MD Simulation of Deformation and Fracture in Less Brittle Glass

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MD simulation was carried out for investigating deformation and fracture behavior under pressure of -5 to 6 GPa and stress -6 to 5 GPa. Two kinds of glasses with different brittleness were used. Under pressure, both glasses showed mostly elastic behaviors for contraction and expansion caused by changing bond angle of Si-O-Si, but they did not fracture in the pressure region. On the other hand, under uni-axial stress, both glass showed inelastic behaviors, i.e., flow and densification besides elastic behavior, and then fractued. Maximum strain and volume change just before fracture were estimated. From these results, deformation and fracture behaviors in less brittle glass were discussed in terms of glass network structure and distribution of modifier ions.

Introduction

It is believed that glass is one of the typical brittle materials. However, glass is also known to take place permanent deformation due to flow[1,2] and densification[3,4]. Such deformation in glass is very important factor for developing a high tough glass. Recently, we found a less brittle glass in the system of Na_2O-MgO-CaO-Al_2O_3-SiO_2.[5] The glass showed about 10 times higher crack initiation load in Vickers indentation test than a commercial window glass. This means that the less brittle glass shows about 30 times larger volume deformation than the window glass before fracture. Although the physical properties except brittleness for two glasses are quite similar, both glasses show different behaviors of deformation and fracture,. Therefore, in order to clear deformation and fracture behaviors in glass, it is very important to know glass structure change under pressure and stress. However, it is generally difficult to know network structures and distibution of modifier ions in network during deformation and fracture of glass under pressure and stress by real experimental method. To obtain such informations, it is very useful to use molecular dynamics (MD) simulation[6], because we can see the configuration of atoms in glass.

In this study, MD was carried out to investigate the difference of glass structure change between LB and SL during deformation and fracture under pressure and uni-axial stress.

Calculation Method

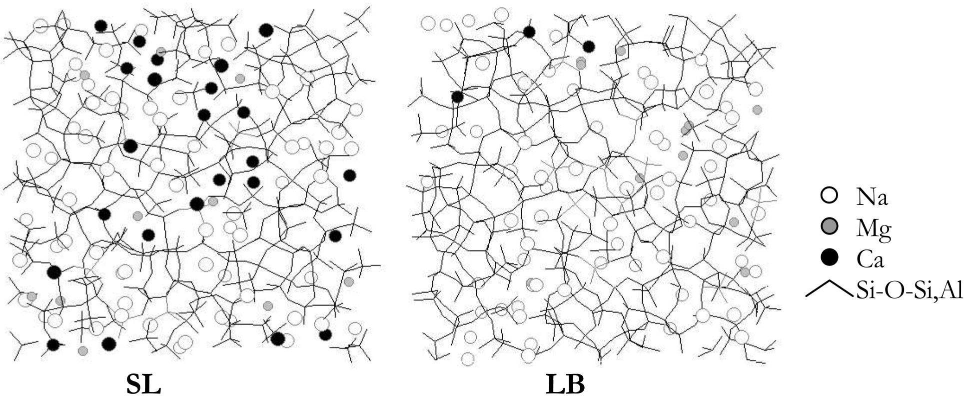
We investigated the deformation and fracture behavior of the two glasses; a soda-lime-silica glass (SL) and a less brittle glass (LB). The glass compositions and their properties are shown in Table 1.

Table 1. Glass compositions and their properties

	Na2O	MgO	CaO	Al2O3	SiO2	•(g/cm^3)	E(GPa)	B(•m$^{-1/2}$)
SL	12.3	5.5	8.9	1.1	72.2	2.5	72	7.1
LB	13.5	4.0	1.0	2.0	79.5	2.4	68	5.0

composition : mol%, •: density, E : Young's Modulus, B : Brittleness

We used MXDORTO developed by Kawamura[7] as a MD program and the empirical potential parameter sets developed by Matsui[8]. Temperature and pressure was controled by normal scaling method under the isothermal-isobatic ensemble; constant temperature T, constant pressure P, and constant number of particles N in the system. N was taken to be about 3000 for the glass samples. The usual periodic boundary conditions were imposed with orthorhombic cell, and the equations of motion were solved numerically with the time increment of 1 fs. The system was equilibrated at 3000 K after starting from a random configuration. The structures for two glasses shown in Fig.1, which was obtained by gradual cooling from 3000K to 300K, were used as initial configurations.



