Discussion on the structural origins of the fracture toughness and hardness changes in rapidly quenched borosilicate glasses: a molecular dynamics study

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Abstract

Understanding radiation effects in nuclear glasses is important in order to assess their long term behaviour in a geological repository. In this paper, the results obtained by classical molecular dynamics about the mechanical properties of a simplified SiO\textsubscript{2} – B\textsubscript{2}O\textsubscript{3} – Na\textsubscript{2}O glass with the same molar proportions as in the real French nuclear glass were reviewed. A pristine and a disordered structure, representative of the irradiated one, were prepared in order to address the question of the radiation effects on the fracture toughness and hardness.

In a first step, fracture simulations were performed to compare the atomistic mechanisms in the pristine and disordered glasses. In a second step, nanoindentation was simulated using a diamond tip and again the pristine and disordered glass behaviors were compared.

The depolymerisation associated to the glass disordering, in particular the increase of the tri-coordinated boron concentration relative to the tetra-coordinated boron concentration improves the fracture resistance by favouring the plastic flows. On the contrary, the swelling of the disordered glass limits the fracture resistance by facilitating the cavity formation. The first effect is dominant in the case of the glass investigated here because, experimentally, the fracture toughness increases after irradiation.

Concerning the hardness, both the decrease of the boron coordination in parallel with non-bridging oxygen formation and free volume accumulation lead to a hardness decrease because the more disordered and open structure facilitates the tip penetration.

Keywords: silicate glass; mechanical properties; radiation; molecular dynamics
1. Introduction

In France, nuclear waste (fission products and minor actinides) is aimed to be confined in complex alkali borosilicate glasses. For this application, the use of the R7T7-type nuclear glass is envisaged [1]. These glasses are proposed to be stored permanently in a deep geological repository, and their behavior must be predictably safe for several thousand years, in order to limit the radionuclide release in the environment.

The nuclear glasses will be exposed to different radiation sources during their long term storage [2]. The decay of fission products is responsible for $\beta$ and $\gamma$ radiations, while the minor actinides are responsible for $\alpha$ disintegrations. Each $\alpha$ disintegration corresponds to the emission of one recoil nucleus and one $\alpha$ particle. It has been shown [3,4] that the ballistic effects associated with the recoil nuclei are the origin of the mechanical property changes during irradiation. When the energy deposited by the heavy ions increases, density and hardness progressively decrease, while fracture toughness progressively increases [5]. Above a critical dose, these mechanical properties stabilize at saturation values.

In order to better understand the long term behaviour of nuclear glasses and to explain these saturation effects, different studies have been carried out to correlate the macroscopic property changes to the structural modifications [6,7,8]. Concerning the density, it has been shown that the swelling is closely related to the modification of the polymerization level, more specifically to the tri- and tetra-coordinated boron atom relative concentrations, as well as to the non-bridging oxygen concentration.

More recently, classical molecular dynamics simulations have been performed in order to determine the atomistic origins of the hardness and fracture toughness changes under ballistic effects [9,10]. In this scope simplified nuclear glasses, containing the major components of the real glass, SiO$_2$, B$_2$O$_3$ and Na$_2$O, have been used and the role of the depolymerisation induced by ballistic effects has been again underlined.

In this paper, a synthesis of these previous studies is proposed, in order to compare the origins of the hardness and fracture toughness changes under irradiation. We present comprehensive results for the SBN14 sodium borosilicate glass, which is the one with the closest composition to the R7T7 glass. Alongside, we also present selected results for two more glasses, SBN12 and SBN55, in order to highlight composition effects on the mechanical properties.

2. Computational procedure for glass preparation

Using classical Molecular Dynamics (MD) simulations, one can gain access to the microstructure of ternary SiO$_2$-B$_2$O$_3$-Na$_2$O glass systems. MD simulations have been performed using the empirical interatomic potentials developed by Kieu et. al. [11]. These potentials have a Buckingham form and are completed by Coulomb interactions which are treated via the Ewald summation method [12] using composition dependent charges. A more detailed discussion about the potential form and its validation can be found in reference [11].

All the calculations have been performed with the DLPOLY code [13]. The timestep was chosen to be equal to 1 fs for all the simulations and the precision for the Ewald summation calculation has been set to $10^{-5}$.

In order to prepare the glasses, Si, B, O, and Na atoms were randomly placed in a computational cell reproducing the different chemical compositions listed in Table 1. Small cells with $10^5$ atoms were used to investigate the fracture behavior and larger ones with approximately $2*10^5$ atoms for the hardness calculations. The systems were equilibrated for 100 ps at 5000K with a density $5\%$ lower than the experimental one. Subsequently the systems were cooled to 300 K at a quench rate equal to $5*10^{12}$ K/s using the NVT ensemble. Then the equilibrium volumes at ambient temperature were determined by an NPT calculation (20 ps). Finally, the structures were equilibrated using NVE for 5 ps at the equilibrium volumes determined previously. This process was repeated for all the systems.
Table 1. Glass chemical compositions used for the MD simulations (in molar percentages)

<table>
<thead>
<tr>
<th>Glasses</th>
<th>SiO₂</th>
<th>B₂O₃</th>
<th>Na₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBN12</td>
<td>59.66</td>
<td>28.14</td>
<td>12.20</td>
</tr>
<tr>
<td>SBN14</td>
<td>67.73</td>
<td>18.04</td>
<td>14.23</td>
</tr>
<tr>
<td>SBN55</td>
<td>55.30</td>
<td>14.71</td>
<td>29.99</td>
</tr>
</tbody>
</table>

Computationally, it is not practical to irradiate the glass systems by accumulating displacement cascades [7,14] because of the significant time required. For this reason, a method based on accelerating the quench rate has been implemented in order to obtain disordered structures representative of the ones subjected to displacement cascades [9].

