ATOMISTIC SIMULATIONS OF BOROSILICATE GLASSES:
MECHANICAL RESPONSE UNDER DIFFERENT LOADING CONDITIONS

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ABSTRACT

It has been challenging to understand the cracking behavior of oxide glasses under sharp contact due to the complicated stress state in the samples and compositional dependence of the mechanical behavior of glasses. Molecular dynamics (MD) is a powerful technique to study materials structure and properties. By taking advantage of its capability of providing the time-dependent trajectories of all atoms in the system, the in-situ observation of mechanical deformation can be achieved. In this research, we used MD simulations to study the mechanical response of two commercial multi-component borosilicate glasses, Borofloat®33 (Boro33) and N-BK7® (N-BK7), under different loading conditions to obtain a more complete picture of the deformation mechanism of the indented glass from the perspective of atomic scale.

This dissertation can be divided into five parts. In the first part, the performances of two sets of classical interatomic potentials for borosilicate glasses were evaluated in terms of structural and elastic properties for the two glass compositions. The results were also compared with available experimental data. It was found that the potential by Wang et al. [M. Wang, N.M. Anoop Krishnan, B. Wang, M.M. Smedskjaer, J.C. Mauro, and M. Bauchy, J. Non. Cryst. Solids, 498 294–304 (2018)] provides a closer $N_4$ value for Boro33 but underpredicts the $N_4$ value for N-BK7. In contrast, the $N_4$ value of N-BK7 using the potential of Deng and Du [L. Deng and J. Du, J. Am. Ceram. Soc., 102 [5] 2482–2505 (2019)] agrees well with the experimental data, but that of Boro33 is overpredicted. Our result also indicates that Wang’s potential gives a better prediction in the short-range structure, while Du’s potential provides a closer medium-range structure compared with the experimental data. Neither set of potentials is able to provide accurate predictions of elastic moduli. Wang’s potential predicts lower elastic modulus due to the underpredicted $N_4$ value, whereas Du’s potential yields higher elastic modulus compared with the experimental values, resulting from its overpredicted $N_4$ value.
The second part presents the results from cold compression-decompression MD simulations of the borosilicate glasses. Our results suggest that the densification of these two borosilicate glasses involves different types of structural changes. The fraction of permanent densification can be correlated to the change in intermediate-range structure. By performing Voronoi analysis, the contributions to densification from different cation types in these two multicomponent borosilicate glasses were qualified. It was found that 3-coordinated cations facilitate the densification process, and higher-coordinated cations are relatively stable and can even show a slight expansion in their Voronoi volume.

The third part describes the shear behaviors of the borosilicate glasses under different pressures. It was found that the addition of alkali ions lowers the yield stress and changes the pressure dependence of shear modulus. Moreover, shear-induced densification was observed in both glasses. The results show that the decreases of the oxygen-centered bond angle and the coordination number change of B are responsible for the density changes at low pressures, and the increase of 5-coordinated Si is the dominant mechanism for densification at high pressures. The atomic shear stress was calculated the results suggest that B is able to relax mechanical stress more easily under pressurized shear compared to other element types. By analyzing the nonaffine displacement of atoms, it was found that N-BK7 exhibits more localized plastic deformation compared to Boro33 at low pressures and the local rearrangements in both glasses become more homogeneous with increasing pressure. The mean squared nonaffine displacement curves show that alkali ions have the highest mobility induced by shear compared to the network formers and B is more mobile than Si for both glasses. It was also observed that plastic deformation tends to take place around boron atoms for Boro33, whereas it occurs in the alkali-rich regions for N-BK7, indicating that these two glasses have different atomic-scale deformation mechanisms.
In the fourth part, the plasticity of the two glasses under tension was investigated by implementing a uniaxial tension test using MD simulations. A bond-switching mechanism is found to be responsible for the plastic response of both glasses and is governed by the increasing rate of non-bridging oxygen (NBO) production during the uniaxial tension. It was found that the amount of B\textsuperscript{4}O\textsubscript{Si\textsuperscript{4}} linkages in the glass governs the stress drop after yielding, due to its higher tendency to create NBOs compared to Si\textsuperscript{4}O\textsubscript{Si\textsuperscript{4}}. Also, the initial existence of NBOs weakens the critical stress for breaking the B\textsuperscript{3}-O bond in B\textsuperscript{4}O\textsubscript{Si\textsuperscript{4}}, which in turn lowers the yield strength of the glass.

The last part describes the effects of pressure on elastic properties, surface energy, and fracture toughness ($K_{IC}$) of the borosilicate glasses. It was found that the impact on $K_{IC}$ is mainly dominated by the change of Young’s modulus under pressure, which is proportional to the relative change in density. Between the two glasses under investigation, $K_{IC}$ can be improved more effectively by the hot-compression process for Boro33, due to its higher concentration of 3-coordinated boron (B\textsuperscript{3}), which facilitates densification via B\textsuperscript{3} to B\textsuperscript{4} conversion under compression.
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Chapter 1

Introduction

1.1 Motivation

Oxide glass is easily subject to brittle failure due to the lack of plasticity carriers, such as dislocations in crystalline materials. While under sharp contacts, such as during an indentation experiment, it has been shown that two types of plastic deformation can take place: densification and plastic flow. These two mechanisms play an important role in the mechanical energy dissipation which decreases the driving force of crack formation. However, the relationship among composition, structure, and deformation behavior in oxide glasses is still not fully understood. The focus of this dissertation is to provide a deeper understanding of the deformation mechanism of borosilicate glasses under sharp contact and obtain a more complete picture of the cracking behavior of the indented glass. To achieve this, we investigate the mechanical response of borosilicate glasses under different loading conditions using molecular dynamics (MD) simulations for bridging up the atomic-scale changes and macroscopic properties.

1.2 Background

1.2.1 Composition-Structure-Properties

In boron (B)-containing glasses, the addition of modifiers, such as alkali or alkali earth oxides, can cause two opposite modifications of the glass network: (a) the creation of non-bridging oxygen (NBO) by breaking the bonding between bridging oxygen (BO) and network formers, and (b) the conversion of the B coordination state from 3 to 4 by acting as a charge
compensator. These two mechanisms lead to either a decrease or an increase of the connectivity of glass, respectively, and the competition between the two mechanisms results in the so-called ‘boron anomaly’. Since the structure of glass governs its properties, such as viscosity, fragility, electrical conductivity, diffusion, etc., considerable research has been devoted to developing models to capture this complex composition-structure relationship of boron-containing glasses so that direct prediction of glass properties from composition becomes possible.

For borate glasses, the random-pair model proposed by Gupta\(^1\) makes an accurate prediction of \(N_4\) value (the number of four-coordinated boron (B\(^4\))/total boron number) which reaches the maximum at alkali amount = 33.3 mol\%, in good agreement with the NNR data. The model was developed based on three rules:

1. B\(^4\) occurs in pairs sharing a corner where the B-O-B bond angle is random.
2. Pairs of B\(^4\) cannot be connected.
3. NBOs only occur in BO\(_3\) (B\(^3\)) units and not in B\(^4\) units.

These rules suggest that the B\(^4\)-O-B\(^4\) linkages are unfavorable compared to B\(^3\)-O-B\(^4\) linkages, which has been demonstrated by the results from the double quantum \(^{11}\)B NMR and the MD simulation\(^2,3\). Krogh-Moe’s pioneering theory\(^4\) in the structural model of glass suggests that borate glasses are constructed from at least some of the structural groupings which occur in their crystalline counterparts (or the nearest compositions) and are randomly oriented. The relative quantity of these structure groupings in glass can then be predicted by applying the level rule to the corresponding position on the equilibrium phase diagram. The model states that the primary grouping types in alkali and silver borate glasses are boroxol, tetraborate, and diborate groups when modifier amounts < 34%. The model also qualitatively explains the inconsistency between the maximum of \(N_4\) value and the minimum of thermal expansion coefficients (15~20 mol\% alkali) of alkali-borate glasses where the amount of boroxol units and tetraborate structural units are about to reach their minimum and maximum, respectively. Note that the contribution of each
structural group to thermal expansion is still unclear. Bray et al. extended Krogh-Moe’s idea by fitting simulated NMR spectra to the experimental data and the relative amount of each structural group can be derived. In Bray’s et al. model, they assumed that the composition range can be divided into three regions in terms of $R$, where $R = \text{mol}\% \text{Li}_2\text{O}/\text{mol}\% \text{B}_2\text{O}_3$:

1. $0 \leq R < 0.4$: only boroxol, tetraborate, and diborate units can exist.
2. $0.4 \leq R < 1$: only diborate, tetraborate, metaborate, and loose BO$_4$ units can exist.
3. $1 \leq R < 1.86$: only metaborate, loose BO$_4$, pyroborate, and orthoborate units can exist.

The result predicted by the Bray et al. model is consistent with the experimental data. Although there are some objections against the Krogh-Moe and Bray theories, their work offers influential insights in the understating of the glass structure. Recently, Mauro et al. proposed a statistical mechanical model, applying noncentral multivariate hypergeometric distribution with Boltzmann weighting factors, to understand the mixed network former effect. Bødker et al. applied the same approach to predict relative amounts of structural units in the lithium borate glasses, and the result showed good agreement with the experimental data.

For borosilicate glasses, Dell et al. proposed a structural model to determine the relative amounts of different boron states, i.e., B$^4$, B$^3$ with 3 NBO or 0 NBO, and B$^3$ with 1 NBO or 2 NBO, of ternary borosilicate glasses with different $R$ and $K$ ($K = \text{mol}\% \text{B}_2\text{O}_3/\text{mol}\% \text{SiO}_2$) values in light of their previous works. The model suggests that there are four stages upon addition of alkali:

1. $R < 0.5$: The addition of Na$_2$O creates B$^4$, and it is assumed that the same amount of B$^3$ and B$^4$ may form diborate groups.
(2) $0.5 \leq R \leq R_{max} = \frac{1}{2} + \frac{1}{16}K$: The additional $\text{Na}_2\text{O}$ associates with the diborate groups formed in the first stage to form reedmergnerite groups until $R_{max}$, at which all the $\text{SiO}_2$ is part of the reedmergnerite group and the $N_4$ reaches the maximum.

(3) $R_{max} \leq R \leq \frac{1}{2} + \frac{1}{4}K$: All the extra $\text{Na}_2\text{O}$ creates NBOs on $\text{SiO}_4$ ($\text{Si}^4$) in the reedmergnerite groups until each reedmergnerite group associates with 1.5 $\text{Na}_2\text{O}$ molecules. The $N_4$ will not change in this stage.

(4) $\frac{1}{2} + \frac{1}{4}K \leq R \leq 2 + K$: In this stage, the additional $\text{Na}_2\text{O}$ molecules are shared by the diborate groups and the reedmergnerite groups to form pyroborate groups and $\text{Si}^4$ with 2 NBO on each Si. The $\text{Na}_2\text{O}$ is shared based on the relative proportions between the diborate groups and the reedmergnerite groups.

Based on these assumptions, the Dell et al. model can capture the experimental trend over a wide composition very well.

Glass properties are well known to be structural dependent. Phillips and Thorpe\textsuperscript{9–13} originally developed topological constraint theory, in which the topology of glass network is estimated by the average difference between the three translational degrees of freedom (in 3-dimension network) and the number of constraints, i.e., linear and angular constraints, of each atom, and can be connected to the compositional dependence of glass properties at zero temperature. Mauro and Gupta\textsuperscript{14,15} further included the temperature dependence of constraints, which can account for the impact of thermal energy on the glass network. The model has successfully been applied to quantitatively predict important glass properties, such as glass transition temperature ($T_g$), fragility ($m$), Young’s modulus, and hardness\textsuperscript{14–18}, and has been shown to provide good predictions of those properties. According to this work, $T_g$ is inversely proportional to the number of degrees of freedom per atom, $m$ is proportional to the changing rate of the number of degrees of freedom per atom at $T_g$, hardness is proportional to the number of
constraints per atom, and Young’s modulus is related to the free energy density of the topological constraints.

For both borate and borosilicate glasses, the initial increase of $N_4$ causes the increase of the connectivity of glass leading to the increase of density, $T_g$, elastic properties and hardness, and the decrease of Poisson’s ratio ($\nu$)\textsuperscript{19-28}. However, the trends of some properties upon alkali addition start to deviate from the $N_4$ evolution in borate glasses when $R<0.5$. For example, $T_g$ starts to level off at $R>0.2$\textsuperscript{14}. By using temperature-dependent constraint theory, Mauro et al.\textsuperscript{14} suggested that the phenomenon is due to the restriction of the onset temperature of the $\beta$ constraint, i.e., O-B-O angular constraint. Doweidar\textsuperscript{25} studied the density and microhardness of sodium borate glasses for $R<0.5$, and found that the increasing rate of microhardness is higher at $R<0.2$ than $R>0.2$, which can be attributed to the increasing and decreasing amount of tetraborate groups, respectively, according to Krogh-Moe’s model. He thus concluded that the tetraborate group has a higher contribution to the hardness compared to the other groups, such as the boroxol and diborate group. Shibata et al.\textsuperscript{28} also attributed the less increasing rate in density over the region $0.4 \leq R \leq 0.5$, compared to that at $R \leq 0.4$, to the formation of NBO on the metaborate groups. However, the NBO amount is too small to be detected at $R \leq 0.5$\textsuperscript{29} by NMR. In the maximum region ($R_{\text{max}} \leq R \leq \frac{1}{2} + \frac{1}{4} K$), the $T_g$\textsuperscript{16,26,27,30}, hardness\textsuperscript{16}, density\textsuperscript{26-28,30}, elastic moduli\textsuperscript{26,30,31}, and fracture toughness\textsuperscript{31} also reach a maximum even though it is assumed that the NBO is created on Si\textsuperscript{4} in the reedmergnerite group leading to the decrease of $\nu$\textsuperscript{26}. After passing this region, $T_g$, hardness, and elastic moduli decrease significantly and $\nu$ increases due to the further formation of NBO (on both the diborate groups and the reedmergnerite groups for borosilicate glasses), but the density only slightly decreases because of the replacement of boron with heavier alkali\textsuperscript{26,28,30}. 
1.2.2 Indentation

Glass is subject to brittle fracture, particularly under sharp contact loading, and indentation is a technique that has been widely used to understand the deformation behavior of glass under this scenario. Besides the crack formation, glasses can also exhibit two types of plastic deformation, densification and plastic flow, in response to stress, which provides an alternative means for the dissipation of applied mechanical energy. Since the activation energy associated with volume recovery is much less than the energy required to activate plastic flow\textsuperscript{32}, the contributions of both mechanisms to displaced volume can be separated by a heat treatment at around 0.9 $T_g$ during which only the displaced volume induced by densification will recover\textsuperscript{32,33}. The magnitudes of the densification and plastic flow mechanisms then can be quantified by the volume recovery ratio ($V_R$) and the pile-up ratio ($V_P$), respectively.\textsuperscript{33} Overall, glasses can be roughly classified as anomalous glasses (e.g., pure silica), normal glasses (e.g., most silicate glass), and intermediate glasses (e.g., N-BasF from SCHOTT). The plastic response of anomalous glasses is dominated by densification, leading to ring/cone cracking under indentation. In contrast, the plastic deformation of normal glasses is mainly driven by plastic flow causing radial-median cracking and apparent pile-up\textsuperscript{33,34}.

The indentation problem can be approached by assuming that the plasticity is only limited to the region in contact with the indenter\textsuperscript{35}. This yielded zone which is assumed to be uniform should accommodate the volume of the indenter tip and experience compressive stress so that no crack can happen within this region during the indentation process. Then, the region outside the yielded zone can be treated as the problem of linear elasticity. Yoffe\textsuperscript{35} developed a model which combines the Boussinesq’s elastic stress field for a point load normal to the flat surface of a semi-infinite body with the blister filed (plastic filed) stemming from the strain...
nucleus located on a free surface. Yoffe’s stress field is given in spherical coordinates referred to Figure 1-1 as follows:

\[
\sigma_{rr} = \frac{P}{2\pi r^2} [1 - 2v - 2(2 - v)\cos\theta] + \frac{4B}{r^3}((5 - v)\cos^2\theta - 2 + v) \quad \text{Eq. (1)}
\]

\[
\sigma_{\theta\theta} = \frac{P}{2\pi r^2} \frac{(1-2v)\cos^2\theta}{(1+\cos\theta)} - \frac{2B}{r^3} (1 - 2v)\cos^2\theta \quad \text{Eq. (2)}
\]

\[
\sigma_{\phi\phi} = \frac{(1-2v)P}{2\pi r^2} \left[ \cos\theta - \frac{1}{1+\cos\theta} \right] + \frac{2B}{r^3} (1 - 2v)(2 - 3\cos^2\theta) \quad \text{Eq. (3)}
\]

\[
\tau_{r\theta} = \frac{P}{2\pi r^2} \frac{(1-2v)\sin\theta\cos\theta}{(1+\cos\theta)} + \frac{4B}{r^3} (1 + v)\sin\theta\cos\theta \quad \text{Eq. (4)}
\]

where \( P \) is the load and \( B \) is the strength of the blister field which is expressed as

\[
B = \frac{3E}{4\pi(1+v)(1-2v)}(1 - V_R - V_P)V_i^- \quad \text{Eq. (5)}
\]

where \( V_i^- \) is the indentation volume, which is related to \( v \), the ratio between Young’s modulus and hardness \((E/H)\), and the value of the apical angle of the indenter. During the loading period, ring and median cracks can be driven by \( \sigma_{rr}(\theta = \pi/2) \) and \( \sigma_{\theta\theta}(\theta = 0) \). Upon unloading, \( P \) decreases gradually and \( B \) stays the same, leading to radial and lateral cracks driven by \( \sigma_{\phi\phi}(\theta = \pi/2) \) and \( \sigma_{rr}(\theta = 0) \). Therefore, the magnitude of \( B \) plays an important role in the cracking pattern. Among the factors determining the \( B \) value, we are most interested in the \((1 - V_R - V_P)\) term since it is a measure of the residual stress. It has been shown that the dependence of \((1 - V_R - V_P)\) value on \( v \) exhibits a maximum around \( v = 0.3^{34} \). The plastic deformation is dominated by densification when \( v < 0.3 \), while it is dominated by plastic flow when \( v > 0.3^{33,34} \). Sellapan et al.\(^{34}\) investigated the relationship between the glass properties and crack pattern based on Yoffe’s model. They found that the crack patterning of glass mainly depends on \( v \) and slightly on the \( E/H \) ratio. Besides glass’s properties, the indenter angle can also have significantly influence on the degree of densification and plastic flow, i.e., \( V_R \) and \( V_P \). With the indenter angle decreasing, the dominant deformation mechanism transits form densification toward plastic flow, and the elastic recovery degree also decreases\(^{33,36,37}\).
It has been shown that $V_R$ and $V_P$ can be correlated with $\nu$ of glass with a sigmoidal relation\textsuperscript{33}, providing a handy way to predict the indentation response from material properties. However, the distributions of $V_R$ and $V_P$ within the range of $\nu$ from 0.2 to 0.3 are wide. Furthermore, the data in the $V_R$ ($V_P$) and $\nu$ relation is scattered, especially when the data of boron-containing glasses are included, indicating that Poisson’s ratio alone is not sufficient to describe the glass deformation\textsuperscript{33,34,38}. Also, the analysis based on Yoffe’s model only provides qualitative prediction because it considers neither the change of mechanical properties nor the change of stress field due to crack formation during the indentation process. Therefore, a deeper understanding of the deformation mechanism of glass under sharp contact is desired. In this study, we focused on two commercial multicomponent borosilicate glasses, Borofloat 33 (Boro33) and N-BK7. Both of these compositions are silica-rich borosilicate glasses with a similar amount of boric oxide. They have similar $\nu$ (0.2 and 0.206 for Boro33 and N-BK7, respectively) and $E/H$ ratio; however, they exhibit different mechanical responses and fracture patterns under indentation\textsuperscript{26,34}, which makes them a good pair of models for comparison.