SL **LB**

Fig. 1. Glass structure of SL and LB glasses

Static pressure of –5 to 6 GPa and uni-axial stress of -6 to 5Gpa were applied to the glass structures for less than 150 ps. Then, pressure and stress were released and the structure was stabilized for 50 ps. Quantum corrections to MD simulations were applied in all runs. The bulk modulus at 300 K and 0 GPa was estimated by fitting a third-order Birch-Murnaghan's equation of state to instantaneous deformed volumes under pressure from -2 to 2 GPa, where the glass showed elastic deformation. The Young's modulus at 300 K and 0 GPa was estimated by approximation of a third-order equation to instantaneous strain change under stress from -1 to 1 GPa, where the glass showed elastic deformation. Under static pressure and uni-axial stress, the constant temperature and pressure methods proposed by Nose [9] and Andersen [10] were applied for the correct time-dependence of deformation of glass.

Results and discussion

Figure 2 shows volume change of the two glasses with static pressure. It can be seen that the volume of both glasses decreased almost linearly with increasing positive pressure, while it increased first linearly and

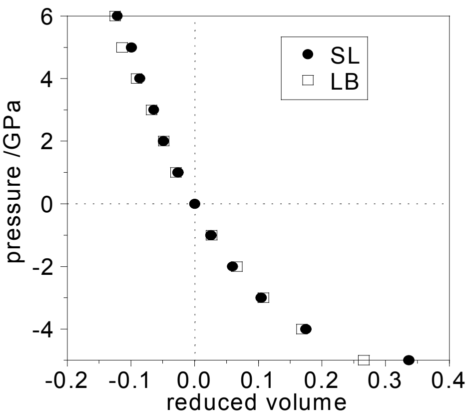


Fig.2 Volume change as a function of pressure for SL and LB glasses

then nonlinearly with increasing negative pressure. The volume increased by about 17 % under negative pressure of -4 GPa, whereas it decreased by about 9 % under positive pressure of 4 GPa. This means the expansion of both glasses occures much easily compared to contraction. The volume change of glassses disappeared after released pressure of -4 to 3 GPa, although a part of the volume change remained after released pressure of less than -4 GPa and more than 3 GPa. Therefore, both glasses are elastic in the former pressure region, but inelastic in the latter pressure regions. From the deformation in elastic region, we calculated bulk modulus for the glasses. The values were 47 and 41 GPa for SL and LB, respectively. The values are almost comparable to the observed values, 46 and 39 GPa, respectively, for SL and LB. Both glasses exihibited almost similar behavior under static pressure of -4 to 6 GPa, although there is a little defference of bulk modulus between both glasses. However, the expansion of SL became larger than that of LB at -5 GPa. SL began permanent deformation at this pressure, but LB did not.

To clear the mechanism for volume change under static pressure, change of network structure and distribution of modifier ions were investigated. Figure 3 shows Si-O-Si bond angle as a function of pressure. It can be seen from the figure that the angle for both glasses changed from about 155° to 140° with pressure from -5 to 6 GPa, but the angle recovered to original angle of about 146° after released pressure. The pair distibution function for modifier ions suggested that the modifier ions migrated during applied and released pressure. From these results, it was concluded that both glasses expanded and shrunk under static pressure by changing bond angle and distribution of ions in the network. Consequently, both glasses did not show so much different behavior under pressure applied in this study.

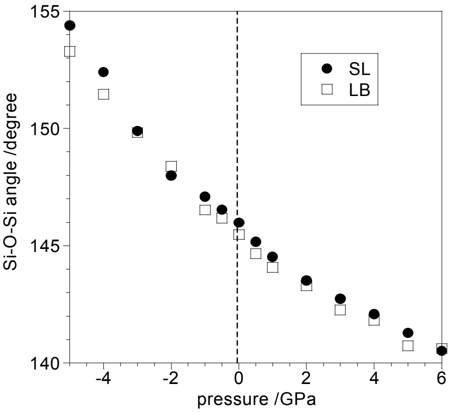


Fig. 3. Change of bond angle of Si-O-Si as a function of pressure for SL and LB glasses.

