3 were mixed in proper weight and ground within Al_2O_3 mortar for ~ 1 hour. Then the oxide mixtures were decarbonized and melted in the platinum crucible at 1200°C for 2 hours. Finally, the melts were quenched on the iron plated heated $\sim 150^\circ\text{C}$ to be glass state. The glasses obtained were all color-less and transparent. In order to remove the residual stress in glass sample, the heat treatment at T_g plus 10°C was performed for an hour (T_g : glass transition temperature). The glass samples were cut into plate with the dimension about $5 \times 5 \times 3$ mm for structural measurements.

2.2 Mg K-edge XAFS spectroscopy

X-ray absorption fine structure (XAFS) analysis was performed using ultra-soft x-ray in AURORA, SR center, Ritsumeikan University. Mg K-edge EXAFS spectroscopy has been conducted at BL-13 by fluorescence yield method. The white x-ray from synchrotron is monochromated (x-ray from 1250 to 1900 eV was used in this measurement) with double crystalline spectrometer made of KTP (110). Finally, the monochromatic x-ray is irradiated to the sample located under high-vacuum condition. The fluorescence line was detected with silicon drift detector located at $90-60^\circ$ against the direction of irradiated x-ray.

3. Results and discussion

3.1 Mg K-edge XAFS spectra

Mg K-edge EXAFS spectra were successfully collected as shown in **Figure 1**. Overall, the configuration of the spectra showed no striking change. However, minor change in the XANES region shown in **Figure 2** was observed. Specifically, the position of absorption edges of the sample varied modifier content shift toward lower-energy side with the modifier content (**Figure 3**), implying that the coordination state of Mg changes with modifier content. As for the samples changed $\text{MgO}/\text{Na}_2\text{O}$, the absorption edge locates almost the same position.

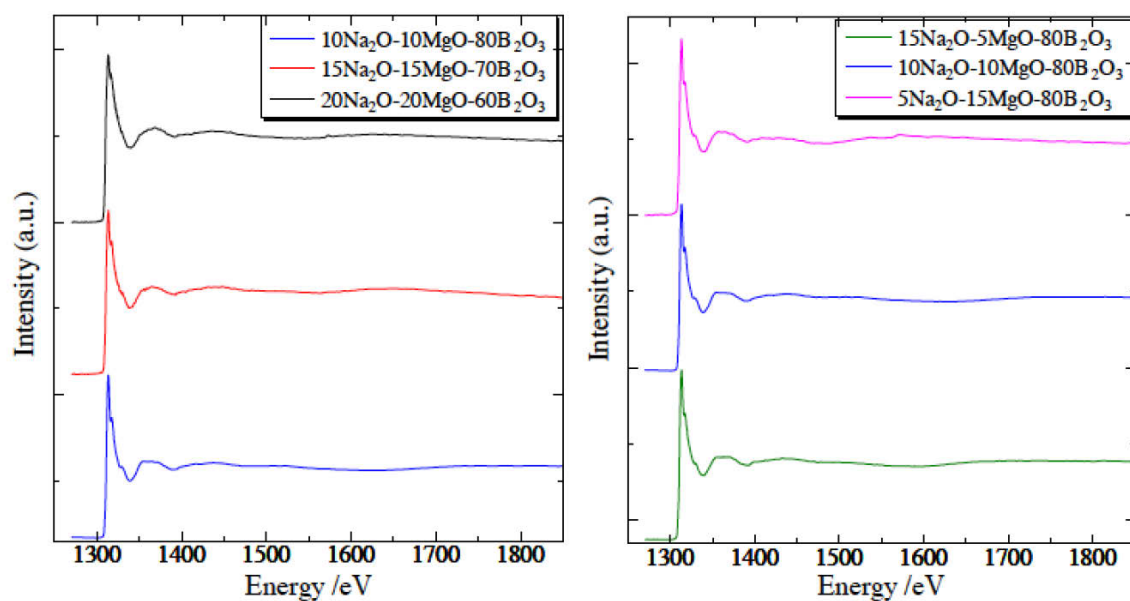


Figure 1. Mg K-edge EXAFS spectra for the samples that content of both network modifiers were varied (left) and that $\text{Na}_2\text{O}/\text{MgO}$ was varied (right).