Figure 1-1 The spherical coordinate systems of an indented sample.
Chapter 2

Research Methods

2.1 Overview

With the tremendous growth of computing power, computational materials science has drawn more attention over the past several decades. The goal of computational materials science is to model materials and understand their properties and behaviors, which accelerates the design and development of new materials. Moreover, understanding the response of materials to extreme conditions becomes possible via computational methods, such as extremely high strain rates or high temperatures or pressures. There are different methods for calculation depending on the length and/or time scale, and the properties that we want to model. For example, first-principles methods can model electronic, optical, and magnetic properties since they consider explicit electrons and nuclei as the basic particles. The interactions of the particles can be described by quantum mechanics, so the methods do not require any external parameters. However, large system sizes and dynamic conditions are difficult for first-principles methods to handle due to their expensive computational cost. In contrast, finite element analysis (FEA) is suitable for the full-scale problems by dividing the sample into small elements, but it is not able to capture the evolutions of material properties during a dynamical process, such as the density change of glass under indentation.

Molecular dynamics is an atomic-scale computational technique, which considers the atom as the basic unit and enables tracking of each atom’s position and velocity over time.
Therefore, molecular dynamics is a suitable tool to investigate the atomic-scale origin of different material behaviors. The successive configurations during the simulation are obtained by solving the differential equation of Newton’s second law:\(^39\):

\[ \mathbf{F}_i = m_i \frac{d^2 \mathbf{r}_i}{dt^2} \quad \text{Eq. (1)} \]

where \( \mathbf{F}_i \) is the force acting on an atom with the mass of \( m_i \), and the position of \( \mathbf{r}_i \) at a time \( t \). The most widely used method for integrating Newton’s second law of motion is finite difference techniques. The basic idea of this method is dividing the integration into a finite number of stages with a fixed timestep, \( \delta t \), during which the force acting on each atom is a constant and can be derived by taking the gradient of the total interatomic potential, \( U \), with other atoms:

\[ \mathbf{F}_i = -\nabla U \quad \text{Eq. (2)} \]

Therefore, the interatomic potential is the most important input which governs the precision of simulation results in molecular dynamics. The acceleration of the atoms can be determined by dividing \( \mathbf{F}_i \) by the mass of atom \( i \), and the positions and velocities can then be obtained at a time \( t+\delta t \). Then, the procedure can be repeated starting from the new position.

The output of molecular dynamics are configurations with information of each atom’s position, from which abundant structural properties can be provided, such as radial distribution function, bond angle distribution, the coordination number of atoms, etc. Also, the trajectory generated from molecular dynamics allows us to observe the time-dependent properties in response to the thermal, mechanical, or chemical gradients \textit{in-situ}.

To study the mechanical responses to the complex stress state under indentation, our approach is to break them down into different loading conditions. We carried out pure compression (Chapter 3), pure shear, and their combinations (Chapter 4) on the glasses to study the plastic zone. Also, we performed uniaxial tension (Chapter 5) and fracture toughness (Chapter 6) simulation to investigate the crack initiation and propagation behaviors.
2.2 Potentials

The main subjects of this research are commercial multicomponent borosilicate glasses. Many potentials have been developed for B-containing glasses. However, the development of interatomic potentials for B-containing glasses covering a wide compositional range has proved challenging due to the changes in the coordination number of B atoms with composition. There are only two sets of potentials including the elements contained in our samples and specifically developed for simulation of borosilicate glasses, which are developed by Bauchy et al. and by Deng and Du respectively. Bauchy potential was developed based on the parametrization of silicate oxides introduced by Guillot and Sator, and Du’s potential is based on the Teter potential, which has been previously used for simulating various silicate glasses. To reduce the number of fitting parameters, both potentials adopt partial charge pairwise functional forms. Moreover, there are no composition-dependent parameters in the Bauchy potential, and only the B-O interaction is composition-dependent in Du potential. Therefore, both potentials are promising and attractive for the study of borosilicate glasses. The B-related parameters in the Bauchy potential are generated by reproducing the evolutions of the coordination number of B and density over a range of borosilicate compositions. The parameters in the Du potential are developed by fitting to the structures of boron oxide and different sodium borate crystals first, and then are refined by reproducing the trend of the structural parameters and the coordination number of B over a range of borosilicate glasses and sodium borate.

Both potentials adopt the same form of Buckingham potential:

\[ U(r) = \frac{z_i z_j e^2}{r_{ij}} + A_{ij} e^{-r_{ij}/\rho_{ij}} - C_{ij} / r_{ij}^6 \]  

Eq. (3)

where \( r_{ij} \) is the distance between atom \( i \) and atom \( j \), \( z_i \) is the effective (partial) charges of atom \( i \), and \( A_{ij}, C_{ij}, \) and \( \rho_{ij} \) are the fitting constants. To avoid the problem caused by the Buckingham
potential at small values of $r_{ij}$, a splice correction is included at low distance in Du’s potential, which is shown as follows:

$$U(r) = \frac{B_{ij}}{r_{ij}^n} + D_{ij}r_{ij}^n$$  Eq. (4)

The details of the parameters in Eqs. (3) and (4) can be found in Ref. [43] and Ref. [44]. It should be noted that there is no correction or extra term added into Bauchy potential for avoiding Buckingham catastrophe since the potential was developed and tested at relatively low temperature (3000K). However, it is found that the glass system is stable at 6000K when the simulation is conducted in the NVT ensemble. A cutoff of 11 Å was used for both the short-range and Coulombic interactions, and the Particle-Particle Particle-Mesh (PPPM) algorithm where accuracy of $10^{-5}$ was used for the long-range force calculation. Periodic boundary conditions were applied at all faces of the simulation cell in all of the simulations. The Nosé-Hoover thermostat and barostat were used to control the temperature and pressure if needed.

A comparison between the performance of the two potentials in describing the structure, mechanical properties, and mechanical responses of Boro33 and N-BK7 is presented in Chapter 3 and Chapter 4. Based on the results in Chapters 3 and 4, we applied the Du potential for the following chapters since it shows a better overall mechanical response.

### 2.3 Sample preparation

MD simulations were performed using LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator)\textsuperscript{48}. Two of SCHOTT’s commercial borosilicate glasses, Boro33 and N-BK7, were simulated. The compositions of the two glasses are provided in Table 1. Note that BaO and CaO are not included in the simulation of N-BK7 since both potentials do not contain
Ba-O interaction and for simplicity. They are not considered to affect the major conclusions in this study due to the small amounts of them (<1mol%). The samples in our study were all obtained by the melt-quench method following the procedure from Deng and Du \textsuperscript{44} for comparison. The initial configurations for each composition were randomly generated in the simulation box. For potential evaluation (Chapter 3) and the unit sample for fracture toughness calculation (Chapter 7), five and three parallel initial configurations for each composition with around 3000 atoms were created in a cubic box. For other deformation processes (Chapter 4~6), 9000 atoms are created in a rectangular box with a size of 3.4 nm×10.2 nm×3.4 nm, and 3 parallel samples were used for each composition. The starting configurations were first energy minimized at 0 K followed by equilibration at 300 K for 60 ps. Then, they were melted at 6000 K for 100 ps and at 5000K for 100 ps to eliminate the memory of the initial configuration. The samples were subsequently quenched from 5000 K to 300 K with a quench rate of 5 K/ps. All of the above processes were conducted in the NVT ensemble, where the initial density is chosen to match the experimentally known density (given by 2.23 and 2.51 for Boro33 and N-BK7, respectively). A subsequent relaxation was carried out at 300 K using the NPT ensemble for 60 ps before an NVT run of 60 ps for statistical averaging. The integration timestep is 1 femtosecond (fs) throughout all of the simulations.
Chapter 3

Evaluation of classical interatomic potentials for molecular dynamics simulations of borosilicate glasses

The work in chapter 2 was previously published in the following journal article:


3.1 Introduction

Boric oxide (B$_2$O$_3$) has been widely used as a glass network former due to its low melting temperature and ability to tailor favorable properties in many industrial glasses. Glasses with B$_2$O$_3$ display an interesting phenomenon where two opposite and competing mechanisms occur with the addition of network modifiers, which may lead to the non-monotonic scaling of many properties with composition. The first of the two competing mechanisms is the creation of non-bridging oxygens (NBOs), which decrease the rigidity of the network. The second mechanism is the conversion of boron coordination from 3-fold to 4-fold coordination with no NBOs created, which increases the connectivity of the glass network. The competition of these reactions leads to the so-called boron anomaly in borate and borosilicate glasses. Glass systems containing B$_2$O$_3$ have been of great interest because the evolution of the boron speciation enables a wide range of tunability of macroscopic properties, including glass transition temperature, fragility, elastic modulus, hardness, etc. Borosilicate glasses are the most important family of boron-containing glasses and have various industrial applications, including laboratory glass containers, optical components, substrates for liquid crystal display, and glasses for nuclear
waste immobilization. The topology of borosilicate glasses consists of three types of network forming cations: tetrahedral Si (Si\(^4\)), tetrahedral B (B\(^4\)), and trigonal B (B\(^3\)), connected by bridging oxygens (BOs). With the addition of modifiers, there are three options for the modifiers in borosilicate glasses to associate with, creation of NBOs on Si\(^4\), creation of NBOs on B\(^3\), and conversion from B\(^3\) to B\(^4\). Therefore, borosilicate glasses also exhibit a boron anomaly, and the fraction of the 4-coordinated boron is affected by both modifier content and the ratio between silica (SiO\(_2\)) and B\(_2\)O\(_3\) (K).

Understanding composition-structure-property relationships is of primary importance to design new borosilicate glass compositions for emerging applications. However, it is still challenging to extract complete and detailed structural information from existing characterization techniques, such as solid-state NMR and neutron or X-ray diffraction. Molecular dynamics (MD) simulations provide a powerful and complementary means to investigate glass properties, including structural, transport, and mechanical properties\(^{52,53}\), enabling researchers to connect the microscopic structure to the macroscopic properties.

The key input governing MD simulations is the interatomic potential, which governs the interactions between atoms and therefore the validity of the simulation results. It is hence necessary to evaluate the reliability of potentials in terms of the properties of interest before conducting any further studies. Due to the complicated behavior of the changes in the coordination number of B atoms with composition, the development of classical interatomic potentials for B-containing glasses covering a wide compositional range has proved challenging. To describe the boron coordination change, a potential usually requires incorporating composition-dependent charges and/or B–O interaction parameters\(^{51,54}\), which would make the use of the potentials tedious and reduce their transferability to other compositions. In this study, we investigate the accuracy of two recently developed B-containing potentials on the structure
and elastic properties of two commercial borosilicate glasses, Boro33 and N-BK7, and compare the simulation-obtained values with experimental data.

3.2 Results and discussion

3.2.1 Neutron structure factor

Neutron scattering is an important and common technique to probe glass structures. Therefore, to compare the structure produced by MD simulations with its experimental counterpart, a comparison between the calculated structure factor and the data from neutron scattering is necessary. The partial structure factors were first calculated from the Fourier transform of the pair distribution functions (PDF), \( g_{ij}(r) \)

\[
S_{ij}(Q) = 1 + \rho_0 \int_0^R 4\pi r^2 (g_{ij}(r) - 1) \frac{\sin(Qr)}{Qr} F_L(r) dr \tag{1}
\]

where \( Q \) is the scattering factor, \( \rho_0 \) represents average number density, and \( R \) is the upper limit of the real-space integration part (17 Å is used here, which is about half of the cubic simulation box). The function \( F_L(r) = \frac{\sin(\frac{\pi r}{R})}{(\frac{\pi r}{R})} \) is a Lorch-type window function, which is used to reduce the effect of the finite-size simulation box but causes broadening of the peaks. The total structure factor can then be calculated by:

\[
S_N(Q) = \left( \sum_{i,j=1}^n c_i c_j b_i b_j \right)^{-1} \sum_{i,j=1}^n c_i c_j b_i b_j S_{ij}(Q) \tag{2}
\]

where \( c_i \) is the concentration of the atom \( i \) and \( b_i \) is the neutron scattering length of each element (given by 5.803, 4.1491, 5.3, 3.449, 3.63, and 3.87 fm for O, Si, B, Al, Na, and K, respectively).
Figure 2-1 shows the comparison of the computed neutron structure factor from MD simulations with the experimental results from neutron diffraction. Here it can be seen that both potentials show good overall agreement with the experimental data. In the total structure factor pattern, the first sharp diffraction peak (FSDP) generally reflects the intermediate-range structure. Shi et al. found that the FSDP contains ring size information and developed a method to extract the ring size distribution from these data. The second diffraction peak corresponds to the size of the structural unit, and the peaks at higher $Q$ correspond to the local structure of the structural unit, such as Si-O, B-O, and O-O bonds. Micoulaut et al. found that the characteristic features of the FSDP change with the pressure and can be correlated with the transport properties of liquid silicate. As shown in Figure 2-1, Du’s potential predicts a closer FSDP than Wang’s potential in terms of position and magnitude compared with the experimental data, indicating that Du’s potential reproduces a more realistic ring structure (ring distribution), while Wang’s potential provides a better agreement with the neutron scattering result at high $Q$, with the exception of the third peak, which suggests that Wang’s potential reproduces a short-range structure in better agreement with the experimental result. It should be noted that Want et al. also compared the structure factor obtained from experiments and simulations and found that the medium-range structure of the glass is well reproduced. However, the samples they compare have different compositions from what we use (different K values and different modifier ions), which might imply that the potential is not able to capture the medium-range structure for our compositions.
3.2.2 Density

Table 1 compares the experimental densities of the samples with the final densities obtained through MD simulations using the two sets of potentials. The calculated densities of two samples agree well with the experimental values (less than 5% difference), especially the simulated N-BK7 (< 1%) even though BaO and CaO are not included in our simulation.

Table 3- 1: Density of the glass samples

<table>
<thead>
<tr>
<th>Condition</th>
<th>Boro-33</th>
<th>N-BK7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment</td>
<td>2.23</td>
<td>2.51</td>
</tr>
<tr>
<td>Wang</td>
<td>2.35±0.06 (+5 %)</td>
<td>2.51±0.01 (+0%)</td>
</tr>
<tr>
<td>Du</td>
<td>2.3±0.01 (+3.14 %)</td>
<td>2.48±0.01 (-0.8 %)</td>
</tr>
</tbody>
</table>
3.2.3 \( N_4 \) fraction

The coordination environment around boron is an especially important property when analyzing the structure of any boron-containing glass since the boron speciation has a major impact on the connectivity of the glass network. The coordination number of boron was computed by enumerating the number of neighbor atoms with respect to each boron within the first coordination shell. The cutoff was determined by the distance of the minimum after the first peak of the pair distribution function.

The use of Du’s potential requires the fraction of \( B^4 \) to total B \( (N_4) \) as an input parameter, which can be expressed as:

\[
N_4 = \frac{c(B^4)}{c(B^4)+c(B^3)}
\]

Eq. (3)

where \( c(B^4) \) and \( c(B^3) \) are the numbers of the three- and four- coordinated B units. Therefore, we use the model developed by Dell et al.\(^8\) (DBX model) and the two-state statistical mechanical model\(^16\) to predict the \( N_4 \) values and also as a comparison. Here we assume that \( Na_2O \) and \( K_2O \) have the same effect on the glass structure. It has been shown that the effect of types of alkali ion on \( N_4 \) value is insignificant when the ratio between alkali ion and \( B_2O_3 \) \( (R) \) is low.\(^59\) According to the DBX model, the variation of boron’s coordination can be divided into four stages:

(5) The \( Na_2O \) goes to create \( B^4 \) when \( R \) is smaller than 0.5.

(6) The additional \( Na_2O \) combines with the diborate groups formed in the first stage to form reedmergnerite groups when \( 0.5 \leq R \leq R_{max} \), where \( R_{max} \) is the ratio at which the \( N_4 \) reaches the maximum and is a function of the ratio between \( SiO_2 \) and \( B_2O_3 \) \( (K) \).

(7) The additional \( Na_2O \) creates NBOs on \( Si^4 \) in the reedmergnerite groups, which will not change the \( N_4 \) value, and this process is assumed to end when each reedmergnerite group has associated with 1.5 \( Na_2O \) molecules.
At the final stage, the additional Na₂O molecules will be distributed to the diborate groups and the reedmergnerite groups according to the relative proportion and form NBOs on Si⁴ and B³.

For the two-state statistical mechanical model, the roles of modifiers are divided into two states, formation of NBO on Si⁴ and conversion of B³ to B⁴. The model takes the competing contributions between enthalpic and entropic effects into consideration, i.e. the enthalpy difference between two states and the ratio between SiO₂ and B₂O₃. The borosilicate system in the two-state statistical mechanical model can be expressed as:

\[ xA₂O \cdot yBO \cdot zAl₂O₃ \cdot tB₂O₃ \cdot (1 - x - y - z - t)SiO₂ \]  \hspace{1cm} \text{Eq. (4)}

where A and B are alkali and alkali earth ions, respectively. Then, the equation for \( N₄ \) derived from the two-state statistical mechanical model can be expressed as follows:\(^{16}\):

\[ N₄ = \left( \min \left\{ \frac{2(x+y-z)z}{z+(1-x-y-z-t)\exp\left[-\Delta H/kT_f\right]} , z + \frac{2}{3} (1 - x - y - z - t), 2z \right\} \right) / 2z \]  \hspace{1cm} \text{Eq. (5)}

where \( k \) is Boltzmann’s constant, \( \Delta H \) is the enthalpy difference between NBO-on-Si⁴ formation and B³-to-B⁴ conversion, which is 0.072 eV\(^{16}\), and \( T_f \) is the fictive temperature. For a glass obtained with a normal cooling rate (~10 K/s), the fictive temperature can be seen as equal to the glass transition temperature\(^{60}\).

A comparison of the \( N₄ \) value predicted by two models, the \( N₄ \) values of the MD simulated samples, and the experimental values is shown in Table 3. As can be seen in Table 3, the two-state statistical mechanical model underestimates the \( N₄ \) fraction of both samples and is also smaller than the simulated \( N₄ \) fractions using both potentials. The result indicates that the two-state model might be too simple for the current glass system. For example, there are more states instead of two states, such as NBO-on-B³, existing in realistic glass systems, and also the mixed-alkali effect isn’t considered in this model. Therefore, the noncentral hypergeometric
distribution model may be a better statistical mechanical model for our samples since more factors can be taken into consideration with flexibility. The DBX model shows good agreement with the experimental data, even though the model was developed based on ternary sodium borosilicate glasses. Based on the comparison above, the $N_4$ values predicted by the DBX model are used as input parameters for the MD simulation using Du’s potential.