Figure 4 shows stress-strain curves from -4 to 4 GPa for both glasses. The strain under stress after 150 ps was plotted in the figure. From the figure, it can be seen that both glasses show linear strain change from –2 to 1 GPa and nonlinear large strain change outside of the stress region. From the linear region of the cuves, Young's moduli were calculated to be 65 and 61, respectively, for SL and LB glass. The observed values are 72 and 68 for SL and LB, respectively. Therefore, the calculated vales were about 10% lower than the observed values. Under tension and compression of more than 3 GPa, the strain change for SL and LB became very large. According to Marsh's theory[1], yield stress can be estimated from hardness. The estmated yield stress is about 3 GPa for both glasses. Therefore, the large strain for both glasses is considered to be due to flow in glass as described below. However, it is important to note that the strain of LB has smaller than that of SL at higher stress region of compression and tension, although LB has smaller Young's modulus than SL. After released stress, the strain formed by stress of –3 to 3 GPa mostly disappered, while a part of strain formed by compression and tension of over 3 GPa remained. The residual strain of SL was larger than

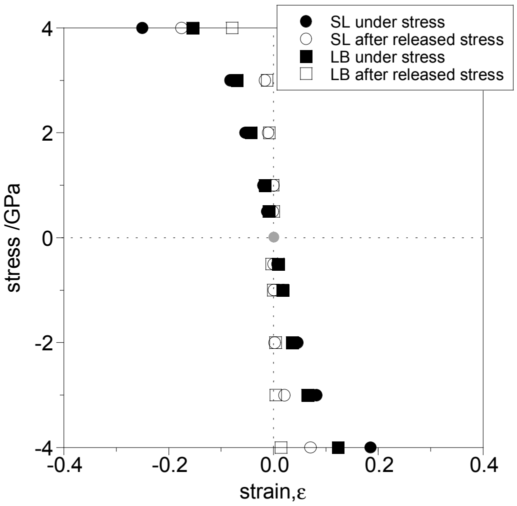


Fig. 4. Stress-strain curves for SL and LB glasses under stress of -4 to 4 GPa.

that of LB at ±4 GPa. During deformation by uni-axial stress, a little change of bond angle of Si-O-Si was observed.

Figure 5 shows volume change as a function of stress. From the figure, it can be seen that the volume for both glasses increased with increasing tensile stress, while the volume decreased with increaseing compressive stress. The volume change of LB under tension of more than 3GPa was larger than that of SL. After released stress, the permanet volume change can not be observed under tension, although the residual strain can be observed for both glasses as shown in Fig. 4. This means that flow in glass took place under tension. On the other hand, SL and LB show almost the same contraction under compression of 4 GPa. A part of the volume change fomed by compression of more than 2 GPa remained after released stress; the permanent densification took place. The densification of LB was smaller than that of SL.

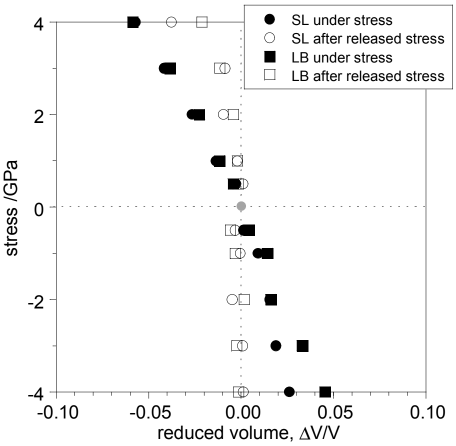


Fig. 5. Volume change as a function of stress for SL and LB glasses.