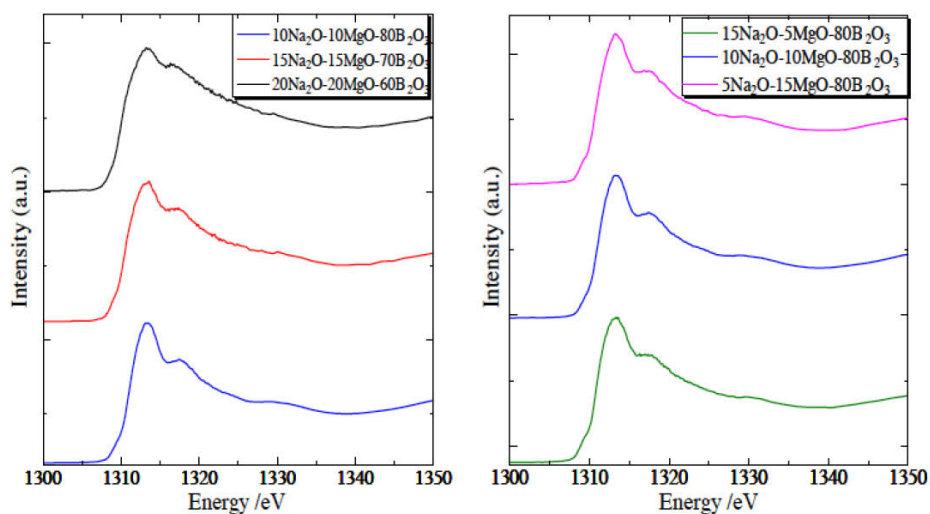


Figure 2. Mg K-edge XANES spectra for the samples that content of both network modifiers were varied (left) and that $\text{Na}_2\text{O}/\text{MgO}$ was varied (right).

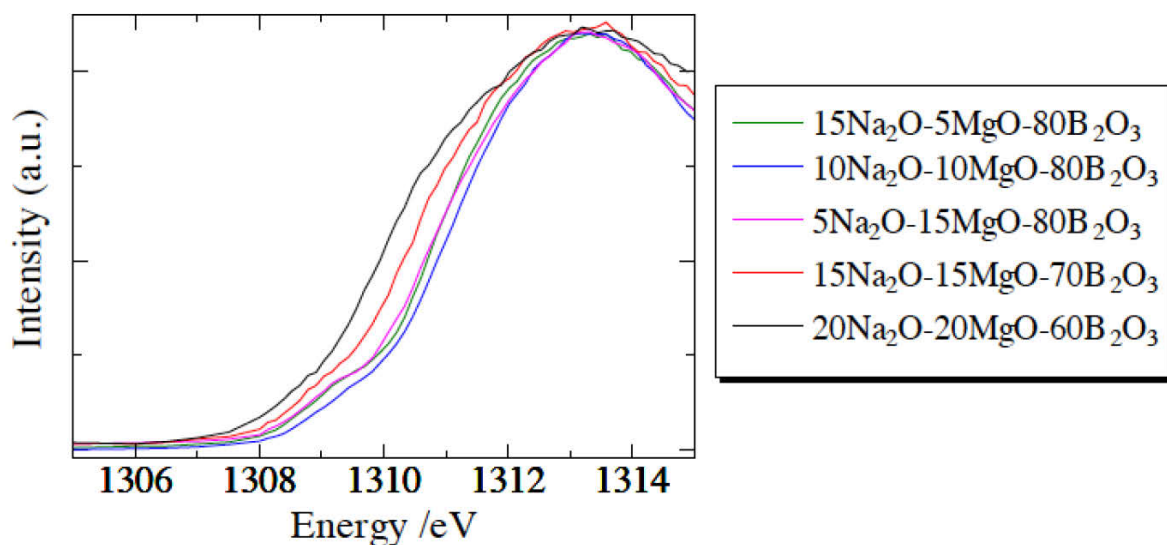


Figure 3. Comparison of absorption edge region in XANES spectra.

3.1 Radial structure function

The radial structure function can be derived from Fourier transformation of Mg K-edge EXAFS spectra (**Figure 4**). The phase shift in the radial structure functions for glass sample was estimated from MgO and MgCr₂O₄, which were prepared as standard material and include 6- and 4-coordinated Mg, respectively. The uncertainty due to the estimation of the phase shift could be ± 0.02 Å. All the functions consist of the relatively sharp intense peak at

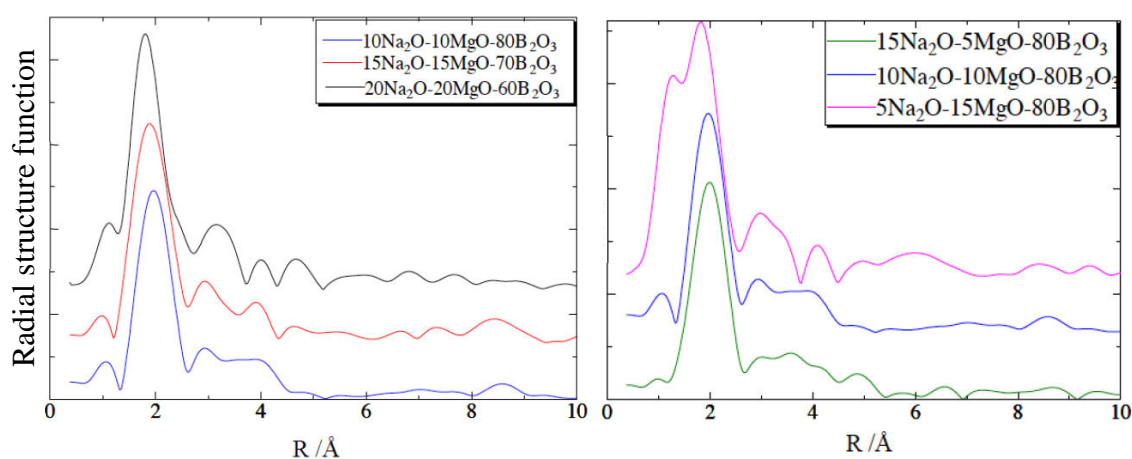


Figure 4. Radial structure function for the samples that content of both network modifiers were varied (left) and that Na₂O/MgO was varied (right)