For the $N_4$ values of MD simulated samples, N-BK7 has a higher $N_4$ fraction due to higher modifier content compared to Boro-33. This trend is reproduced by all of the models. It is also found that Wang’s potential gives a closer $N_4$ value for Boro-33, while Du’s potential predicts a more accurate value of $N_4$ for N-BK7. The lower $N_4$ value of the N-BK7 sample predicted by Wang’s potential might result from a lower B$^3$-to-B$^4$ conversion rate. Therefore, the use of a high cooling rate in the MD simulation would affect the final coordination environment in the glass state. For Du’s potential, the $N_4$ value is an input parameter obtained from the DBX model, so the higher $N_4$ value of the Boro-33 sample predicted by Du’s potential might be generated from a higher input $N_4$ value. It is worth noting that the $N_4$ values predicted by Du’s potential are already close or higher than the experimental values, so the cooling-rate effect on Du’s potential might be less significant than that on Wang’s potential.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Boro-33</th>
<th>N-BK7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment</td>
<td>23 %$^{55}$</td>
<td>91 %$^{61}$</td>
</tr>
<tr>
<td>Wang</td>
<td>19.8±2.1 %</td>
<td>66.7±3.6 %</td>
</tr>
<tr>
<td>Du</td>
<td>52.3±2.4 %</td>
<td>90±1 %</td>
</tr>
<tr>
<td>DBX model</td>
<td>33 %</td>
<td>95 %</td>
</tr>
<tr>
<td>Two-state model</td>
<td>7.4 %</td>
<td>59.5 %</td>
</tr>
</tbody>
</table>

Table 3-2: The N4 value of simulated samples and experimental data
3.2.4 Pair distribution functions

To further investigate the potential effects on the glass structures, the local structural environment around each element is investigated by computing the pair distribution functions (PDFs). Figure 2-2 shows the Si-O, B-O, Na-O and K-O PDFs. The average Si-O distance is around 1.64 Å for both Boro33 and N-BK7 regardless of which potential is used, in good agreement with the experimental values. For the B-O PDFs, it is found that the B-O distance of samples using Du’s potential is larger than that using Wang’s potential; however, both potentials exhibit bimodal distributions and have similar differences between the two peaks (~0.06 Å). The peaks are around 1.39 Å and 1.46 Å for Wang’s potential, and 1.54 Å and 1.60 Å for Du’s potential, which correspond to the B-O bond length of 3- and 4- coordinated B atoms, respectively. The peak positions of Wang’s potential are found to be closer to the experimental values obtained from neutron diffraction experiments on alkali diborate glasses and ab initio simulation results for borosilicate glasses (3Na₂O·B₂O₃·6SiO₂), which are found to be around 1.37-1.385 Å and 1.47-1.48 Å, respectively. Similar values from different compositions may indicate that the B–O distance is not sensitive to composition. It should be noted that the A₄ parameter in Du’s potential is a function of composition and the N₄ value, which can be obtained by either experiment or model (here, we use DBX model), so that the repulsive term of the interaction force will change with these factors, resulting in the variance of B-O bond length. Since N-BK7 has more B⁴, the intensity of the peak at the higher distances (1.60 Å) is much greater than that of Boro-33. However, in the previous section, it is shown that the N₄ value of the sample using Du’s potential is always higher than that using Wang’s potential. Therefore, for the N-BK7 sample, the peak of B⁴ is less obvious for the sample using Du’s potential with N₄ > 90%. For the Boro-33 sample, Wang’s potential yields only 18% B⁴, so there is a greater difference between the two peaks compared with the sample using Du’s potential.
Figure 2-2 (c) and (d) show the local environment of the modifier. The Na-O bond length depends on Na’s role in the structure and ranges from 2.29 Å when Na forms an NBO to 2.62 Å when Na is in a charge compensator role. The Na-O peaks of Boro33 and N-BK7 are centered around 2.52 Å and 2.42 Å for Du’s potential, and 2.52 Å and 2.47 Å for Wang’s potential. The N-BK7 sample has a lower Na-O bond length because it has excess modifiers after converting all of the B3 to B4, resulting in a higher fraction of NBOs even though it has a higher $N_4$ value. The difference in K-O bond length between Boro33 and N-BK7 is small, but the peaks of the Boro33 have less clearly defined positions compared to that of the N-BK7 samples due to the small number of alkali ions. The differences in the local environment of Na and K atoms are not significant between these two sets of potentials.

Figure 3-2: (a) Si-O, (b) B-O, (c) Na-O, (d) K-O PDFs of Boro33 and N-BK7 samples using different potentials. The curves have been shifted for comparison.
Figure 3-3: (a) Si-Si, (b) B-B, (c) Na-Na, (d) O-O PDFs of Boro33 and N-BK7 samples using different potentials.

Figure 3-4: Decomposition of the B-B PDF according to B coordination.
Figure 3-3 (a) shows the Si-Si PDF calculated by two potentials. For both potentials, both Boro33 and N-BK7 show asymmetric distributions whose peaks are at 3.2 Å, similar to the values obtained from MD simulation on calcium aluminosilicate glasses, ranging from 3.17 Å to 3.2 Å depending on which potential is used\textsuperscript{68}. The experimental first-neighbor Si-Si distance for pure SiO\textsubscript{2} is 3.08 Å\textsuperscript{69}.

Figure 3-3 (b) shows that the first peak in the B-B PDF of samples using Du’s potential split into two peaks, one at around 2.31-2.39 Å and the other is at 3.03 Å, respectively. However, there is only one broad peak around 2.75-2.79 Å with Wang’s potential, which is in better agreement with the neutron scattering result on B\textsubscript{2}O\textsubscript{3} and alkali borate glasses, having the B-B distance of 2.77 Å and 2.85 Å\textsuperscript{70,71}. To account for the peak split using Du’s potential, the B-B PDF is decomposed into contributions from B\textsuperscript{3}-B\textsuperscript{3}, B\textsuperscript{4}-B\textsuperscript{4} and B\textsuperscript{3}-B\textsuperscript{4} PDFS as shown in Figure 3-4, where the superscripts represent the coordination number of a B atom. It is found that the first peak is mainly attributed to B\textsuperscript{4}-B\textsuperscript{4} PDF, and all the decomposed PDFs have contributions to the second peak. Pedesseau et al.\textsuperscript{70} found the same feature in their borosilicate glasses obtained from ab initio simulation and indicated that the peak split results from the edge-sharing polyhedra defects due to the high cooling rate, which cannot be observed in the sample obtained with experimental cooling rate. We can also see that, for samples using Wang’s potential, the first peaks of B\textsuperscript{3}-B\textsuperscript{3}, B\textsuperscript{4}-B\textsuperscript{4} and B\textsuperscript{3}-B\textsuperscript{4} PDFs are located at similar positions.
According to Fig 3-3 (c), the Na ions tend to agglomerate to form clusters, especially in the N-BK7 sample, which can be seen in Figure 3-5. This nano-segregation of alkali ions from the network, as indicated by Greaves’ modified random network (MRN) model\textsuperscript{72,73}, would be inevitable because alkali ions and NBOs tend to be coordinated to each other. This alkali-rich channel may have lower activation energy for the transport of alkali\textsuperscript{72} and also be the preferential path for crack propagation.\textsuperscript{74} For both potentials, the first peak between two sodium ions is located around 3.1 Å, which is slightly shorter than the result from \textit{ab initio} simulation, 3.25 Å. The curves of Boro-33 samples are fluctuating due to the small number of Na ions.
Figure 3-3(d) shows the O–O PDFs. As can be seen in the figure, the first peak of Wang’s sample splits into two peaks located at 2.4 Å and 2.63 Å; while only one peak at 2.6 Å exists in Du’s samples. To explain the difference, the O–O PDF is decomposed into the contributions from B³, B⁴, and Si⁴), as given in Figure 3-6. It can be seen that the first peak in the O–O PDF of Wang’s sample consists of two peaks attributed to the first-neighbor O–O distance in B³ and B⁴ at 2.41 Å and 2.39 Å, respectively. These values are in good agreement with the result from the neutron diffraction on B₂O₃ and binary borate glasses⁷¹ ranging from 2.38 to 2.42 Å and also the result from ab initio simulation on borosilicate glasses⁶⁵,⁷⁰ which found the distance of 2.38 Å and 2.42 Å for B³ and B⁴. The second peak is contributed from Si⁴ located at 2.63 Å, which agrees well with the result from x-ray diffraction for calcium aluminosilicate glasses⁷³ and for SiO₂⁶⁹, giving the values of 2.65 Å and 2.62 Å, and also the results obtained from ab initio simulations of pure SiO₂⁷⁶ and borosilicate glass⁶⁵, which are 2.59 Å and 2.66 Å, respectively. The geometry of the silicon tetrahedra can be affected by the existence of non-bridging oxygen or other network formers. However, SiO₂ is a strong network former, and also there is a significant amount of SiO₂ in our glass sample resulting in a close value to that of pure SiO₂. For Du’s potential, the O–O PDFs contributed from all of the structural units are located at around the same distance compared to that of Wang’s potential, as seen in Figure 3-6(b). This difference results from the different B–O distance between the two potentials as shown in Figure 3-2(b). For Wang’s potential, the lower B–O distance compared with Si–O distance makes the O–O distance contributed from boron units and silicon units distinguishable; while for Du’s potential, the B–O distance is close to the Si–O distance causing the unimodal distribution of O–O PDF. Therefore, we believe that Wang’s potential predicts a better local-range structure than Du’s potential, consistent with the structure factor result.
3.2.5 Bond angle distributions

The bond angle distributions are also investigated. As shown in Figure 3-7 (a), the average O-Si-O angle is around 109° for both compositions and potentials, which is expected for the Si-O tetrahedral geometry. For O-B-O angle distributions, shown in Figure 3-7(b), samples using Wang’s potential exhibit bimodal distribution, as is the case of B-O PDFs shown in Fig 2 (b). Two peaks are located at around 109° and 120°, corresponding to the O-B-O angle in the B4 and B3 units, respectively. However, samples using Du’s potential do not exhibit a bimodal distribution of the O-B-O angle because the $N_4$ value of Boro-33 using Du’s potential is about 52% so that the median value of the distribution is at between 109° and 120°, and the $N_4$ value of N-BK7 is over 90% as a result of which the peak corresponding to 3-coordinated boron units can be barely seen.
Figure 3-7: (a) O-Si-O and (b) O-B-O angle distributions of Boro-33 and N-BK7 sample using different potentials.

Figure 3-8 (a), (b), and (c) show the Si-O-Si, B-O-B, and Si-O-B angle distributions. The Si-O-Si angle distributions using the two sets of potentials show a broad spread (ranging from 110° to 180°), but the peaks are located at different positions, viz., around 151° for Du’s potential and around 140° for Wang’s potential. Both angles are close to the range of the experimental values, which are around 142°-151°.54,77,78 The lower Si-O-Si angle of Wang’s sample compared with that of Du’s sample can be related to the lower average Si–Si distance, as given in Figure 3-3(a), and it might also account for the higher density of Wang’s samples due to its less open structure.

Du’s potential also leads to bimodal distributions in the B-O-B angle, as in the B-B PDF., which are located at 90° and around 130°. The decomposition of B-O-B angle distribution is given in Figure 3-9. The peak at 90° mainly originates from the B^4-O-B^4 distribution and partially from the B^3-O-B^4 distribution and the broad peak at a higher angle is contributed from all of the angle distributions. By contrast, Wang’s potential yields a broad B-O-B peak around 155° consisting of three peaks from B^3-O-B^3, B^3-O-B^4 and B^4-O-B^4 distributions. For both potentials, the peak shape of the bond angle distributions depends on composition due to the different contributions from three bond angles, with the order of the angles as follows: B^3-O-B^3 > B^3-O-B^4 > B^4-O-B^4. We also calculate the Si-O-B angle distribution, as shown in Figure 3-8(c). The difference in peak locations for the two potentials is relatively small, which are located at 139° and 143°.
3.2.6 Elastic properties

Table 3- 3: Elastic properties

<table>
<thead>
<tr>
<th>Condition</th>
<th>Young’s modulus (GPa)</th>
<th>Bulk modulus (GPa)</th>
<th>Shear modulus (GPa)</th>
<th>Poisson’s ratio</th>
</tr>
</thead>
</table>
Table 4 shows the elastic properties of the samples obtained by different conditions. The elastic properties, viz., Young’s modulus \( E \), bulk modulus \( K \), shear modulus \( G \), and Poisson’s ratio \( \nu \), are calculated using the LAMMPS package\(^4\). The elastic compliance constant matrix is obtained by deforming the glass samples along six directions (x, y, z, xy, yz, and xz) and measuring the resulting strains. The number of matrix elements is reduced to 21 due to symmetry. The Young’s modulus and Poisson’s ratio of isotropic materials can be calculated by:

\[
E = \frac{3}{(S_{11} + S_{22} + S_{33})} \quad \text{Eq. (6)}
\]

\[
\nu = -\frac{(S_{12} + S_{13} + S_{23})E}{3} \quad \text{Eq. (7)}
\]

where \( S_{ij} \) is the element in the elastic compliance constant matrix. Since there are only two independent constants among the four elastic properties for isotropic materials, \( G \) and \( K \), can then be determined from:

<table>
<thead>
<tr>
<th>Sample</th>
<th>( E ) (GPa)</th>
<th>( K ) (GPa)</th>
<th>( G ) (GPa)</th>
<th>( \nu )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boro-33</td>
<td>64</td>
<td>35.5</td>
<td>26.5</td>
<td>0.2</td>
</tr>
<tr>
<td>(Experiment)</td>
<td>85.8±2.7</td>
<td>51.3±3.5</td>
<td>35.1±1.1</td>
<td>0.22±0.02</td>
</tr>
<tr>
<td>(Du, NVT)</td>
<td>(+34%)</td>
<td>(+45%)</td>
<td>(+32%)</td>
<td>(+10%)</td>
</tr>
<tr>
<td>Boro33</td>
<td>51.9±3.4</td>
<td>29.1±1.2</td>
<td>21.6±1.7</td>
<td>0.202±0.02</td>
</tr>
<tr>
<td>(Wang, NVT)</td>
<td>(-18%)</td>
<td>(-18%)</td>
<td>(-18%)</td>
<td>(+1%)</td>
</tr>
<tr>
<td>N-BK7</td>
<td>82</td>
<td>46.5</td>
<td>34</td>
<td>0.206</td>
</tr>
<tr>
<td>(Experiment)</td>
<td>89.4±7.4</td>
<td>60.7±4.2</td>
<td>35.6±3.25</td>
<td>0.258±0.015</td>
</tr>
<tr>
<td>(Du, NVT)</td>
<td>(+9%)</td>
<td>(+30%)</td>
<td>(+5%)</td>
<td>(+25%)</td>
</tr>
<tr>
<td>N-BK7</td>
<td>59.2±5.9</td>
<td>37.5±1.8</td>
<td>23.9±2.7</td>
<td>0.238±0.017</td>
</tr>
<tr>
<td>(Wang, NVT)</td>
<td>(-27%)</td>
<td>(-19%)</td>
<td>(-30%)</td>
<td>(+15%)</td>
</tr>
</tbody>
</table>
\[ G = \frac{E}{2(1+\nu)} \quad \text{Eq. (8)} \]
\[ K = \frac{E}{3(1-2\nu)} \quad \text{Eq. (9)} \]

As shown in Table 4, Du’s potential consistently overestimates the elastic moduli while Wang’s potential underestimates the elastic moduli compared with the experimental values even though the curvature of B-O interaction of Wang’s potential is larger than that of Du’s potential and the curvatures of Si-O interactions of both potentials are close, which can be seen in Figure 3-10. The reason for the overpredicted elastic modulus of the samples using Du’s potential might result from the overpredicted \( N_4 \) value. It should be noted that the elastic moduli of the N-BK7 using Du’s potential are closer to the experimental data than that of the Boro33 using the same potential, which might be due to the closer \( N_4 \) value. The lower elastic modulus of samples using Wang’s potential might result from the lower \( N_4 \) value.

Figure 3-10: (a) B-O (b) Si-O interaction energy of Wang's and Du's potential.
3.3 Conclusion

Two borosilicate glasses are simulated using two different sets of interatomic potentials. Overall, Wang’s set of potentials gives better agreement with experimental data in terms of local-range structure, but Du’s potential provides a better prediction of medium-range structure. It is also found that Wang’s potential offers a closer $N_4$ value of Boro33 sample to the experimental values but underpredicts the $N_4$ value for the N-BK7 sample. On the contrary, the $N_4$ value of the N-BK7 sample using Du’s potential agrees well with the experimental data, but that of the Boro33 sample is overpredicted. For elastic properties, both potentials are not able to predict accurate values compared with experimental data. Wang’s potential predicts a lower elastic modulus, which might be due to the underpredicted $N_4$ value, and Du’s potential provides a higher elastic modulus, which may result from a higher $N_4$ value. This benchmark work allows us to have a better understanding of the effects of potentials on the simulated borosilicate glasses.
Chapter 4

Atomic-Scale Mechanisms of Densification in Cold-Compressed Borosilicate Glasses

The work in chapter 3 was previously published in the following journal article:


4.1 Introduction

Glass is subject to brittle failure, particularly under sharp contact loading. However, glasses can also exhibit densification and plastic flow in response to stress, which provides an alternative means for dissipation of the applied mechanical energy. The fraction of the densification vs. flow mechanisms depends on the composition and structure of a glass. In an indentation experiment, the magnitudes of the densification and plastic flow mechanisms can be quantified by the volume recovery ratio ($V_R$) and the pile-up ratio ($V_P$), respectively, after a heat treatment at around $0.9 \ T_g$. Since the activation energy associated with volume recovery is much less than the energy required to activate plastic flow, the heat treatment enables researchers to separate the displaced volume induced by these two mechanisms. It has been shown that $V_R$ and $V_P$ can be correlated with Poisson’s ratio ($\nu$), and the magnitude of residual stress arising from the indentation process can be estimated from $\xi=1-V_R-V_P$, which is related to the driving force for cracking under indentation. However, the wide distribution of $V_R$ and $V_P$ within the range of $\nu$ from 0.2 to 0.3 and the scatter of the data in the $V_R$ ($V_P$) and $\nu$ relation indicate that
Poisson’s ratio alone is not sufficient to describe the glass deformation. For this reason, understanding the underlying structural changes of glass during the deformation process is of great importance.

Concerning the densification accompanying indentation or compression, much previous research has been devoted to investigating the structural response of oxide glasses. One mechanism for structural change under pressure is a decrease in bond angles, which was observed in both experiments and MD simulations. Another densification mechanism under pressure is an increase in the coordination number of atoms. For example, it was found using in-situ high-pressure x-ray diffraction that the Si coordination number in SiO$_2$ glass increases starting around 8 GPa of compression, and the coordination number approaches 6 at 42 GPa. It was also observed that the fraction of 4-coordinated boron ($N_4$) increases with pressure for B$_2$O$_3$-containing glasses, and Al can also exhibit various coordination numbers from 4 to 6 in Al$_2$O$_3$-containing glasses. Lee et al. reported the results of in-situ pressure-induced changes in the boron and oxygen environments of B$_2$O$_3$ glass at ambient temperature and found that the increase of $N_4$ is reversible up to 24 GPa. They also indicated that the type of modifier cations in a borate glass affects the energy barrier for the boron coordination. The conversion from B$^3$ to B$^4$ (B$^3$ and B$^4$ represent 3- and 4-coordinated boron) can be achieved by either consuming non-bridging oxygen or forming 3-coordinated oxygen triclusters. The change in the intermediate-range structure under pressure is more difficult to probe than the changes in the short-range structure. Martinet et al. used micro-Raman spectroscopy to investigate the structural changes of the densified SiO$_2$ glasses generated from cold compression and observed that the percentage of 3-membered rings increases with density. The phenomenon of the increase of 3- and 4- membered rings at the expense of the large rings was also observed in the MD simulation result of SiO$_2$ glass and borosilicate glasses. Based on the X-ray
scattering result, Meade et al. found that the first sharp diffraction peak (FSDP) of the cold-compressed SiO\textsubscript{2} glass is significantly altered under pressure. Regarding the homogeneity of the glass structure under pressure, Januchta et al. found that more random mixing of Al\textsuperscript{4} and B\textsuperscript{3} happens in the lithium aluminoborate glass under pressure, and Kilymis et al. also showed that the mixing of Si and B subnetwork increases during compression.