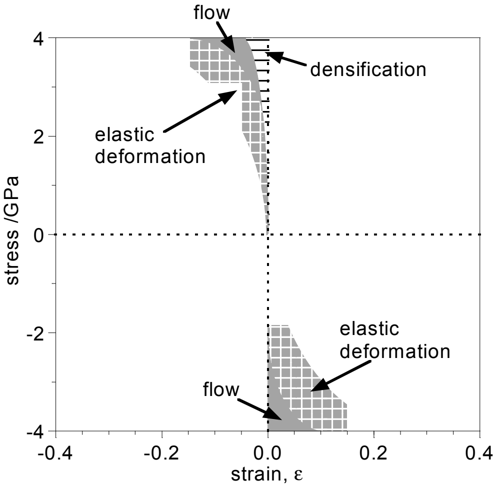


Fig. 6. Schematic diagram of deformation in glass under stress.

The strain calculated from the densification at 2 and 3 GPa was almost the same with the residual strain in Fig. 4. However, the strain calculated from the densification at 4 GPa was smaller than the residual strain. Therefore, the strain of both glasses under compression of 2 to 3 GPa is due to mainly densification and the larger residual strain under compression of 4 GPa is due to flow and densification in glass. Consequently, both glasses show elasticity and flow under tension, while they show elasticity, flow and densification under compression, as shown schematicaly in Fig. 6.

Figure 7 shows strain change with time as a function of stress. At ±2 GPa, the strain of both glasses was independent of time. However, at ±4 GPa, both glasses showed time-dependence of strain and the dependence for SL was larger than that for LB; SL tends to flow more easily than LB.

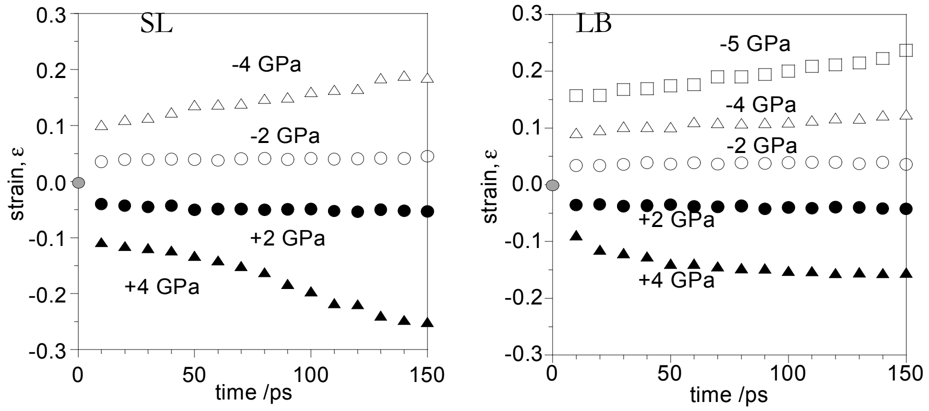


Fig. 7. Strain change with time for SL and LB glasses.

All these results described above suggest that LB is more elastic than SL under higher stress such as 2 to 4 GPa of tension and compression, although Young's modulus of LB at zero stress is lower than that of SL. The difference in deformation behaviors at the higher stress region between two glasses is considered due to the difference of polymerization of network in the glasses.

When much higher stress was applied to the glasses, they fractured. The fracture stresses under tension were -5 and –6 GPa, respectively, for SL and LB, whereas both glasses did not fracture under compression. Figure 8 shows strain and volume change as a function of time for both glasses. Under tension of -5 GPa, SL glass strained gradually and then began to fracture after 80 ps, while LB glass strained only 25% within 150 ps (Fig. 7) and did not fracture. However, LB glass also fractured at -6 GPa after 90 ps, accompanied by large strain. The final strain of LB was much larger than that of SL. The volume change, i.e. expansion