around 2 Å and weak broad oscillation in higher-R region (the peak for 5Na₂O-15MgO-80B₂O₃ has additional peak on the left-hand side, which could be the noise cannot be removed). The sharp peak can be assigned to Mg-O atomic pair from the ion radius. Similarly, the broad peak at around 3 Å could indicate second neighbor atomic pair such as Mg(-O)-Mg and/or Mg(-O)-B, which look to become slightly intense with Mg content. Although, the peaks from second neighbor are clearly weak compared to those of crystalline material, suggesting lack of periodic linkage of MgO_n polyhedra.

The mean bond length of Mg-O is obtainable from the peak position of radial structure function. The change in the bond length with MgO content is plotted in **Figure 5**. Overall, the MgO bond length shift to short-distance side with MgO content. Especially, the bond length of the glass that content of modifiers are varied monotonically and significantly decreases with MgO content, implying the decrease in coordination number. According to the crystallographic data, for instance, mean Mg-O bond length of MgB₂O(OH)₆ (Pinnoite), which consists of octahedrally coordinated Mg, has 2.02 Å. On the other hand, MgAl₂O₄ (Spinel), which includes MgO₄ tetrahedra, has shorter bond length to be 1.92 Å. Thus, the shortening of the bond length indicates the possibility of decrease in the mean coordination number of MgO_n polyhedra in the glass. This interpretation could be supported by the result of XANES spectra, which shows low-energy shift of the absorption edge for the sample varied modifier content. In general, tetrahedral site is more suitable for the construction of the

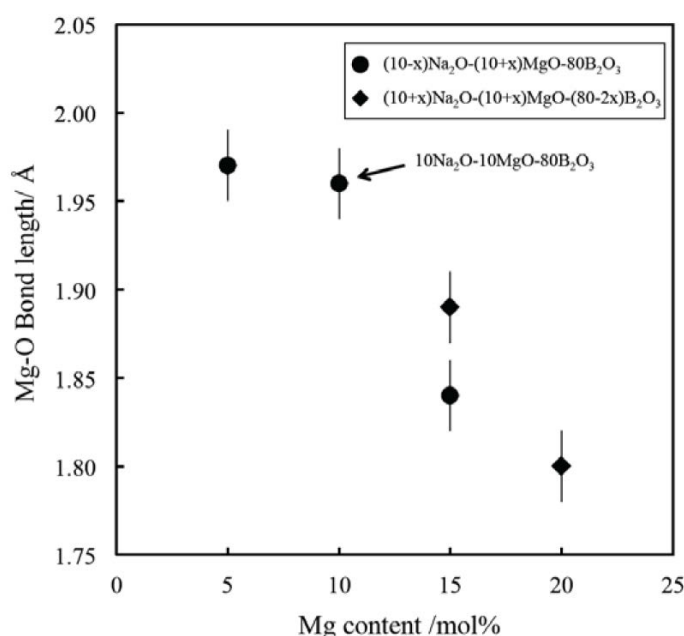


Figure 5. Change in Mg-O bond length with MgO content. 10Na₂O-10MgO-B₂O₃ is the base composition.

network than highly coordinated one such as octahedral and/or pentahedral unit. Enhancement of linkage over the glass structure should contribute to the improvement of mechanical strength. Actually, significant weakening of SiO₂ glass has been reported when the structural change of SiO₄ tetrahedron to SiO₆ octahedron occurs [4]. In addition to the high bond strength of Mg-O, the formation of tetrahedral unit may influence the strengthening of glass. Of course, since “network former” should mainly dominate the properties of glass, it is necessary to investigate other component with multiple techniques for the further understanding of glass structure and the mechanical properties.

Summary

Mg K-edge EXAFS spectroscopy has been conducted to investigate the local structure of Mg in the alkaline borate glass (Na₂O-MgO-SiO₂). From radial structure functions, overall, MgO bond length decreased with MgO content. The trend was more pronounced in the sample that the network modifiers (i.e., Na₂O and MgO) were varied. The shortening of the bond length could be interpreted as decrease in mean coordination number of MgO_n as from MgO₆ to MgO₄. Tetrahedral coordination is suitable for the formation of network structure, which can enhance the mechanical properties of glass material. Improvement of mechanical properties of glass by addition of MgO could be due to the formation of tetrahedrally coordinated MgO and the linkage. In order to understand totally the mechanism of the hardening of glass, it is necessary to investigate the effect of the addition of MgO on the borate network structure.

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