Nonetheless, studies related to structural changes in multicomponent borosilicate glasses are rare. In this study, we present results of MD simulations of loading-unloading hydrostatic compression for two commercial borosilicate glasses, Boro33 and N-BK7, which are silica-rich borosilicate glasses with similar Poisson’s ratios (0.2 and 0.206 for Boro33 and N-BK7, respectively) but showing different mechanical responses under indentation. We report the deformation mechanisms in these two glasses induced by pressure, including analysis in both short-range structure and medium-range structure. The contribution of each element to the densification is also investigated using Voronoi analysis.

### 4.2 Method

In the loading-unloading process, the samples are compressed isotropically at 300 K controlled by the NPT ensemble. The compression starts from 0 GPa and then the pressure gradually increases with a step of 0.5 GPa followed by a 25 ps equilibration until the pressure reaches 20 GPa. The rate is 0.02 GPa/ps following the rate used in the previous work of Kilymis et al. \textsuperscript{81}. The unloading process uses the same parameters as the loading process. Throughout all of the simulations, the integration timestep is kept at 1 femtosecond (fs) and the Nosé-Hoover thermostat and barostat were used to control the temperature and pressure (when necessary). The periodic boundary conditions are applied along all directions in each of the simulations.
It has been shown that the first sharp diffraction peak (FSDP) in the neutron scattering structure factor can reflect the intermediate-range order. For example, Shi et al. \textsuperscript{56} demonstrated that the ring size distribution can be extracted from the FSDP. Therefore, we calculated the structure factor to get a better understanding of the structural response under pressure. The partial structure factors were calculated from the Fourier transform of the pair distribution functions (PDF), $g_{ij}(r)$

$$S_{ij}(Q) = 1 + \rho_0 \int_{0}^{R} 4\pi r^2 \left( g_{ij}(r) - 1 \right) \frac{\sin(Qr)}{Qr} F_L(r) dr \quad \text{Eq. (1)}$$

where $Q$ is the scattering factor, $\rho_0$ represents average number density, and $R$ is the upper limit of the real-space integration part (17 Å is used here), and the function $F_L(r) = \sin\left(\frac{\pi r}{R}\right)/\left(\frac{\pi r}{R}\right)$ is a Lorcher-type window function used to reduce the effect of the finite-size simulation box but causes peaks broadening. The total structure factor can then be calculated by\textsuperscript{43}:

$$S_N(Q) = \left( \sum_{i,j=1}^{n} c_i c_j b_i b_j \right)^{-1} \sum_{i,j=1}^{n} c_i c_j b_i b_j S_{ij}(Q) \quad \text{Eq. (2)}$$

where $c_i$ is the concentration of the atom $i$ and $b_i$ is the neutron scattering length of each element (given by 5.803, 4.1491, 5.3, 3.449, 3.63, and 3.87 fm for O, Si, B, Al, Na, and K, respectively\textsuperscript{43}).

To understand the contributions of different elements to the densification, Voronoi analysis is performed\textsuperscript{96}. In the Voronoi analysis, the simulation box is partitioned into polyhedra (one is centered on each atom) by bisectors between each atom and its surrounding ones. By analyzing the difference in the volumes of polyhedral before and after compression, the contribution of each structural unit to permanent densification can be deduced.
4.3 Results

4.3.1 Pressure-induced densification

Figure 4-1 shows the evolution of density changes under pressure. For both potentials, Boro33 shows a large change in density during the loading-unloading process and also more permanent densification after decompression than N-BK7. This trend is in agreement with the trend of $V_R$ ratio in the indentation experiment. We can also see the samples using Bauchy potential have more densification than those using Du potential, which is probably due to the shallower pair potential well of the Bauchy potential as shown in the previous study.
The relationship between the final density after decompression and the maximum pressure applied during the process is shown for both potentials in Figure 4-2. The general trend between the two potentials is that the slope of Boro33’s curve (0.008 g/cm$^3$/GPa and 0.025 g/cm$^3$/GPa for Boro33 with Du and Bauchy potentials, respectively) is larger than that of N-BK7’s (0.0015 g/cm$^3$/GPa and 0.0054 g/cm$^3$/GPa for N-BK7 with Du and Bauchy potentials, respectively), i.e., Boro33 requires less pressure to reach the same amount of permanent density increase compared to N-BK7. The ratios between the slopes of Boro33 and N-BK7 are similar with both potentials, which are $5.69 \pm 1.59$ and $4.74 \pm 0.7$ for the Du and Bauchy potentials, respectively. It should be noted that there exists a critical maximum pressure, 5 GPa, at which the plastic deformation starts to happen for Boro33 with the Du potential, which is absent in Boro33 using the Bauchy potential.
4.3.2 Short-range structure

Coordination number

Figure 4-3: The evolutions of (a) Si$^{5}$ and (b) N$_{4}$ during the compression-decompression process where Si$^{5}$ represents 5-coordinated Si and N$_{4}$ is the ratio of the number of 4-coordinated borons to the total boron number.

Since the coordination change serves as an important response accounting for the densification, the coordination number changes of the main network formers are investigated. The amount of 5-coordinated Si (Si$^{5}$) increases during compression, which can be seen in Figure 4-3(a). It should be noted that there are insignificant amounts of 6-coordinated Si (Si$^{6}$) appearing in all the samples during compression, which are about 0.02% and 0.26% in Du’s Boro33 and N-BK7, and about 1.62% and 0.56% in Boro33 and N-BK7 using the Bauchy potentials at 20 GPa. The appearance of Si$^{6}$ may be related to the formation of silicon octahedra as seen in Figure A-1, which has also been observed in compressed SiO$_{2}$ glass$^{82}$. We notice that Boro33 and N-BK7 have a similar variation of Si$^{5}$ for Du potential (~3% at 20GPa). In contrast, the increasing amount of Si$^{5}$ in Boro33 is higher than that in N-BK7 for Bauchy potential (17.3% and 11.4% for
Boro33 and N-BK7 at 20GPa. The degree of Si\textsuperscript{5} change using Du potential is closer to what has been reported previously \textsuperscript{81}. The permanent increases of Si\textsuperscript{5} of the samples using Bauchy potential are around 0.8~2 % while for the samples using Du potential, the coordination change of Si is reversible. Lin et al. \textsuperscript{87} applied the x-ray Raman scattering method to probe the bonding state in SiO\textsubscript{2} under pressure, and they found that the coordination environment of Si is reversible after decompression from 22 GPa. This reversibility is more consistent with the results from Du potential even though our results show less amount of Si\textsuperscript{6} compared to the experiment, which may be attributed to the small timescale in the simulations. For the B environment, the variation of \(N_e\) in Boro33 is higher than that in N-BK7 for both potentials due to more initial B\textsuperscript{3} in Boro33, and samples using Bauchy potential also have more changes than Du potential, as seen in Figure 4-3(b). Note that there are only B\textsuperscript{3} and B\textsuperscript{4} existing in the glasses. Lee et al. \textsuperscript{89} investigated the bonding changes of B\textsubscript{2}O\textsubscript{3} under cold-compression using inelastic X-ray scattering and found that the coordination change of B is reversible after decompression from 22.5 GPa. Therefore, the less permanent change of B coordination of samples using Du potential is in better agreement with the experimental result compared to Bauchy potential.

The coordination environment around oxygen is also calculated. As can be seen in Figure 4-4, there are more NBOs in N-BK7 than in Boro33 due to the existence of more alkali ions in N-BK7. Also, a small concentration of oxygen triclusters is observed at 0 GPa in all the samples, and Boro33 has more oxygen triclusters compared to N-BK7 for both potentials. During compression, the NBOs are consumed and the amount of triclusters increases with pressure, which results from the increase of Si and B coordination numbers. However, we can see there is a larger decrease in the percentage of NBO in N-BK7 than that in Boro33 due to the higher initial NBO amount in N-BK7 while the concentration of oxygen triclusters in Boro33 increases more rapidly than that in N-BK7 resulting from the more free volume in Boro33 (can be correlated with Voronoi volume (Sec. D)), enabling an easier increase in O coordination number.
In sum, the above coordination analysis suggests that Du potential provides a more realistic behavior in terms of the mechanical response of the coordination of Si and B. The higher rate of coordination change with pressure of samples using Bauchy potential may result from its shallower potential well. It causes more increase in small rings (see section III.c.ii) and also leads to unrealistic increases of mechanical properties, such as hardness and elastic moduli, with pressure.

**Pair distribution function (PDF)**

Figure 4-4: The evolutions of the percentage of NBOs and oxygen triclusters during the whole process, where solid lines represent Boro33 and dash lines represent N-BK7. (a) and (b) are the results of the simulations using Du and Bauchy potential, respectively.
Figure 4-5 shows the Si-O and B-O PDFs during the process, including the initial PDFs, the PDFs at 20 GPa, and the PDFs after decompression of the two types of glasses. It can be seen that the Si-O peaks shift to smaller distances and the distributions become broader at 20 GPa.
all of the samples. It is worth noting that the amount of Si-O pair with larger bond distance increases slightly for Bauchy potential, which corresponds with the result of the increasing coordination number of Si. After decompression, the peak positions almost restore to their initial positions, but the magnitudes decrease slightly. Boro33 has a more permanent change in peak magnitude than N-BK7 for both potentials.

The B-O PDF usually exhibits two sub-peaks corresponding to B³-O and B⁴-O pairs, which are more discernable between Boro33 and N-BK7 using Bauchy’s potential due to the difference in $N_d$ value. The distributions generally have a right-shift due to the conversion from B³ to B⁴ with the exception of Du N-BK7 as a result of its high $N_d$ value (~90%). Therefore, the left-shift of Du N-BK7 indicates the decrease of B⁴-O bond distance by 0.04 Å, and this change can also be observed in the PDF of Bauchy N-BK7 where the peak position of B⁴-O shifts from 1.467 to 1.447 Å (Figure 4-5(h)). After the loading-unloading process, all of them have permanent changes except N-BK7 using the Du potential, which is in agreement with their $N_d$ changes (Figure 4-3(b)).

![Figure 4-6](image): The Na-O PDFs of N-BK7 in (a) Du potential and (b) Bauchy potential.
The Na-O PDFs of N-BK7 are also presented in Figure 4-6. It can be seen that the Na-O distances decrease significantly and the peak magnitudes increase for both potentials at 20 GPa. The large decreases in Na-O distance (by 4.5% and 6% for N-BK7 using the Du and Bauchy potentials, respectively) contribute a big portion of densification during compression. However, they almost recover to their initial states after decompression.

**Average bond angle**

![Figure 4-7: The average bond angle evolutions of different bond angle types in (a) Du Boro33, (b) Bauchy Boro33, (c) Du N-BK7, and (d) Bauchy N-BK7. In every compression-decompression curve where the decompression paths are under the compression paths.](image)
In Figure 4-7, we present the average bond angle evolutions with pressure for both compositions and potentials. We can see that the bond angle of O-Si-O has insignificant change during the whole process for all conditions, indicating the strong angular constraint of O-Si-O. It should be noted that the distribution of the O-Si-O bond angle becomes wider under pressure, indicating a distortion in the Si tetrahedral units. Also, the O-Si-O with the bond angle of low angles (~90°) emerges during compression, which is in agreement with the coordination number results that Si octahedron appears at high pressures (Figure A-2, 3, 4, 5 (a)). The main change of the O-B-O bond angle mainly results from the B$_3$-B$_4$ conversion. Therefore, the average bond angles decrease toward 109°, and the Boro33 glass exhibits a higher decrease in the O-B-O bond angle than the N-BK7 for both potentials due to the higher proportion of B$_3$, in agreement with the result from Figure 4-2(B). Again, samples using the Bauchy potential have a more bond angle decrease compared to those using the Du potential.

For the mechanical response of oxygen-centered bond angles, such as Si-O-B and Si-O-Si, larger changes in response to pressure are shown during the compression/decompression process compared to O-Si-O and O-B-O bond angles. The order of the changes of these bond angles is in agreement with the order of the relative strength of these constraints in temperature-dependent constraint theory (TCT). TCT has been applied to predict the glass transition temperature ($T_g$) of borosilicate glasses, which shows that the angular constraint centered on oxygen, i.e., the γ constraint, is more flexible compared to other angular constraints. We also observe that the Si-O-B bond angle decreases more than the Si-O-Si bond angle, and the Si-O-B is further decomposed into Si-O-B$_3$ and Si-O-B$_4$ distributions. It is observed that the Si-O-B$_4$ bond angle decreases more significantly with pressure and has a higher permanent change than the Si-O-B$_3$ bond angle, which reflects the weaker angular strength of Si-O-B$_4$ compared to that of Si-O-B$_3$. The weaker angular strength of Si-O-B$_4$ may be due to the lower bond strength of B$_4$-O (B$_4$-O: 373 kJ/mol; B$_3$-O: 499 kJ/mol) and needs further study.
4.3.3 Medium-range structure

**Structure factor**

As shown in Figure 4-8, all the structure-factor distributions shift to the higher frequency at 20 GPa, representing the overall densification, except for the positions of the third peak, which have no change during the process. Besides the peak position, the magnitude of FSDP decreases with increasing pressure (Figure 4-9). After decompression, the permanent changes of the FSDP of Boro33, i.e., peak position and magnitude, are larger than those of N-BK7 for both potentials. The structure factor of N-BK7 using the Du potential almost recovers to its initial state, similar to the changes in the short-range order. For other samples (Du’s Boro33, Bauchy’s Boro33 and N-BK7), the peaks at high frequency restore to their initial positions mostly with a slight decrease in magnitude, but the FSDPs exhibit much larger permanent changes compared to other peaks, suggesting that the permanent densification may result from the change in the intermediate-range order. The permanent changes at high frequency in Boro33 with the Bauchy potential are much larger than that in other samples, which may reflect the largest permanent change in short-range structure among all the samples as we have seen previously.
Figure 4-8: The structure factor of (a) Du Boro33, (b) Bauchy Boro33, (c) Du N-BK7 and (d) Bauchy N-BK7 at different stages.

Figure 4-9: The FSDP in the structure factor of (a) Du Boro33, (b) Bauchy Boro33, (c) Du N-BK7, and (d) Bauchy N-BK7 at different stages.
Ring statistics

Figure 4-10: The ring distributions of (a) Du Boro33, (b) Bauchy Boro33, (c) Du N-BK7 and (d) Bauchy N-BK7 at different stages. The lines in Figure 4-10 are for visual guidance only and the numbers in parentheses represent the total ring numbers.

The ring statistics during the loading and unloading process are carried out using the R.I.N.G.S code. In our analysis, we take all the network formers, including Si, B, Al, and O into consideration. The results are shown in Figure 4-10 where the ring size represents the number of network former cations in a ring. First, we can see that the total ring number of Boro33 is more than that of N-BK7 due to the lower non-bridging oxygen content of Boro33 using both potentials. We can observe a general trend that the 2- to 7-membered rings increase with increasing pressure and the numbers of the ring sizes larger than 7-membered decrease for
Boro33, and for N-BK7, this critical ring size is the 8-membered ring. By calculating the number ratio of non-Si elements (i.e., B and Al) in a ring (Figure A-6), we notice that the increasing number of smaller rings is accompanied by the increasing number ratio of non-Si elements, suggesting that the coordination number changes of B and Al play an important role in the change of ring statistics under pressure. The trend of the increase of the small rings at the expense of large rings is in agreement with the previous studies 81,83,95. Interestingly, the population of some large rings increases after unloading, which has also been observed in the work of Kilymis et al. 81. It is also found that Boro33 has a larger relative change in the ring distribution compared to N-BK7.

4.3.4 Voronoi volume
To understand the contributions of different elements to the densification, Voronoi analysis is performed. Figure 4-11 shows the percentages of the total Voronoi volume change of different element types after decompression. It can be seen that oxygen contributes the most amount of densification since it is the most abundant element in both glasses. In terms of cations, B leads to more densification in Boro33 compared to that in N-BK7 even though they have similar B$_2$O$_3$ concentrations. In contrast, the modifiers, i.e., Na and K, result in more change in N-BK7 than in Boro33. This result shows that the dominant elements responsible for the densification are different in the two compositions.

Since oxygen is the dominant species in both glasses, we further look into the relationship between the initial Voronoi volume per O atom and the permanent volume difference per O atom after decompression, as shown in Figure 4-12. We can see that these two properties have an approximately linear relation with a negative slope, i.e., a higher initial Voronoi volume leads to a higher degree of permanent densification. Note that some oxygens with smaller initial Voronoi volumes expand after decompression. Boro33 has a wider distribution over the initial Voronoi volume compared to N-BK7 for both potentials, which explains the higher densification degree of Boro33. It can be also seen that the Baauchy potential provides wider distributions for both compositions than the Du potential and in turn leads to a higher densification degree.
Figure 4-12: The relations between each oxygen’s Voronoi volume difference/atom after decompression and their initial Voronoi volume/atom.
Since a Voronoi cell is constructed based on the distance between the central atom and its surrounding atoms, the average densification degrees after decompression of different cation types are also worth investigating to understand the effects of different cations on the densification. As can be seen in Figure 4-13, besides alkali ions, 3-coordinated cations, such as B$^3$ and Al$^3$, have the highest densification degree than other network former cations. In contrast, cations with higher coordination number, such as Si$^4$, B$^4$ or Si$^5$, have smaller change or even exhibit expansion behavior and the expansion degree increase with the non-bridging oxygen amount. The silicon tetrahedron is relatively stable, which has only a slight change in Voronoi volume. By comparison, the trend is similar between the two compositions using both potentials.

4.4 Discussion
In this study, we performed the loading-unloading hydrostatic compression simulations on two multicomponent borosilicate glasses, Boro33 and N-BK7, which have similar boron concentrations but different amounts of alkali ions, and two potentials were used for comparison in the simulations. By analyzing the difference in structural response between two glasses in terms of short-range structure, intermediate-range structure, and also the Voronoi volume, we have a better understanding of the composition dependence of the structural changes induced by densification.

Oxygen-centered bond angle change has been shown to play an important role in the densification process of oxide glasses\textsuperscript{80,81,83–86}. In this study, we also observed that Si-O-Si and
Si-O-B bond angles have more permanent changes compared to other bond angles. However, as can be seen in Figure 3-14, the permanent change of Si-Si distance, associating with the Si-O-Si bond angle, is tiny, which can only account for a small portion of the densification after decompression if the linear change of the Si-Si distance is used. Therefore, the coordination number function is also presented in Figure 3-15, and we can see that the difference between the initial state and the final state mainly starts from the distance of the first valley in the SiSi PDFs, suggesting that the densification may mainly result from changes in intermediate-range order. In the structure factor calculation, the change in FSDP can be correlated to the length scale of the intermediate periodicity with the expression

\[
\left(\frac{V}{V_0}\right)^{1/3} = \frac{d}{d_0} \sim \frac{q_0}{q}
\]

Eq. (2)

where \(V/V_0\) is the volume strain, \(d/d_0\) is the linear strain, \(q\) is the FSDP position, and the subscript 0 indicates the values at 0 GPa. Table 2 shows the comparison between the permanent densification amount and the values calculated from the changes of FSDP. The decreases in the length scale of intermediate-range order are commensurate with their densification degree, indicating that the change in intermediate-range structure is responsible for densification which may result from the accumulative changes in the short-range structure. The ring statistics show that the amount of smaller rings increases in response to the increase of density, and Boro33 has more permanent change than N-BK7.