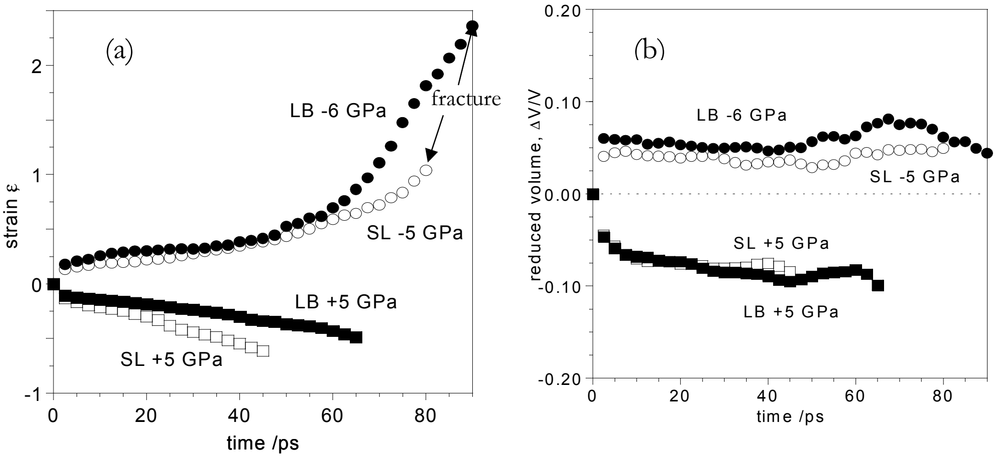


Fig. 8. Strain (a) and volume (b) change with time under high stress for SL and LB.

under tension of –5 and -6 GPa, respectively, for SL and LB took place instantaneously and then did not change so much with time. The maximum expansion of LB was a little bit larger than that of SL before fracture. On the other hand, under compression of 5 GPa, SL and LB became thiner gradually with time. Their volume decreased quickly by densification during first 10 ps and then did not decrease so much due to flow. However, we could not simulate the structure after 45 and 65 ps, respectively for SL and LB because of a limitation in cell size used in this study. The compressed strain rate of LB was smaller than that of SL. The contraction of LB was a little bit larger than that of SL. These results also suggest that LB is more elastic and deformable than SL before fracture.

From the simulation of structure change by tension, it was found that the glasses deformed gradually with time by mainly flow, which was caused by breaking larger network ring and forming smaller ring, repeating breaking and forming of bonds in network. During this flow, the volume was almost constant. After a ceratain time, some open space such as hole shown in Fig. 9 appeared in the network. Then, the hole became larger and hence fracture started.

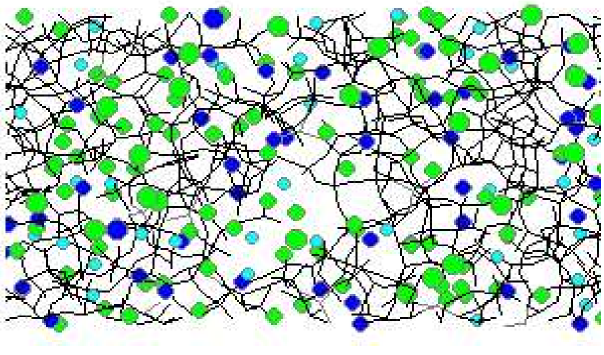


Fig. 9. Fracture origin in glass network structure.

Sodium ions gathered in the hole and the distribution of modifier ions in the network was also changed. We think this ion migration can help flow in glass. On the other hand, under compression, the glasses showed increase in compressed strain first by densification and then flow with migration of modifier ions. Finally, network was broken sporadically and hole appeared in network as well as under tension. Since LB has higher polymerized network structure than SL, the formation of hole in the network become more difficult. Therefore, LB can stand higher stress and can take place larger deformation until fracture compared to SL. Consequently, LB has lower brittleness because of its larger deformable network structure without the formation of hole, i.e., origin of fracture, compared to SL.

Conclusion

Deformation and fracture of less brittle glass LB were investigated by MD method, compared to soda-lime-silica glass SL. Both glasses showed more inelastic behaviors by flow and/or densification under uni-axial stress compared to static pressure. However, LB showed more elastic behavior than SL before fracture, although LB has smaller Young's mudulus than SL. Maximum deformation just before fracture for LB was much larger than that for SL and fracture stress of LB was larger than that of SL. These results were related to glass network strucuture and ion migration. Consequently, it can be concluded that the lower brittleness of LB is caused by suitable elasticity and flow which are attributed to higher polymerized network and appropriate distribution of modifier ions.

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