By performing the Voronoi volume analysis, an approximately linear relation between Voronoi volume difference/oxygen atom after decompression and the initial oxygen Voronoi volume/atom is observed. The existence of more modifiers leads to N-BK7 having a smaller initial average Voronoi volume/atom and narrower initial oxygen Voronoi volume/atom.
distribution compared to Boro33, causing less structural changes in response to pressure as we have seen in the analyses of short- and intermediate-range structure.

A detailed analysis of the permanent difference in Voronoi difference/atom of each cation type reveals that 3-coordinated network former cations can contribute more densification, but a higher coordination number provides a minor or negative effect on the densification. The result is consistent with the conclusions by Januchta et al. that $\text{B}^3$ and $\text{Al}^3$ have better abilities to self-adapt in response to pressure, i.e., via increase of coordination number, and the crack resistance increases with increasing self-adaptivity of a glass network. Our analysis provides a quantitative way to compare the contributions to the densification from different cations.

<table>
<thead>
<tr>
<th></th>
<th>Du Boro33</th>
<th>Du N-BK7</th>
<th>Bauchy Boro33</th>
<th>Bauchy N-BK7</th>
</tr>
</thead>
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<td>0.952</td>
<td>0.989</td>
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<td>1</td>
<td>0.921</td>
<td>0.975</td>
</tr>
</tbody>
</table>
Chapter 5

Pressure Effects on Shear Deformation of Borosilicate Glasses

The work in chapter 4 was previously published in the following journal article:


5.1 Introduction

Understanding the cracking behavior of oxide glasses under sharp contact is challenging due to not only the complicated stress field in the samples, but also the composition dependence of the mechanical behavior of glasses. Characterized by the cracking pattern and the dominant plastic response under the indentation experiment, glass compositions can be roughly classified as anomalous glasses (e.g., pure silica), normal glasses (e.g., most silicate glass) and intermediate glasses (e.g., N-BasF from SCHOTT). The anomalous glasses exhibit cone cracking under the indentation experiment, where the plastic response is dominated by densification. In contrast, normal glasses feature radial-median cracking and apparent pile-up which results from plastic flow. It has been shown that this difference in the mechanical response to indentation can be ascribed, at least in part, to the glass’s Poisson ratio: densification is preferred in glasses with relatively low Poisson’s ratio while the plastic flow is preferred in glasses with high Poisson’s ratio. Although this classification method is simple and attractive, exceptions can be observed if the prediction is solely based on this criterion. To improve the crack resistance of glasses, a better understanding of the link between composition, structure, and mechanical response is necessary.
The densification behavior under pressure has drawn a lot of attention including its mechanism and impacts on the mechanical properties from both experimental and simulation research. It has been shown that the densification process may involve two mechanisms: a decrease of oxygen-centered bond angle and an increase of coordination number. Densification is an important mechanism to dissipate the mechanical energy under sharp contact, and hence the addition of the atoms with high self-adaptivity in terms of its coordination environment, such as boron (B), has been shown to be able to increase the crack resistance of oxide glass. However, in comparison with densification, the plastic flow behavior of oxide glasses has received less attention and is not clearly understood yet.

Unlike many crystalline materials where dislocations are the main plasticity carrier, in glasses, it is difficult to identify the structural response for the plasticity. Some models have been proposed to account for the shear mechanism under shear for non-crystalline materials, but most of them are developed based on metallic and colloidal glasses. Mantisi et al. investigated the mechanical response of silica glass under shear and hydrostatic pressure and found that the shear yield stress decreases with increasing pressure within a threshold pressure of 8 GPa due to the homogenization of atomic displacement. Molnar et al. studied the effects of composition and pressure on the elastic moduli and shear response of sodium silicate glasses. They observed the same phenomenon where the shear stress decreases under pressure, but this behavior gradually disappears with increasing sodium amount. By introducing the density as an internal variable, a yield function evolves from the elliptic surface into a Drucker-Prager criterion with increasing density. They also found that sodium weakens the local elastic properties and acts as a catalyst for the local plastic rearrangement. Nevertheless, the shear behavior of multicomponent borosilicate glasses has been rarely studied in the literature.

In this study, we applied pure shear deformation to two multicomponent borosilicate glasses, Boro33 and N-BK7, at different pressures using molecular dynamics simulations to study
the composition and pressure effects on the mechanical responses of these two borosilicate glasses. Boro33 and N-BK7 are both silica-rich glasses with a similar amount of boric oxide (B$_2$O$_3$), but different ratios between silica and alkali ions. They have similar Poisson’s ratios (0.2 and 0.206 for Boro33 and N-BK7, respectively) but different mechanical responses to the indentation, which makes them a good pair of models for comparison.

5.2 Methods

In the deformation process, the generated samples were compressed first to the specified pressures at 300 K by gradually increasing the pressure with a small increment of 0.5 GPa followed by a 25 ps equilibration controlled by the NPT ensemble. This pressurization rate follows the rate used in our previous work. The samples were then subjected to pure shear deformation to the strain of 0.8 under the specified pressures achieved in the prior process. An integration time step of 1 fs and periodic boundary conditions along all directions are used in all simulations.

To evaluate the average shear stress experienced by each element type during the deformation, the virial stress is calculated by:

$$\sigma_i = \frac{1}{V_i} \left( m_i v_i^2 + \vec{r}_i \cdot \vec{F}_i \right)$$  (1)

where $\sigma_i$ is the stress experienced by the atom $i$, $V_i$, $m_i$, $v_i$ and $\vec{r}_i$ are the volume, mass, velocity, position vector of the atom $i$, and $\vec{F}_i$ is the resultant force applied by all the other atoms (1 …$i$-1, $i$+1 … $N$) on the atom $i$. Since the volume of each atom is not well-defined, the Voronoi volume calculated from LAMMPS is used to assess the volume of each atom. The atomic shear stress applied to each atom then can be estimated according to:
\[ s^2 = \frac{1}{6} \left[ (\sigma_{xx} - \sigma_{yy})^2 + (\sigma_{xx} - \sigma_{zz})^2 + (\sigma_{yy} - \sigma_{zz})^2 + 6(\sigma_{xy}^2 + \sigma_{xz}^2 + \sigma_{yz}^2) \right] \] \hspace{1cm} \text{……(2)}

where \( \sigma_{ij} \) represents the components of the stress tensor calculated from eq (1). The average shear stress of each element type is then calculated by averaging the shear stress over the atoms of the same element type.

\[ \text{5.3 Results} \]

\[ \text{5.3.1 Shear deformation} \]

Figure 5-1 shows the stress-strain curves of pure shear deformation at different pressures for Boro33 and N-BK7. For both glasses, the softening behavior, followed by the flow phase, happens at low pressures, and gradually disappears with increasing pressure. In contrast to the samples at low pressures, the stresses of the samples at high pressures continuously increase until reaching the plateau at high strains. It can be observed that the pressure effect also influences the yield strength and strain, which decreases when the pressure is either greater or smaller than 0 GPa.

The shear modulus was evaluated as the slope within a small strain (0.02) from the stress-strain curves at different pressures for both glasses, as shown in Figure 5-2. At 0 GPa, the calculated shear modulus (37 GPa) of N-BK7 is close to its experimental value (34 GPa) and higher than the calculated shear modulus of Boro33, which is in agreement with the experimental trend even though the calculated shear modulus of Boro33 is overpredicted by ~20%, might be due to the overpredicted N\textsubscript{4} value. In the tensile region, the shear modulus of N-BK7 and Boro33 have opposite trends in response to the tensile stress. The shear modulus of N-BK7 decreases with increasing tensile stress, whereas that of Boro33 increases first followed by a
decrease when the stress is larger than 6 GPa. In the compressive region, the pressure has little effect on the shear modulus of N-BK7 when the pressure is smaller than 10 GPa, but the shear modulus of Boro33 has a minimum of around 2 GPa. The shear moduli of both Boro33 and N-BK7 increase when the pressure is above 10 GPa.

The maximum shear stresses as a function of the applied pressure for both glasses are shown in Figure 5-3. Solid symbols represent the samples that exhibit ductile behavior during the deformation, and the open symbols indicate that the fracture behavior happens at the end of the deformation. N-BK7 has a smaller shear strength compared to Boro33 in both tensile and compressive sides, indicating that N-BK7 has less resistance to shear deformation and crack initiation. Moreover, N-BK7 also has a lower critical pressure at which the transition between brittle and ductile behavior happens than Boro33.

Figure 5-1: Stress-strain curves of Boro33 and N-BK7 under shear deformation at different pressures.
Figure 5-2: Pressure dependence of the shear modulus for Boro33 and N-BK7. The error bar represents the standard deviation of the data. The cross symbols represent the experimental data points at 0 GPa.

Figure 5-3: Maximum shear stress during shear deformation as a function of pressure for Boro33 and N-BK7. The solid symbols represent the samples exhibit ductile behavior during the
deformation, and the open symbols indicate that the fracture behavior happens at the end of the deformation. Some error bars are the same size or smaller than the symbols.

5.3.2 Density, coordination number, and bond-angle changes induced by shear deformation

Figure 5-4 shows the density evolution during shear deformation at different pressures for Boro33 and N-BK7. It can be seen that the shear-induced densification happens in both glasses except N-BK7 at 0 GPa and -2 GPa. The difference in initial density and its evolution between the two glasses becomes less with increasing pressure. The strain interval at which the density change rate is accelerated matches the transition region in the stress-strain curves, which is around 0.2 ~ 0.3, and the density also reaches a steady-state in the flow phase for all glasses except the N-BK7 at -2 GPa which keeps decreasing with strain.

The coordination number evolution of each network former is analyzed as shown in Figure 5-5. Generally, with increasing strain, the fractions of oxygen triclusters (3-coordinated O), NBO (non-bridging O), Si\(^5\) and Si\(^3\) (the superscript represents the coordination number) increase for both glasses. Besides, the fractions of tricluster and Si\(^5\) increase, and NBO and Si\(^3\) decrease with increasing pressure. One major difference between Boro33 and N-BK7 is the boron-coordination evolution: the fraction of B\(^4\) increases in Boro33 but decreases in N-BK7 during the deformation. However, this difference decreases with increasing pressure due to the saturation of B\(^4\). It can also be observed that, for the O coordination environment, Boro33 has a higher amount of oxygen triclusters due to the existence of Al, but N-BK7 has more NBO due to its higher alkali amount. Regarding the Si coordination environment, Boro33 has a higher increase in Si\(^3\) but a lower increase in Si\(^5\) with pressure and strain compared to N-BK7.
The bond angle change has been shown to be another mechanism accounting for densification. Thus, the average bond angle evolutions of Si-O-B, Si-O-Si, O-Si-O, and OBO at different pressures are calculated, as shown in Figure 5-6. The initial bond angles of Si-O-B and Si-O-Si of N-BK7 are less affected by the applied pressure compared to that of Boro33 due to the existence of the alkali. At low pressures, the average bond angles of Si-O-B and Si-O-Si decrease with increasing strain, and the evolutions of the average bond angle of O-B-O reflect the changes in the coordination environment of B. With increasing pressure, the changes in the bond angle of Si-O-B, Si-O-Si, and O-B-O become less during shear deformation. However, the decrease of O-Si-O bond angle increases, reflecting the increase of Si$^5$ at higher pressures.

Figure 5-4: The density evolutions under shear deformation at different pressures for Boro33 and N-BK7.
Figure 5-5: Coordination evolution of each network formers during shear deformation at different pressures. (Dash-dotted lines: -2 GPa, solid lines: 0 GPa, dotted lines: 10 GPa, and dashed lines: 20 GPa).
Figure 5-6: The bond angle evolutions of (a) Si-O-B, (b) Si-O-Si, (c) O-Si-O, and (d) O-B-O at different pressures for Boro33 and N-BK7. Solids lines represent Boro33, and dashed lines represent N-BK7.

5.3.3 Microscopic analysis

Atomic shear stress

Figure 5-7 shows the average shear stress evolution of each element type during the deformation. For B and Si (Figure 5-7 (a)-(d)), the yield stresses decrease with increasing pressure. However, in the flow phase, the shear stress of Si is less affected by the applied pressures compared to B. It can be seen that the shear stress of Si in N-BK7 at 20 GPa even
exceeds that at 0 GPa at the end of the process. One can find that the stress level of Si in N-BK7 is lower than that in Boro33, which may be ascribed to the higher amount of NBO (Figure 5-5(b)). However, the stress levels of B are similar in both glasses even though they have very different B⁴ concentrations at small pressures. In comparison to B and Si, the shear stress of O is insensitive to pressure and composition during the whole process, and the stress levels in Boro33 and N-BK7 are also similar (Figure 5-7 (e) and (f)). Figure 5-7 (g) and (h) show the shear stress evolutions of alkali, i.e., Na and K. The stress level of alkali is much smaller than that of network formers, explaining the lower yield stress of N-BK7. In contrast to B and Si, the shear stress of alkali increases with increasing pressure, especially for K.
Figure 5-7: Average shear stress of each element type during shear deformation at different pressures. In (g) and (h), solid lines and dashed lines represent Na and K, respectively.
Nonaffine displacement analysis

To measure the plastic deformation degree in the sample, the nonaffine displacement, which is a good measure of plastic deformation as shown in the previous study [118], is calculated. By subtracting the affine deformation, the nonaffine displacement reflects the diffusion behavior induced by shear deformation. Figure 5-8 shows the nonaffine displacement distributions at strain=0.2 and 0.4 and 0 GPa and 20 GPa for Boro33 and N-BK7. One can observe a general trend in Boro33 and N-BK7 that at strain=0.2, which is when samples are about to yield, more plastic deformations happen in the samples at 20 GPa. However, at strain=0.4, these local plastic deformations develop within confined regions at 0 GPa while distributing more homogeneous at 20 GPa. Also, the nonaffine displacement distributions in N-BK7 are more inhomogeneous than Boro33. For visualizing the shear localization more clearly, the samples were sliced and the nonaffine displacements were averaged over each slice along the shear direction, as shown in Figure 5-9. We can see that the distributions become more homogeneous with increasing pressure for both glasses except the N-BK7 at -2 GPa, which exhibits more homogeneous distributions compared to that at 0 GPa. The possible explanations for this exception are proposed in the Discussion section. The mean-squared displacement (MSD) evolutions during the deformation are calculated, as shown in Figure 5-10. It can be seen in Figure 5-10(a), the MSD curves can be divided into three phases according to their slopes for both glasses: an initial stage (phase I) with low MSD, a transition region (phase II) in which the slope changes abruptly, and a final stage (phase III) where the MSD increasing rate is in between that in phase I and phase III. The slope in phase II is affected by pressure more significantly compared to phase I and phase III, and it increases with decreasing pressure except for the N-BK7 at -2 GPa whose slope in phase II is lower than that at 0 GPa. This trend can be correlated with the trend of the pressure dependence of the inhomogeneity degree of nonaffine displacement distributions, which is characterized by
calculating the difference between the maximum and minimum in the sliced nonaffine displacement profile at strain = 0.4 (Figure 5-9), as shown in Figure 5-11. This correlation indicates that the steep MSD increase in phase II at low pressures can be associated with the formation of the shear localized region. Interestingly, it is observed that the slope reflects the stress level in the stress-strain curve. In the flow phase (phase III), the slopes of MSD are not affected by the applied pressure apparently for both glasses, consistent with their pressure dependences of the flow stress. Also, the slopes of phase III in N-BK7 are higher than those in Boro33, in agreement with its relatively lower resistance to shear flow (See Figure 5-1). Figure 5-10(b)(c)(d) shows the MSD evolution curves of the individual element type. The MSD values of alkali ions are ~5 times as high as that of network formers, i.e., Si and B, and B is more mobile than Si in both glasses.

Figure 5-8: The nonaffine displacement distributions at strain=0.2 and 0.4 and at 0 GPa and 20 GPa for Boro33 and N-BK7.
Figure 5-9: The average nonaffine displacement profiles along the shear direction of Boro33 and N-BK7 at different pressures. The peaks in the profiles are where shear localizations happen.

Figure 5-10: The average nonaffine MSD evolutions for (a) all atoms, (b) alkali atoms, and (c)(d) B and Si atoms, during shear deformation for Boro33 and N-BK7 at different pressures. The three shaded areas in (a) approximately designate three phases during shear deformation. Please note that the widths of phases in Boro33 and N-BK7 are slightly different.
To understand the dynamic heterogeneity during shear deformation, the nonaffine displacement determined by the current configuration and the previous configuration with a time interval of 10 ps is used for the following analysis. The participation ratio (PR) is defined by

$$P_R = \frac{\langle u^2 \rangle^2}{\langle u^4 \rangle}$$

where $u$ is the nonaffine displacement magnitude and the angular brackets mean the averages over all atoms, to characterize the dynamic heterogeneity. $P_R$ ranges from $1/N$ for the isolated movement of an atom with a finite $u$ to 1.0 for the full correlated motion of all atoms with the same $u$, and $P_R = 3/5$ for a Gaussian distribution of displacement. Figure 5-12 shows the evolutions of $P_R$ at different pressures for both glasses. The $P_R$ increases with increasing pressure indicating that the structural response within a short time interval becomes more

Figure 5-11: Maximum nonaffine displacement difference in Figure 5-9 and the MSD difference in phase II in Figure 5-10(a) as functions of pressure.
homogeneous under pressure and the accumulation of the movement of atoms within each time
interval causes the difference in the final plastic deformation distribution between different
pressures (Figure 5-9). This trend has also been observed in other materials. It can also be seen
that the increase in $P_R$ due to the pressure for N-BK7 is less than that for Boro33.

The plastic deformation in non-crystalline materials has been shown to be induced by
localized rearrangements. Therefore, the extreme values of the nonaffine displacement
distribution are crucial to induce localized rearrangements since the atoms with large strain can
no longer be accommodated by the matrix elastically. The nonaffine displacement of each
atom is arranged in ascending order, and the value of 1 Å at which the nonaffine displacement
curve is about to take off is chosen as the threshold value to filter out the atoms with significantly
large displacement, which are referred to as local maxima. Figure 5-13 shows the evolutions of
the cumulative number of local maxima during the deformation and two regions can be
distinguished by the different slopes. The increasing rate of local maxima is slow in the elastic
part and increases when the system enters into the flow phase. N-BK7 has more local maxima
compared to Boro33 at every pressure, but for both glasses, the local maxima number decreases
with increasing pressure. The reduction of local maxima numbers combined with the increase of
participation ratio with pressure suggests that the atoms in the samples at high pressures can
rearrange more efficiently to reach the same strain level compared to the samples at low
pressures.

To understand the element type responsible for the plastic deformation, the concentration
of local maxima is analyzed. The local concentration of each element type is normalized to its
global concentration, so the normalized value of an element type greater than 1 means the
localized rearrangements tend to be initiated by it. Figure 5-14 (a) and (b) show the normalized
concentration evolutions of B, Si, and alkali ion at 0 GPa, and Figure 5-14(c) and (d) are the
zoom-in figures for B and Si in Figure 5-14(a) and (b). For both glasses, the alkali concentrations
in local maxima are much higher than the concentration of Si and B, especially in the elastic region. However, the alkali concentration decreases gradually and reaches a steady state in the flow phase. Note that the alkali concentration of local maxima in Boro33 is much larger than that in N-BK7 even though the alkali amount in Boro33 is little, which may result from the larger molar volume in Boro33 enabling easier movement. As to the network formers, the Si and B concentrations increase with increasing deformation and also reach plateaus when entering into the flow phases. The Si concentrations in both glasses are smaller than 0.5, indicating that the Si structural unit is relatively stable during shear deformation. However, an interesting difference can be observed in the B concentration between the two glasses. The B concentration in the flow phase fluctuates above 1 for Boro33, whereas it fluctuates below 1 for N-BK7. The difference indicates that the deformation mechanisms for Boro33 and N-BK7 are different. Plastic deformation tends to take place around B ions for Boro33 while it tends to occur around alkali ions for N-BK7 due to the difference in their alkali amount. The nano-segregation of alkali ions from the network in N-BK7 was observed in our previous study. Thus, we can also deduce that plastic deformation is prone to taking place at the alkali-rich regions for N-BK7. We further investigate the average cumulative nonaffine displacement of each type of structural unit, as shown in Figure B-3 and Figure B-4. It is found that $B^3$ and $Si^5$ have relatively higher mobility compared to other structural units, and $B^4$ is also more active than $Si^4$. 
Figure 5-12: The PR evolutions at different pressures for (a) Boro33 and (b) N-BK7.

Figure 5-13: Evolutions of the cumulative number of local maxima during the deformation. The solid lines represent Boro33, and the dashed lines represent N-BK7.
Discussion

In this study, pure shear deformation is applied to two multicomponent borosilicate glasses, Boro33 and N-BK7, at different pressures to investigate the pressure effects on their mechanical response. We observed that the pressure effects on shear moduli of the two glasses are different. The shear modulus of N-BK7 is more sensitive to the tensile stress than that of Boro33, which can be ascribed to more B⁴⁺ in N-BK7 induced by a higher amount of alkali ion. It has been shown that the bond-breaking event associated with B⁴⁺OSi⁴⁺ → Si⁴⁺O⁻ is much more preferential compared to others under tension stress causing N-BK7 to lose its rigidity more

Figure 5-14: The normalized concentration of alkali, B and Si in local maxima for (a) Boro33 and (b) N-BK7 at 0 GPa. (c) and (d) are the zoom-in figures of (a) and (b).
easily with increasing tensile stress \(^{124}\). However, the shear modulus of N-BK7 is relatively stable from the pressure of 0 GPa to 10 GPa, but that of Boro33 exhibits a minimum at 2 GPa. In the previous work \(^{98}\), it was found that alkali ions tend to form clusters in N-BK7. These alkali-rich regions tend to densify preferentially under pressure \(^{118}\), but the densification of these regions does not affect the number of constraints (rigidity) in the sample \(^{125}\). For Boro33, its minimum in modulus is in agreement with the elastic moduli anomaly found in silica \(^{126-128}\) and also silicate glasses \(^{118}\). It has been shown that the critical composition at which the transition between anomalous and normal behavior happens is located at 15 \% \(\text{Na}_2\text{O}\) \(^{129}\) and the anomalous behavior mainly results from the isotropic collapse of the glass’s network due to more free volume in the structure \(^{115,118}\) rather than the coordination change \(^{127}\). This anomaly is thus not observed in N-BK7 because of more alkali amount. When the pressure is beyond 10 GPa, the shear moduli of the two glasses have an apparent increase, which matches with the increase of Si\(^3\) starting from \(~10\) GPa \(^{120}\).

The maximum shear stress-pressure plot shows that Boro33 is more resistant to deformation compared to N-BK7. In the previous work by Molnar et al. \(^{118}\), they studied the composition effects on the shear behavior of sodium silicate glasses and found that the addition of sodium shrinks the area under the maximum shear stress-pressure curves. It should be noted that the addition of alkali ion in the borosilicate glasses creates B\(^4\) instead of NBO even though they have a similar effect on the maximum shear stress-pressure plot. We also find that the phenomenon that pressure increases the maximum shear stress, which has been observed in silica, silicate glasses, and metallic glasses \(^{115,118,130}\) is not clear in both of the borosilicate glasses under 20 GPa. Since the main difference between our glasses and the sodium silicate glasses (NSx5 and NSx15) studied by Molnar et. al. \(^{118}\) is the existence of boron in our glasses, we hypothesized that the absence of this pressure dependence may result from the different response of boron to the applied pressure compared to Si. By calculating the atomic stress experienced by each atom, we
find that the shear stresses of B and Si decrease with increasing pressure, and indeed the stress level of B is more sensitive to pressure compared to Si. This result indicates that B can not only facilitate the densification behavior under pressure, as shown in the previous work \(^{79}\), but also the plastic flow mechanism due to the ability to decrease the shear stress under pressure. Gross et al. \(^{131}\) investigated the effect of B\(_2\)O\(_3\) content on the indentation response of 15CaO-15Al\(_2\)O\(_3\)-xB\(_2\)O\(_3\)-(70-x)SiO\(_2\) and found that both the replaced volumes contributed from densification and plastic flow increase with increasing B\(_2\)O\(_3\). The crack resistance also increases from 1 kgf for \(x=5\) to 3 kgf for \(x=25\) due to the higher shear band density causing less displacement along with shear, which is the direct experimental evidence to support our conclusion. It is also found that the stress level of B is insensitive to its composition (coordination state), which may be due to the ease of B\(^4\)-O bond-breaking \(^{124}\). However, it is worth noting that the softening behavior can be observed in the stress-strain curve of B for Boro33 but not for N-BK7 at small pressures (Figure 5-6(c) and (d)). Since Mantisi et al \(^{116}\) have shown that the suppression of the softening behavior can be related to the spatial homogenization of the atom displacements, we thus infer that the absence of the softening behavior in N-BK7 can be ascribed to its high amount of B\(^4\) causing the local rearrangements related to B to be more homogeneous, which in turn suppresses the softening behavior. It is also found that the much lower stress experienced by alkali compared to the network formers can explain the origin of the lower yield stress of N-BK7.

Shear-induced densification, which has been observed in other oxide glasses \(^{119,132}\), is also observed in our study. The density of Boro33 increases by \(\sim 7.9\ \%\) after shearing, while the density of N-BK7 barely changes at 0 GPa. However, this difference disappears with increasing pressure. The model proposed by Mackenzie \(^{132}\) suggests that the shear effect may be induced by the entanglement effect between two parts of the network under pressure. However, the shear-induced densification is also observed without pressure and even under tensile stress in our results and the previous work on the silicate glasses \(^{119}\). By analyzing both coordination number and
bond-angle evolutions, it can be seen that the decreases of the oxygen-centered bond angle, i.e., Si-O-B and Si-O-Si, and the coordination number change of B are responsible for the density changes during shear deformation for both glasses. The different density evolution trends at low pressures between Boro33 and N-BK7 can be attributed to the different evolutionary trends of the coordination number of B. The decrease of the B\(^4\) unit in N-BK7 accompanies the increase of B\(^3\) and NBO, which in turn decreases the density and competes with the densification mechanism caused by the bond-angle decrease. Therefore, as can be seen in Figure 5-4, the density decrease caused by the decrease of B\(^4\) unit reaches a balance with the density increase contributed by the bond-angle changes at 0 GPa, and becomes dominant under the tensile stress. In contrast to N-BK7, the amount of B\(^4\) increases with the deformation in Boro33 when the applied pressure is larger than 0 GPa, and has insignificant change at -2 GPa, causing the shear-induced densification can still be observed under small tensile stress. This difference explains the lower crack resistance in the tensile region. With increasing pressure, the initial oxygen-centered bond angle and the coordination number of B reach their saturated states and the increase of Si\(^5\) becomes the dominant densification mechanism at high pressures.

The coordination number evolutions show that the fractions of oxygen triclusters, NBO, and Si\(^5\) follow similar evolution trends as the stress-strain curves in terms of their slope changes, suggesting that these structural units may play crucial roles in the shear deformation of glasses. We found that NBOs become more important under tensile stress. In contrast, triclusters are more prevalent at high pressures. Indeed, it was found in the previous study that, during tensile loading, the plastic response of glass relies on the bond-switching mechanism governed by the increasing rate of NBO\(^{124,133,134}\). In addition, the formation of oxygen triclusters may accompany the formation of Si\(^5\) which has also been shown to act as a “catalyst” for plastic flow for densified silica glass, enhancing its plasticity under deformation\(^{127,135,136}\). Since the system is under constant-pressure shear simulation, the higher flexibility of the B structural unit may lead to
different coordination-evolution trends of B between Boro33 and N-BK7 to maintain constant pressures. However, this difference vanishes with pressure accompanied by the saturated B⁴ amount for both glasses.

The nonaffine displacement analysis provides the diffusion information induced by shear deformation. We find that the shear localization behavior accompanies the abrupt MSD increase in phase II in the MSD evolution curves, consistent with the result of the previous study 113,137. Also, the degree of inhomogeneity of the nonaffine displacement distribution and the MSD jump in phase II increase with decreasing pressure, except for N-BK7 at -2 GPa. The possible reason for the exception can be ascribed to the creation of B³ and NBO from the B⁴-B³ conversion during shear deformation, which not only reduces the density but also increases the amount of soft spot for plastic deformation, making the plastic deformation more homogeneous compared to the N-BK7 at 0 GPa. From Figure 5-9, we can see that N-BK7 has a more peak number with a narrower width compared to Boro33, indicating a higher shear band density in N-BK7.

The nonaffine displacement analysis also reveals the difference in the diffusion behavior between different element types. As expected, the mobility of the alkali ions (Na and K) are much higher than that of the network formers during the deformation, which is in agreement with the previous literature 118. Concerning the network formers, B is more active than Si in the structure, which again indicates that B has a better ability to dissipate energy under shear deformation. The further analysis of the cumulative nonaffine displacement of the network former cations (Figure B-3 and Figure B-4) shows that B³ and Si⁵ have relatively high mobility compared to other network former cations, which is consistent with the conclusion drawn from the coordination analysis. By analyzing the extreme value of nonaffine displacement distributions, it is observed that, for both glasses, the local maxima of nonaffine displacement tend to take place in the alkali-rich regions due to their low yield stress (Figure 5-11). However, when the samples enter into the plastic flow phase, the B concentration of the local maxima increases to above 1 in Boro33 but
stays below 1 in N-BK7. Also, we know that the alkali concentration in Boro33 is very small. These differences indicate that Boro33 and N-BK7 have different flow mechanisms. The participation ratio calculation and the cumulative local maxima evolutions also suggest that the motion of atoms caused by shear becomes more homogeneous and efficient under pressure.

5.5 Conclusion

In this study, we conducted shear deformation on the two borosilicate glasses, Boro33 and N-BK7, under different pressures using molecular dynamics simulations. We find that N-BK7 always has lower maximum shear stresses and different pressure dependence of shear modulus due to the higher concentration of alkali ions. Shear-induced densification is observed in both glasses. At low pressure, the decreases of the oxygen-centered bond angle and the coordination number change of B are responsible for the density changes, whereas at high pressures the increase of 5-coordinated Si is the dominant mechanism for densification at high pressures due to the saturation of the oxygen-centered bond angle and the coordination number of B. The average shear stress experienced by each element type is investigated, and it is found that the shear stress of Si and B decreases, and that of alkali ions increases with pressure. The average shear stress of B is more sensitive to the applied pressures compared to Si, suggesting that B has a better ability to relax mechanical stress under pressurized-shear. By calculating the nonaffine MSD, the correlation between the formation of the shear localized region and the abrupt increase in MSD in phase II is found, and the difference between the two compositions vanishes at higher pressures accompanied with more homogeneous atom rearrangement. Besides, alkali ion shows the highest mobility compared to the network formers, and B diffuses faster than Si. From the cumulative nonaffine displacement analysis, Si$^5$ and B$^3$ show relatively higher mobility compared to other network former cations. Our result shows that the plastic deformation mechanism is
composition-dependent: it takes place around boron-rich atoms preferentially in Boro33 and at alkali-rich regions in N-BK7.
Chapter 6

Plasticity of Borosilicate Glasses under Uniaxial Tension

The work in chapter 5 was previously published in the following journal article:

6.1 Introduction

Plasticity is the ability of a material to experience irreversible deformation under applied stress. Even though glass is considered to be a brittle material in a macroscopic sense, it has been shown that glass exhibits ductile behavior at a microscopic scale, and plastic deformation preferentially occurs in local regions leading to stress concentration and eventual cavity nucleation.\textsuperscript{138–140} Also, plastic deformation has been observed under certain loading conditions. Lacroix et al.\textsuperscript{141} observed large plastic deformation by applying uniaxial compression on micron-scale amorphous silica pillars. Plastic deformation under tension is observed in sodium borate glasses and soda lime silicate glasses during the loading-unloading experiments of Matsuoka et al.\textsuperscript{142,143} Frankberg et al.\textsuperscript{134} also found that amorphous Al\textsubscript{2}O\textsubscript{3} can exhibit highly ductile behavior under uniaxial tension at high strain rates at room temperature.

During indentation, the plastic behavior of glass can be observed more easily due to the high compressive stress state that can be achieved. Therefore, indentation experiments are widely used to estimate the plasticity of materials, i.e., via hardness measurements. The plastic deformation of glass under indentation consists of two contributions, permanent densification and shear flow.\textsuperscript{26,38} which can be estimated by the temperature-induced volume recovery ratio ($V_R$).
and the pile-up ratio ($V_p$). The contributions of these two mechanisms depend on the composition of glass. It has been found that these two contributions can be roughly correlated to Poisson’s ratio via a sigmoidal relation, where a higher Poisson’s ratio leads to a lower $V_R$ and higher $V_p$. However, glasses with a Poisson’s ratio from 0.2 to 0.3 have a wide range of $V_R$ and $V_p$, which indicates that Poisson’s ratio alone is insufficient to predict a glass’s mechanical response. Furthermore, the data become more scattered with the addition of the data from boron-containing glasses due to their complex composition-structure relationships making their corresponding mechanical response even more complicated. In boron-containing glasses, boron can exist in either 3-coordinated or 4-coordinated structures. It has been found that 3-coordinated boron has higher self-adaptivity under stress, which enables alleviation of stress to increase crack resistance.

To design improved damage-resistant glasses, a better understanding of the composition-structure-mechanical response relationships in borosilicate glasses is desired. In this study, we carry out uniaxial tension tests on two multicomponent borosilicate glasses, Borofloat®33 (Boro33) and N-BK7®, using molecular dynamics simulations to investigate their plasticity. Both of these compositions are silica-rich borosilicate glasses with similar Poisson’s ratios (0.2 and 0.206 for Boro33 and N-BK7, respectively); however, they exhibit different mechanical responses and fracture patterns under indentation. Our results suggest that the amount of $\text{B}_4\text{OSi}_4$ in glass is responsible for the stress drop after yielding, and that the existence of non-bridging oxygen (NBO), created by modifiers, weakens the critical stress of the bond-breaking of $\text{B}_4\text{OSi}_4$, which in turn affects the yield stress of a glass.
6.2 Method

The samples for uniaxial tension tests are created by duplicating the unit samples along y-direction two times followed by the structural relaxation for 100 ps. The samples are then deformed along the y-direction at the strain rate of $10^9 \text{s}^{-1}$ in the NPT ensemble, and the x and z directions of the simulation box are allowed to move freely to maintain zero stress. The true stress is calculated by using the virial stress definition. A temperature of 5 K is used to avoid thermal effects. The integration timestep is kept at 1 femtosecond (fs) throughout all of the simulations.

6.3 Results and Discussion

6.3.1 Stress-strain curves

Figure 6-1 shows the stress-strain (S-S) curves of Boro33 and N-BK7. Both glasses exhibit plastic deformation and strain-hardening. The plastic yield of Boro33 has also been observed in the scratch test. From the S-S curves, three properties can be obtained: Young’s modulus ($E$), yield stress ($\sigma_y$), and maximum stress ($\sigma_{max}$). Young’s modulus was evaluated as a slope within a small strain (0.02), and the $\sigma_y$ was defined as the stress at which the difference between the stress predicted by the linear function with the slope of $E$ and the stress reaches 10%. This method is purely empirical and also used by Urata and Sato to determine the yield stress of soda-lime silicate glasses. As can be seen in Table 6-1, Boro33 has a lower $E$ compared to N-BK7, which is in agreement with the experimental data even though both $E$ values are overpredicted. The $\sigma_y$ and $\sigma_{max}$ of Boro33 are larger than those of N-BK7.
Table 6-1: Mechanical properties estimated from stress-strain curves. The experimental Young’s moduli are also shown in the third column.

<table>
<thead>
<tr>
<th></th>
<th>$E$ (GPa)</th>
<th>$E_{exp}$ (GPa)</th>
<th>$\sigma_y$ (GPa)</th>
<th>$\sigma_{max}$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boro33</td>
<td>89.8±2.7</td>
<td>64</td>
<td>12.1±0.4</td>
<td>13.2±0.3</td>
</tr>
<tr>
<td>N-BK7</td>
<td>96.9±1.9</td>
<td>82</td>
<td>8.4±0.4</td>
<td>10.2±0.1</td>
</tr>
</tbody>
</table>

Figure 6-1: S-S curves of Boro33 and N-BK7 under uniaxial tension tests from MD simulations.
6.3.2 Bond-change statistics

The evolutions of bond-change events (i.e., the change in the coordination number within the nearest-neighbor shell) of network-former cations and alkali ions during the uniaxial tension are analyzed for both Boro33 and N-BK7, as shown in Figure 6-2. The bond-change events are divided into four categories: unchanged coordination number (U), unchanged coordination number but where at least one of the neighbors is swapped (US), increased coordination number (INC), and decreased coordination number (DEC). Figure 6-2(a) shows just the last three categories for clarity. One can see from Figure 6-2(a) that the rates of bond-loss for both glasses are higher than the other categories resulting in the fracture of samples. Boro33 has a higher percentage of bond-loss and bond-increase atoms compared to N-BK7, while they have similar percentages of bond-switching atoms. For the bond-change events of alkali ions, from Figure 6-2(b), it is found that the four categories of both glasses have similar trends, and their changes are more significant compared to the network-former cations, reflecting the weaker bonding of Na-O. The rises of the U category in Figure 6-2(b) for both glasses after fracture may indicate partial recovery of the structure due to the stress relaxation induced by the crack.

When comparing the evolution of the fraction of bond-switching atoms (Figure 6-3) with the S-S curves (Figure 6-1), we find both curves can be divided into different stages according to the slope during the uniaxial tension test, and the positions of different stages in the two curves can match approximately well, which suggest that the plasticity in borosilicate glasses are dominated by the bond-switching mechanism. It should be noted that the slight increase in the number of bond-switching atoms from the strain of 0.05 to 0.1 in the Boro33 does not reflect clearly in its S-S curves. Since it requires NBO to accommodate the strain in the bond-switching mechanism 133,134, we further compare the evolution of US categories with the evolution of NBO as shown in Figure 6-3. It is found that the trends of NBO evolution agree well with that of bond-
switching atoms for both glasses. For the strain range from 0.05 to 0.1 and 0.1 to 0.175, the rate of change of NBO in N-BK7 is higher than that in Boro33, which causes larger stress relaxation in N-BK7. Interestingly, from Figure 6-3, one can see that the increases of bond-switching atoms of Boro33 and N-BK7 are similar even though N-BK7 has a higher increasing rate of NBO, which results from the higher $Q_{Si}^2$ amount in N-BK7 ($Q_{Si}^j$ represents the ratio of silicon atoms with $j$ number of bridging oxygens to the total silicon atoms), as shown in Figure 6-4, which makes N-BK7 require a fewer amount of bond-switching atoms to achieve more stress relaxation.

Figure 6-2: Changes in the bonding of (a) network-former cations and (b) alkali ions in Boro33 and N-BK7 during the uniaxial tension test. The evolutions of atom numbers in each category in the (a) and (b) are normalized by the total network-former cation numbers, i.e., Si, B, and Al, and total alkali ion numbers, i.e., Na and K, respectively. (U: unchanged coordination number; US: unchanged coordination number but at least one of its neighbors is swapped; INC: increased coordination number; DEC: decreased coordination number)
Figure 6-3: (a) and (b) The comparison between the evolutions of the US fraction and NBO fraction, where the NBO numbers are normalized to the total oxygen numbers. Note that the scales of the right axis of 3(a) and 3(b) are different.

Figure 6-4: QS\(i\) evolutions of Boro33 and N-BK7 during the uniaxial tension. QS\(i\)2 part is zoomed in as shown in the inset.
6.3.3 NBO analysis

To examine the origin of plasticity, we analyze the source of the NBOs. Figure 6-5 shows the evolutions of different bond-breaking events. Boro33 has almost no NBO, whereas N-BK7 has around 6.6% NBO due to its compositional difference, which is in good agreement with the experimental data \cite{29,150}. During the uniaxial tension of Boro33, bond-breaking related to 3-coordinated O atoms has the highest tendency to occur, but the breaking of these bonds does not create NBO. Therefore, the bond-switching events cannot be activated until the bond-breaking events related to 2-coordinated oxygens, such as B^4OSi^4 and Si^4OSi^4, start to happen. The bond-breakings related to 3-coordinated oxygens also account for a higher bond-loss rate in Boro33 due to their instability, as seen in Figure 6-3. 3-coordinated O atoms, which have been observed in aluminosilicate glasses in the previous NMR study and MD simulations\cite{68,151}, tend to form in the aluminum-containing glasses as a role of charge compensator, which may also explain the higher 3-coordinated O atom in Boro33. Note that the existence of 3-coordinated oxygen has not been confirmed in Boro33 and N-BK7, but it would not affect the insight we can obtain from our study since the amount of 3-coordinated oxygen is small, around 3.6% and 0.4% for Boro33 and N-BK7 respectively.

For both Boro33 and N-BK7, the bond-breaking events related to B^4OSi^4 → Si^4O^- are much more probable compared to the others, which also contributes the greatest to the NBO production. The bond-breakings related to Si^4OSi^4 provide the second-highest contribution. We analyzed the initial proportions of these oxygen types and their tendency for bond-breaking, as shown in Figure 6-6. One can see that the initial amounts of B^4OSi^4 are lower than that of Si^4OSi^4 for both glasses (Figure 6-6(a) and Figure 6-6(b)); while the bond-breaking tendency of B^4OSi^4 is higher than that of Si^4OSi^4 (Figure 6-6(c) and Figure 6-6(d)) for both glasses. This result can be explained by the lower single bond strength of B^4-O bonds (B^4-O: 373 kJ/mol; B^3-O: 499 kJ/mol;
Si-O: 444 kJ/mol). Therefore, the higher amount of B\textsuperscript{4}O\textsubscript{4}Si\textsuperscript{4} in N-BK7 is responsible for higher stress drop after yielding in the S-S curves.

We also find that the B\textsuperscript{4}-O in B\textsuperscript{4}O\textsubscript{4}Si\textsuperscript{4} in N-BK7 has lower critical stress at which bond-breaking starts to take place compared to that in Boro33. Since the major difference between Boro33 and N-BK7 is the alkali ion concentration, the difference in critical stress is thus hypothesized to be related to the alkali ion concentration. The continuous coarse-grained expression was used to visualize the NBO density distribution:

\[
\rho(r) = \sum_i n_i \phi(||r - r_i||) \quad \text{and} \quad \phi(r) = \frac{1}{\pi^{3/2} \omega^3} e^{-\frac{(r_\omega)^2}{2}}
\]

Eq. (1)

where \(r\) is the grid position, \(r_i\) is the position of atom \(i\) with \(n_i\) (1 or 0, representing the atom may or may not be an NBO), and \(\omega\) is the coarse-graining scale (here, we use 8 Å, following the work of Molnar et al.\textsuperscript{117,152}). Figure 6-7 shows the evolutions of the NBO density distributions in the Boro33 and N-BK7 during the uniaxial tension. One can first see in Figure 6-7 (a) and 6-7(f) that the initial distributions of NBO are not uniform, resulting in structural heterogeneity. This nano-segregation agrees with Greaves’ modified random network (MRN) model\textsuperscript{72,73}. When the tension is applied, the NBO fronts start to move toward the regions with lower NBO density. The result suggests that the initial existence of NBO may weaken the critical stress for B\textsuperscript{4}-O bond breaking and facilitate the bond-switching event, which in turn lowers the yield strength. It is also found that the NBO concentrations do not recover to their original states after the fracture, as shown in Figure 6-5, Figure 6-7(e), and Figure 6-7(j), indicating that there are some permanent NBOs formed in the glasses during the uniaxial tension test. Similar Poisson’s ratios between N-BK7 (0.206) and Boro33 (0.2) are supposed to lead to a similar mechanical response under indentation; however, the \(V_p\) of BK7-type glasses is much larger than that of Borofloat-type glasses, which are 8.0 and 2.2, respectively\textsuperscript{26}. Our results thus shed some light on the possible origin of this difference.
Figure 6-5: The evolutions of different types of bond-breaking events. (“Other” represents other oxygen-related-bond-breaking events.)

Figure 6-6: The statistics of initial oxygen types for (a) Boro33 and (b) N-BK7 and the tendency of the bond-breaking events related to the groups with the initial amount larger than 5% for (c) Boro33
and (d) N-BK7. Note that the superscript of the element represents the coordination number except the superscript of Si\(^3\) and Si\(^4\) which indicates the number of bridging oxygens (both of them have a coordination number that is still 4).

Figure 6-7: The evolutions of NBO distributions during the uniaxial tension test for Boro33 and N-BK7. The sample has fractured at the strain of 0.21.

### 6.3.4 Local plastic deformation

To identify the distributions of local deformation resulting from the heterogeneity of the glasses, the local deviation from affine deformation \((D_{\text{min}}^2)\) was used here to measure the degree of local plastic deformation. \(D_{\text{min}}^2\), first proposed by Falk and Langer \cite{111}, has been shown to be a
good indicator of local irreversible transformations in non-crystalline solids\textsuperscript{111,134,153}. In this analysis, $D_\text{min}^2$ is calculated by fitting the atomic displacements predicted by a linear deformation to the actual atomic displacements. Therefore, the higher $D_\text{min}^2$ value represent a higher degree of irreversible deformation. The mathematical expression can be found in Ref. [25]. Figure 6-8 shows the $D_\text{min}^2$ evolutions of Boro33 and N-BK7 during the tensile loading. For both Boro33 and N-BK7, yielding takes place at local regions and accumulates during the uniaxial tension. The macroscopic plastic deformations, shown as Figure 6-1, are thus the accumulation of these local rearrangements and the increasing fluctuations after yields in the S-S curves result from these localized plastic deformation events\textsuperscript{134}. It is also found that N-BK7 has a higher degree of plastic deformation compared to Boro33 during tension. This suggests that N-BK7 is able to relax more stresses via these deformations, which is consistent with the S-S curves where N-BK7 has a greater drop in stress after yielding.

Topological constraint theory, which connects the topology of the glass network and the compositional dependence of glass properties, has proven to provide good predictions of important glass properties, such as glass transition temperature, fragility, and hardness\textsuperscript{15–17}. Wang et al.\textsuperscript{74} used topological constraint theory to identify the spatial heterogeneity of the network rigidity in silicate glasses and found that the plastic deformation events mainly result from the under-constrained (floppy) regions. In this study, we analyzed the number of local constraints ($N_c$) of the two samples during the uniaxial tension by considering linear and angular constraints, which can be calculated as follows\textsuperscript{125}:

\[
n_{c,\text{linear}} = \frac{1}{2} CN |_{CN \geq 2}, \quad \text{Eq. (2)}
\]

\[
n_{c,\text{angular}} = (2CN - 3) |_{CN \geq 2}, \quad \text{Eq. (3)}
\]

where $n_c$ is the number of constraints associated with the analyzed atoms, and $CN$ is the coordination number of those atoms. We used the same coarse-grained method as in Figure 6-7 to
visualize the local constraint density and the $D_{\text{min}}^2$ distribution for comparison. The comparisons at the critical strain where the fracture is about to happen are shown in Figure 6-9.

The anti-correlation of constraints and $D_{\text{min}}^2$ can be seen visually in Figure 6-9. To measure the correlation quantitatively, we apply the following expression to calculate the correlation between the two properties:

$$
Corr(A, B) = \frac{\Sigma_{i} \Sigma_{j} \Sigma_{k} (A_{ijk} - \bar{A})(B_{ijk} - \bar{B})}{\sqrt{\Sigma_{i} \Sigma_{j} \Sigma_{k} (A_{ijk} - \bar{A})^2} \sqrt{\Sigma_{i} \Sigma_{j} \Sigma_{k} (B_{ijk} - \bar{B})^2}}
$$

where $A_{ijk}$ and $B_{ijk}$ are two different quantities in grid $(i, j, k)$ and the $\bar{A}$ and $\bar{B}$ stand for the average values of $A$ and $B$ over the total grids. It was found that the $Corr(N_c, D_{\text{min}}^2)$ of Boro33 and N-BK7 at fracture point are -0.75 and -0.87, suggesting that the lower-constrained regions enable local plastic deformation in the glasses, consistent with the conclusion from Wang et al. 74. The result is consistent with the results of Benzine et al. 154, who found that localized deformation is caused by universal structural heterogeneity. It should be noted that the structural heterogeneities include, but are not limited to, the existence of alkali-rich regions.
Figure 6-8: The evolution of $D_{\text{min}}^2$ distributions during the uniaxial tension test for Boro33 and N-BK7. $\langle D_{\text{min}}^2 \rangle$ on the top right corner of each sub-figure is the average $D_{\text{min}}^2$.

Figure 6-9: The comparison between the constraint density distribution and $D_{\text{min}}^2$ density distribution for Boro33 ((a) and (c)) and N-BK7 ((b) and (d)).
6.4 Conclusion

In this study, we carried out a uniaxial tension test on two multicomponent borosilicate glasses, Boro33 and N-BK7, to investigate their plasticity. Bond-switching events and NBO generation during the test were analyzed, and it was found that in these two silica-rich borosilicate glasses the difference in the amount of B\(^4\)-O-Si\(^3\) unit governs the difference in the stress-drop after yielding. This is because the B\(^4\)-O bond has a higher tendency to break under stress compared to Si\(^4\)-O. We also found that the initial existence of NBOs lowers the critical stress for breaking B\(^4\)-O, which may be responsible for the lower yield strength of N-BK7. Lastly, the comparison between constraint density and \(D_{\text{min}}^2\) density was carried out, and these two quantities show a high anti-correlation, indicating that local plastic deformation preferentially occurs in the lower-constrained regions.
Chapter 7

Effect of pressurization on the fracture toughness of borosilicate glasses

7.1 Introduction

According to Griffith’s analysis\textsuperscript{155},

\[ \sigma_f \sqrt{\pi c^*} = \sqrt{2 \gamma_f E} = \text{constant} \quad (1) \]

where \( \sigma_f \) is the strength of a material, \( c^* \) is the critical size of the pre-existing flaw and \( E \) is Young’s modulus. This expression yields the concept of stress intensity factor, defined as \( K = \sigma_a \sqrt{\pi c}, \) in which both the applied stress (\( \sigma_a \)) and flaw size (\( c \)) are taken into consideration. The critical value of this factor, \( K_C \), is called fracture toughness, which is a measure of the resistance to crack propagation of a material. The opening mode, where the crack plane and the direction of crack propagation are perpendicular to the direction of the applied stress, is of primary concern for brittle materials, and the fracture toughness of this loading mode is referred to as \( K_{IC}. \textsuperscript{156} \)

For inorganic glasses, the values of \( K_{IC} \) are usually smaller than 1 MPa\( \sqrt{\text{m}} \) and the compositional dependence of \( K_{IC} \) is typically insignificant\textsuperscript{157}. Therefore, extrinsic methods have been developed to prevent fracture, such as introducing compressive stress in the surface by chemical strengthening, thermal tempering or lamination, protecting the glass from surface damage and water attack by polymeric coatings, or reducing the flaw severity by firepolishing\textsuperscript{156}. On the other hand, it has also been shown that the thermal history can also affect the fracture toughness of glass. Kumar et al.\textsuperscript{158} indicated that the plasticity of some metallic glasses is a strong function of fictive temperature. The work of Malchow et al.\textsuperscript{159} also showed that the indentation fracture toughness of borosilicate glasses decreases with an increasing cooling rate. Nevertheless,
There is currently no comprehensive study related to the effects of pressurization on the fracture toughness of oxide glasses.

Over the last decade, the pressure-induced changes in structure and properties have received greater attention because they provide a new route to tailor the desired properties of glasses, such as optical properties, mechanical response, and chemical durability. Most of the studies can be divided into two categories, pressure quenching and hot compression, at temperatures near or slightly lower than the glass transition temperature, $T_g$. Some studies focused on pressurization at room temperature, but it is found that the pressure required to reach the same degree of densification for high temperature is much lower than that for room temperature pressurization. Among oxide glasses, boron-containing glasses draw special attention due to the existence of both 3-coordinated (B³) and 4-coordinated (B⁴) boron atoms.

Pressurization generally results in the conversion from B³ to B⁴. Lee et al. reported the results of pressure-induced changes in the boron and oxygen environment of B₂O₃ at ambient temperature and found that the coordination transformation is reversible up to 24 GPa. They also indicated that the type of the modifier cations in borate glasses plays a role in determining the energy barrier for the boron coordination conversion. Svenson et al. found that the pressure dependences of hardness, crack resistance and brittleness of hot-compressed borosilicate glasses are different, suggesting different structural origins of these properties. Svenson et al. also found a universal link between densification resulting from hot compression and the changes in elastic moduli, but this relationship may vary with the densification route due to different structural changes. Striepe et al. annealed soda-lime borate glasses at $T_g + 20$ K under pressure (0.1~0.57 GPa) and then quenched them back to room temperature. They found that the atomic factor, elastic modulus, hardness and brittleness increase linearly as applied pressure increases, and the increasing degree is a function of the composition. Although they observed that the
indentation fracture toughness of the glass decreases slightly with pressure, the indentation-based experimental method for measuring fracture toughness is still debated.\textsuperscript{163}

In this study, we applied the hot-compression process to two silica-rich multicomponent borosilicate glasses, Borofloat®33 (Boro33) and N-BK7®, using molecular dynamics simulations, and the pressure dependence of elastic properties, surface energy, fracture toughness, and glass structure are investigated. Using molecular dynamics simulations, we can circumvent the experimental difficulties related to the high-pressurization process and fracture toughness measurements. We find that hot-compression can indeed improve the $K_{IC}$ of borosilicate glasses, and Boro33 has a higher increase in $K_{IC}$ under pressure, despite the similar starting values of $K_{IC}(0.65 \text{ MPa}\sqrt{\text{m}})$ and Poisson’s ratios (0.234.97) in the uncompressed state of the two glasses.

7.2 Methods

7.2.1 Simulation method

In the hot-compression process, the generated samples were heated to 90\% of the fictive temperature (0.9$T_f$) followed by annealing for 2 ns, and then quenched back to the room temperature. $T_f$ is determined by solving the intersection of two linear lines which fit to the high temperature (3000 K ~ 5000 K) and low temperature (300 K ~ 1000 K) sections in the energy-temperature curve. During the annealing and quench processes, pressures from 2 to 10 GPa were applied. All the procedures were conducted in the NPT ensemble to enforce the pressurization, and both the heating and cooling rate are 5 K/ps.
7.2.2 Surface energy

To calculate the surface energy, $\gamma$, free surfaces along a certain direction of a simulation box were created by releasing periodic boundary conditions followed by relaxation for 1 ns at room temperature in the NVT ensemble. The surface energy was then estimated by calculating the energy difference between the original simulation box and the box with the free surfaces divided by the total surface area created.

7.2.3 Elastic properties

The elastic properties are obtained by applying uniaxial tension with a strain rate of $10^9$ s$^{-1}$ on the samples. The Young’s modulus was estimated as a slope within a small strain (0.02) in the stress-strain curve, and the Poisson’s ratio is evaluated as the ratio between the strain along the direction of applies stress and the strain of the lateral direction.

7.2.4 Fracture toughness calculation

With knowledge of the pressure dependence of the surface energy, Young’s modulus, and Poisson’s ratio, we can estimate the pressure effect on fracture toughness using the equation$^{155}$:

$$K_{IC} = \sqrt{\frac{2\gamma E}{1-v}}.$$  \hspace{1cm} (2)

We also conducted a compact tension test, even though the length scale is much smaller than a realistic experimental sample. Following the work of Mei et al.$^{164}$, we constructed the samples with the size of 21 nm $\times$ 21 nm $\times$ 3.5 nm by duplicating the smaller sample, prepared via the procedure described in Sec 2.1, by $6 \times 6 \times 1$ in the three directions. A V-shaped crack
was created in each sample, and then the sample is subsequently relaxed for 20 ps. The crack length is around 5.5 nm and the ratio between crack length and crack height is around 0.25. The plane strain condition is used in the X-Y plane and periodic boundary conditions are applied in all directions. Uniaxial tension was then applied to the samples with a strain rate of $10^9 \text{s}^{-1}$ until the onset of fracture.

Since the crack size introduced in the sample is small, the fracture strength may be higher than the yield strength and a certain degree of plasticity can happen in the sample. Therefore, we adopted the energetic approach to estimate the fracture toughness\textsuperscript{165}. The critical energy release rate, $G_{IC}$, can be estimated by integrating the stress-strain curve after the sample is broken, and the fracture toughness can be calculated by the Irwin formula\textsuperscript{166}:

$$G_c = \frac{1-v^2}{E}(K_{IC})^2. \quad (3)$$

The brittleness can then be estimated by\textsuperscript{167}:

$$B = \frac{2\gamma}{G_c}. \quad (4)$$

where $\gamma$ is the surface energy obtained by the method described in sec. 2.2 and $B = 1$ represents a perfectly brittle material. The detail of this procedure can be found in Ref. 165.

7.3 Results

7.3.1 Macro-properties
Figure 7-1: (a) The final density after the hot compression process as a function of pressure for each sample. (b) The increase rate of Young’s modulus as a function of relative change in density for each sample. The straight lines shown on the graph are fitted lines.

Figure 7-1 (a) shows the final density as a function of the compression pressure. Boro33 has a higher increasing degree under pressure compared to N-BK7, and Bauchy potential is more sensitive to the pressure compared to Du potential, consistent with the previous work. The difference in the results using different potentials may result from structural effect and/or potential effect, and we may consider the results from Bauchy potential as an upper limit for Boro33.

The relationship between the Young’s modulus after hot compression and pressure is shown in Figure 7-2. Young’s modulus increases with increasing pressure overall and the correlation between the Poisson’s ratio and the compression pressure is unremarkable. Note that the elastic properties of Boro33 using the Du and Bauchy potentials are overestimated and slightly underestimated, respectively, compared to the experimental data (64 GPa), which may be related to their structural differences and has been discussed in our previous work. It is found
that the relative change of densities and the increasing rates of Young’s modulus exhibit a linear relationship, as is shown in Figure 7-1(b).

![Figure 7-2: (a) Young’s modulus and (b) Poisson’s ratio as functions of compression pressure for each sample.](image)

Figure 7-3 shows the relationship between the surface energy and the compression pressure. The calculated surface energies are about one-fourth of the experimental fracture surface energy of glass (4~5 J/m²)\textsuperscript{168}. However, they are closer to the theoretical values predicted by the Rouxel model\textsuperscript{169} with the use of the bond strengths from Sun’s model\textsuperscript{100}, which are 2.15 J/m² and 2.02 J/m² for Boro33 and N-BK7 respectively. The higher experimental value of fracture surface energy can be attributed to additional energy dissipated by plastic deformation\textsuperscript{168}. We can also see that the surface energy of Du Boro33 increases at 2 GPa, but becomes insensitive to the pressure when a higher pressure is applied. For Du N-BK7 and Bauchy Boro33, there is no clear correlation found between the surface energy and compression pressure.

The effect of pressure on the fracture toughness calculated by Eq (2) is shown in Figure 7-4 (a). The calculated $K_{IC}$ values in the uncompressed state are smaller than the experimental values (0.65 MPa√m for both Boro33 and N-BK7) due to the smaller calculated
surface energies. Figure 7-4(b) shows the $K_{IC}$ obtained by the compact tension test combined with the energetic approach where the plastic deformation energy has been taken into consideration. It can be seen that the $K_{IC}$ values in the uncompressed state calculated by the fracture toughness simulation (Figure 7-4(b)) are closer to the experimental values, especially for samples using Du potential. Despite this difference, the $K_{IC}$ values obtained by both methods exhibit the same trend with pressure. We can see that the $K_{IC}$ values of both Boro33 simulations increase with compression pressure. Also, the increase degree in $K_{IC}$ is especially higher when the pressure increases from 0 GPa to 2 GPa. In contrast, the fracture toughness of N-BK7 is less affected by pressure. The brittleness as a function of pressure is shown in Figure 7-4(c). It is found that the brittleness for all the samples are smaller than 1, suggesting that, indeed, the fracture energy is not only used to create the fracture surfaces but also dissipated partially in other forms, such as plastic deformation or heat release. Even though it has been observed that the radius of curvature of a flaw in a glass is around 1.5 nm$^{170}$, close to the atomic scale, the length of a Griffith flaw is around 5~50 μm$^{156}$, much larger than the MD length scale. The larger crack size causes larger stress concentration$^{171}$, so that the plasticity is hard to be observed in the experiment. It is also found that the brittleness does not vary a lot with pressure and remains at ~0.5 for all the samples.
Change of microstructures

The bond angle and coordination number of the samples after hot-compression were analyzed since these two are considered as the main mechanisms accounting for the densification. We can see that the Si-O-Si bond angle only slightly decreases with increasing pressure for all of

Figure 7-3: The surface energy of each sample as a function of pressure.

Figure 7-4: (a) The $K_{IC}$ calculated by Eq (2), (b) The $K_{IC}$ obtained from the compact tension tests and (c) Brittleness as functions of pressure. The experimental values are from Ref. [17].

7.3.2 Change of microstructures

The bond angle and coordination number of the samples after hot-compression were analyzed since these two are considered as the main mechanisms accounting for the densification. We can see that the Si-O-Si bond angle only slightly decreases with increasing pressure for all of
the samples (Figure 7-5(a)). The Si-O-B bond angle of Boro33 has a significant decrease with pressure. In contrast, the Si-O-B angle of N-BK7 is less sensitive to pressure. We further decomposed the Si-O-B into Si-O-B\(^3\) and Si-O-B\(^4\) and found that there is no apparent pressure effect on either of these quantities. Therefore, it can be inferred that the decrease of average Si-O-B bond angle is mainly due to the conversion from B\(^3\) to B\(^4\), except that the change of Si-O-B\(^4\) bond in Du Boro33 may combine the effects of the decrease in Si-O-B\(^4\) bond angle and the B\(^3\) - B\(^4\) coordination conversion under pressure (Figure 7-6(a)). The pressure effect on Si\(^5\) and N\(_4\) (the percentage of B\(^4\)) are shown in Figure 7-7. The increase of Si\(^5\) is insignificant with pressure, while N\(_4\) increases with pressures for all the samples. Boro33 has a much larger increase in N\(_4\) due to its higher B\(^3\) amount compared to N-BK7, regardless of the potential used.

Figure 7-5: (a) Mean Si-O-Si bond angle and (b) mean Si-O-B bond angle as functions of pressure.
7.4 Discussion

Figure 7-6: Mean Si-O-B\(^3\) and Si-O-B\(^4\) bond angles of (a) Du Boro33, (b) Du N-BK7, and (c) Bauchy Boro33 as functions of pressure.

Figure 7-7: (a) The percentage of Si\(^5\) and (b) N\(_4\) value as functions of pressure. The experimental N4 values are from Ref. [55] and Ref. [61].
In this study, we found that the hot-compression process is an effective method to improve $K_{IC}$. Based on Eq (2), the increase of $K_{IC}$ is mainly governed by the changes of Young’s modulus and surface energy. The fracture toughness after hot compression can then be expressed as:

$$K_{IC, hc} = \sqrt{\frac{2\gamma_{0GPa}(1+\Delta\gamma)E_{0GPa}(1+\Delta E)}{1-\nu^2}}$$  \hspace{1cm} (5)$$

Where $K_{IC,0GPa}$ is the fracture toughness in the uncompressed state, and $\Delta E$ and $\Delta \gamma$ are the percentage increase of Young’s modulus and surface energy respectively. By rearranging Eq (5):

$$K_{IC, hc} = K_{IC,0GPa}\sqrt{\frac{1+\Delta\gamma + \Delta E + \Delta \gamma \Delta E}{1-\nu^2}} \approx K_{IC,0GPa}\sqrt{1+\Delta x}$$  \hspace{1cm} (6)$$

where $\Delta x = \Delta E + \Delta \gamma$. The Taylor series around $\Delta x=0$ for $\sqrt{1+\Delta x}$ is:

$$\sqrt{1+\Delta x} = 1 + \frac{1}{2}\Delta x + \sum_{n=2}^{\infty} \Delta x^n (-1)^{n-1} \frac{(2n-3)!}{n!(n-2)!2^{n-2}}$$  \hspace{1cm} (7)$$

Truncating Eq (7) after the linear term yields:

$$\sqrt{1+\Delta x} = 1 + \frac{1}{2}\Delta x$$  \hspace{1cm} (8)$$

By substituting Eq (8) into Eq (6), we can decompose the contributions to the increase ratio of $K_{IC}$ into the increase ratio of $\Delta E$ and $\Delta \gamma$ linearly and visualize them as shown in Figure 7-8.
7-8. It should be mentioned that the brittleness is around 0.5 for all the samples and pressures; thus, the contribution of the increase of plastic energy to the increase of $K_{IC}$ is similar to that of $\Delta \gamma$. We find that the $\Delta E$ contributes the most to the $K_{IC}$ increase for all the samples. Note that the $\Delta \gamma$ in Du Boro33 contributes relatively more to the fracture toughness increase, especially at 2 GPa, compared to that in other samples.

Both Young’s modulus and surface energy can be related to energy density. By assuming that a crack propagates along a path with the weakest links of the energy landscape, Rouxel\textsuperscript{169} proposed an expression for surface energy from the bond strength and bond concentration on the crack surface,

$$\gamma = \frac{1}{2} \left( \frac{\rho}{M_0} \right)^{2/3} N^{-1/3} \sum_i x_i n_i U_{oi}$$ \hspace{1cm} (8)

where $\rho$ is density, $M_0$ is molar mass, $N$ is Avogadro’s number, $x_i$ is the stoichiometric fraction of the cation species $i$ involved in bond-breaking between this species and its first-neighbor oxygen with the bonding energy $U_{oi}$, and $n_i$ is the number of bonds that will be broken as the crack front extends to the next cation unit. The hot-compression process leads to the densification and the increase of coordination, which is supposed to increase $\gamma$ according to Eq (9). However, there is no clear trend between surface energy and pressure observed in our result (Figure 7-3). We may infer that the bonding energy decreases with pressure, which competes with the increase of density.

The work by Makishima and Mackenzie\textsuperscript{172} proposed a method to calculate the Young’s modulus of oxide glasses, which can be expressed as

$$E = 2 \left( \frac{\rho}{M_0} \right)^2 \sum_i \frac{4}{3} \pi x_i r_i^3 \sum_i X_i U_{oi}$$ \hspace{1cm} (9)
where $X_i$ is the fraction of each oxide. By comparing Eq (8) and Eq (9), it can be seen that density is weighted more in Young’s modulus than in surface energy, making the difference in the trend with pressure between Young’s modulus and surface energy self-explanatory. Moreover, Collin et al.\textsuperscript{18} offered another possible solution for predicting elastic moduli based on the free energy density of the topological constraint, which is able to account for the effect of topological and temperature changes on elastic moduli. The model indicates that the increase of coordination causes more increase in the number of $\beta$ constraints (e.g., O-B-O angular constraint) compared to other types of constraint. Therefore, the increase of B coordination after hot compression caused a significant Young’s modulus increase. In contrast, the surface energy may be only related to broken linear constraints and is less affected by the coordination increase.

The densification of glass can be mainly attributed to the oxygen-centered bond angles\textsuperscript{81,83} and/or coordination decrease\textsuperscript{82,88,173}. It is found that the Si-O-Si bond angles only decrease slightly under hot-compression for all the samples, and the change in Si-O-B bond angle is mainly due to the $B^3 - B^4$ coordination conversion under pressure. Therefore, more Si-O-B bond angle increase can be observed in Boro33 due to the higher $B^3$ amount. For the coordination change, most Si stayed 4-coordinated after compression, while B coordination increases with pressure for all the samples. From 0 GPa to 2 GPa, Boro33 has the largest increase in $K_{IC}$. However, for both Si-O-Si and Si-O-B bond angles, they have little change at 2 GPa, suggesting that the coordination change of B in Boro33 is the main structural mechanism responsible for the large increase in $K_{IC}$ from 0 to 2 GPa. This conclusion is supported by the recent experimental work by To et al.\textsuperscript{174} Indeed, we can see a linear relationship between the increasing rate of Young’s modulus and the relative change of $N_t$ value, especially for Boro33, as shown in Figure 7-9. The less linear curve for N-BK7 in Figure 7-9 indicates that another densification mechanism, i.e., bond-angle decrease, may play a more important role in densification even though the amount of bond-angle change is small.
Conclusions

The pressure dependence of elastic properties, surface energy, and fracture toughness of Boro33 and N-BK7 are calculated using molecular dynamics simulations. It is found that hot compression can effectively increase the \( K_{IC} \) of Boro33 using both potentials, while having little impact on that of N-BK7. This study also demonstrates that the increase of \( K_{IC} \) mainly results from the increase of Young’s modulus due to densification, and the borosilicate composition with a higher amount of B\(^3\) in the uncompressed state, i.e., Boro33, exhibits a higher degree of densification and, in turn, a higher increase in \( K_{IC} \) as a result of hot compression.

Figure 7-9: The increase rate of Young’s modulus as a function of relative change in density for each sample.

7.5 Conclusions

The pressure dependence of elastic properties, surface energy, and fracture toughness of Boro33 and N-BK7 are calculated using molecular dynamics simulations. It is found that hot compression can effectively increase the \( K_{IC} \) of Boro33 using both potentials, while having little impact on that of N-BK7. This study also demonstrates that the increase of \( K_{IC} \) mainly results from the increase of Young’s modulus due to densification, and the borosilicate composition with a higher amount of B\(^3\) in the uncompressed state, i.e., Boro33, exhibits a higher degree of densification and, in turn, a higher increase in \( K_{IC} \) as a result of hot compression.
Chapter 8

Conclusions and future directions

In this dissertation, different loading conditions using MD simulations were carried out on two commercial borosilicate glasses, including uniaxial tension, compression, pure shear, and also fracture toughness calculation, to understand the deformation behavior of these glasses. It was found that, under tensile conditions, the difference in the degree of stress relaxation after yielding is determined by the difference in the amount of $\text{B}_4\text{O}_3\text{Si}_4^4$, and the critical stress for breaking $\text{B}_4\text{O}$ may be lowered by the initial existence of NBOs. Therefore, although the 4-coordinated B increase the elastic moduli of N-BK7, the higher amount of $\text{B}_4\text{O}$ bond causes more nano-scale plastic deformation, which in turn lowers the strength of N-BK7. Moreover, the ease of $\text{B}_4\text{O}$ bond breaking in N-BK7 leads to the creation of a $\text{B}_3$ and an NBO, which not only reduces the density but increases the number of regions susceptible to plastic deformation, making the shear deformation more homogeneous under tensile stress. In contrast, shear localization becomes more apparent for Boro33 when tensile stress is applied, as seen in Chapter 4. By introducing a crack, the fracture toughness can be calculated by MD simulations, and the results are comparable to the experimental values. We found that the hot-compression process is a promising way to increase fracture toughness, but the increasing degree is composition-dependent, i.e., the higher amount of $\text{B}_3$, the higher increasing degree.

When the samples experience compressive stress, N-BK7 has less densification degree compared to Boro33 due to its higher alkali concentration, in agreement with the indentation experiment. Also, it was found that the fraction of permanent densification can be correlated to the change in intermediate-range structure. To quantify the contribution of each cation structural unit to densification, Voronoi analysis was performed. The results indicate that 3-coordinated
cations, such as B\textsuperscript{3} and Al\textsuperscript{3}, can promote the densification process, while higher-coordinated cations, such as Si\textsuperscript{4} and Si\textsuperscript{5}, are relatively stable and can even exhibit expansion in their Voronoi volumes. The combination of compression and pure shear loading was applied to mimic the plastic zone in the indented sample. The observation of shear-induced densification is corroborated by the previous experimental work on silica. In the atomic shear stress calculation, we observed that the shear stress of Si decreases with increasing pressure at the beginning of shear, but reaches a similar level or even exceeds the magnitude at lower pressures at the end of deformation. The shear stress experienced by B, by contrast, decreases throughout the deformation with pressure. In terms of alkali, the shear stress is much lower than that of network formers, explaining the lower shear strength of N-BK7. Also, pressurization has an opposite effect on the shear stress compared to the network formers, i.e., the shear stress increases with pressure. From the non-affine displacement analysis, it was observed that plastic deformation tends to take place around B-rich regions for Boro33, while around alkali-rich regions for N-BK7, suggesting different deformation mechanisms for the two glasses. Moreover, the results indicate that B\textsuperscript{3} has the highest mobility under shear deformation, and Si\textsuperscript{5} becomes more active with increasing pressure. An interesting observation is that high-coordinated Al, such as Al\textsuperscript{4}, Al\textsuperscript{5}, and Al\textsuperscript{6}, are more mobile than the other high-coordinated network formers. To summarize, B\textsuperscript{3} facilitates both densification behavior and plastic flow; furthermore, B\textsuperscript{3} does not decrease the strength of glass as much as alkali ions. Thus, B\textsuperscript{3} is suitable for the composition design of crack-resistant glass.

From this research project, some future work can be suggested to explore the deformation behavior of oxide glasses. For example, the shear-induced densification may cause the underestimation of the \( V_R \) ratio if it cannot be fully recovered by the heat treatment. Therefore, if the contribution of shear-induced densification can be confirmed experimentally, Yoffe’s model used for cracking pattern prediction can be improved. Furthermore, the responses of glasses to
different loading conditions, e.g., shear strength and elastic properties, obtained in this work can be incorporated into the finite-element modeling of indentation so that a more realistic indentation can be approached.
Appendix A

Supplementary materials for Atomic-Scale Mechanisms of Densification in Cold-Compressed Borosilicate Glasses

Appendix A contains the supporting information and acknowledgments of the following published journal article:


Figure A-1: Snapshot from MD simulation of Boro33 at 20G GPa generated by Bauchy potential. (Blue: Si, Red: O, Yellow: B)
Figure A-2: The bond-angle distributions of Boro33 using Du potential.
Figure A-3: The bond-angle distributions of N-BK7 using Du potential.
Figure A-4: The bond-angle distributions of Boro33 using Bauchy potential.
Figure A-5: The bond-angle distributions of N-BK7 using Bauchy potential.
Figure A-6: The relations between the average non-Si element ratios in a ring (only counting cations) and ring sizes at different pressures for Boro33 and N-BK7 using Du potential. (0 GPa_d represents the state after decompression)
Appendix B

Supplementary materials for Pressure Effects on Shear Deformation of Borosilicate Glasses

Appendix B contains the supporting information and acknowledgments of the following published journal article:


Figure B-1: Size effects on the S-S curves of (a)(c) Boro33 and (b)(d) N-BK7 under shear deformation. The three numbers in the legend represent the replication number along the xxyxz direction.
Figure B-2: (a)(c) The Si-O PDFs and (b)(d) the B-O PDFs of Boro33 and N-BK7 at different pressures.
Figure B-3: (a)(c)(e)(g) The Si-O PDFs and (b)(d)(f)(h) the B-O PDFs of Boro33 and N-BK7 at different strains at 0 GPa and 20 GPa.
Figure B-4: Cumulative nonaffine displacement evolutions of different structural units at different pressures for Boro33. The superscript represents the coordination number, which is also the number of bridging oxygen. $Si_4^3$ represents 4-coordinated Si with 3 bridging oxygens.

Figure B-5: Cumulative nonaffine displacement evolutions of different structural units at different pressures for N-BK7. The superscript represents the coordination number, which is also the number of bridging oxygen. $Si_4^3$ represents 4-coordinated Si with 3 bridging oxygens.
Appendix C

Supplementary materials for Plasticity of Borosilicate Glasses under Uniaxial Tension

Appendix C contains the supporting information and acknowledgments of the following published journal article:

Figure C-1: Size effects on the S-S curves of (a)(c) Boro33 and (b)(d) N-BK7 under uniaxial tension. The three numbers in the legend represent the replication number along the x×y×z direction where the unit sample is a cubic sample with the length of ~33 Å.

Figure C-2: S-S curves of all three sample for Boro33 and N-BK7 under uniaxial tension.
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EDUCATION

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<tr>
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WORKING EXPERIENCE

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<tr>
<td>Ph.D. Candidate/Research Assistant</td>
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<tr>
<td>➢ Modeled the indentation on the metallic glass with embedded nanoparticle using molecular dynamics simulations for improving the crack-resistance of the metallic glass.</td>
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<tr>
<td>➢ Investigating the composition-structure-mechanical response relation and atomic-scale deformation mechanism of borosilicate glasses, Borofloat®33 and N-BK7®, at room temperature using molecular dynamics simulations to have a deeper understanding of the fracture behavior of glasses. Sponsored by SCHOTT AG for 4 years</td>
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<td>➢ Synthesized and sintered aluminum oxynitride (AlON) powders via carbothermal reduction to develop transparent polycrystalline AlON nose domes for the next generation application of missile seeker.</td>
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SELECTED PUBLICATIONS