In a previous work, structural modifications of a simulated SBN14 glass specimen subjected to a series of 600 eV displacement cascades have been identified [7]. After the accumulation of 100 displacement cascades, volume expansion, depolymerization and increasing disorder have been observed. The density diminished by 4%, the mean boron coordination number decreased from 3.75 to 3.53, signifying conversions of tetra-coordinated boron atoms to tri-coordinated boron atoms and a larger number of non-bridging oxygen atoms form.

Moreover, a 6° decrease of the Si-O-Si and Si-O-B angles has been observed. The degree of disorder increased; a fact that has been detected by the broadening of the angular and ring size distributions.

We sought to qualitatively reproduce the phenomena described above by applying a rapid thermal quenching method to produce a structure representative of a glass irradiated by displacement cascades. The approach consisted of heating the glass, equilibrating at room temperature and melting for 50 ps in the NPT ensemble at zero pressure. The melting temperature was 3000K for SBN14 (3000K for SBN12 and 1600K for SBN55). The heated structure was then quenched to room temperature at a rate of \(10^{14}\) K/s in the NVT ensemble. After quenching, the glass has been relaxed in the NPT ensemble for 20 ps to determine its new equilibrium volume and then for 5 ps in the NVE ensemble while maintaining the previously determined equilibrium volume.

This technique produced glasses characterized by a lower density than the initial one, a lower degree of polymerization and a greater degree of disorder.

Hence, this method qualitatively reproduces the effect of displacement cascade accumulation as shown in Table 2 where a comparison of the two methods in the case of the SBN14 glass is presented.

Table 2. Comparison of the effects of accelerated quenching and accumulation of 600 eV displacement cascades in SBN14 glass

<table>
<thead>
<tr>
<th></th>
<th>Accelerated quenching</th>
<th>Displacement cascades</th>
</tr>
</thead>
<tbody>
<tr>
<td>Swelling</td>
<td>7%</td>
<td>4%</td>
</tr>
<tr>
<td>Percentage increase in [3]B</td>
<td>10%</td>
<td>17%</td>
</tr>
<tr>
<td>Decrease in Si-O-Si angle</td>
<td>2.2°</td>
<td>6°</td>
</tr>
<tr>
<td>Decrease in Si-O-B angle</td>
<td>2°</td>
<td>6°</td>
</tr>
<tr>
<td>Mean ring size</td>
<td>Initial: 4.82</td>
<td>Initial: 4.95</td>
</tr>
<tr>
<td></td>
<td>Final: 4.72</td>
<td>Final: 4.79</td>
</tr>
</tbody>
</table>

The rapidly quenched SBN14 glass exhibits the same general structural alteration as the SBN14 glass subjected to a series of displacement cascades, and is thus considered as a good model for assessing the impact of irradiation on the mechanical properties. One has to keep in mind though that some differences do exist between the irradiated glass and the heat-treated glass, a point which will be developed in the discussion.

In the following parts of the paper, the glass prepared using accelerated thermal quench will be called “disordered glass” in contrast to the glass quenched at a slower rate, called “pristine glass”.

3. Effect of thermal quenching on the fracture behavior

3.1 Fracture simulation details
The parallelepiped simulation cell containing the glassy structures with $10^5$ atoms were fractured as follows. First, 2000 atoms were removed in order to notch one face of the simulation cell. The notched samples were then relaxed at 5 K for 50 ps before being fractured.

Afterwards, periodic boundary conditions were eliminated along the vertical Z axis to allow the application of a tensile force. To avoid surface effects following the elimination of periodic conditions along the Z axis, two atomic layers were frozen at the top and bottom of the simulation cell. In these layers, the atom positions were fixed.

To fracture the samples a tensile force was applied by imposing progressive displacements in the Z direction on the frozen layers. A displacement was applied at each time step with a strain rate of $4 \times 10^{-6}$ fs$^{-1}$. This method is classically used in fracture simulation studies \[15,16\]. The temperature was maintained at 5 K using a Berendsen thermostat throughout the duration of fracturing to avoid adding thermal effects to the tensile effects.

3.2 Results

We have compared the pristine and disordered glass behaviors on the basis of the stress – strain curve (Figure 1.). The overall stress tensor of the simulation cell is calculated from the conventional virial formula \[17\]:

$$\sigma_{\alpha\beta}^V = \frac{1}{V} \left\{ \sum_{ij} \frac{1}{2} r_{ij}^\alpha f_{ij}^\beta + \sum_i m_i v_i^\alpha v_i^\beta \right\},$$  \hspace{8mm} (1)

where $V$ is the volume of the simulation cell, $r_{ij}^\alpha$ and $f_{ij}^\beta$ are the $\alpha$ and $\beta$ coordinates of the vector distance between atoms $i$ and $j$ and the force exerted by atom $j$ on atom $i$ respectively. The $m_i$ and $v_i^\alpha$ terms represent the mass of atom $i$ and the $\alpha$ coordinate of its velocity.

The overall deformation along the Z axis when the external tensile stress is applied is measured as the ratio between the displacement applied to the frozen layers in the simulation cell and the sample size in the Z direction. The stress/strain curves are plotted using the $\sigma_{zz}$ component of the stress tensor, i.e. the component measuring the atomic-level tensile force applied.

![Figure 1. Stress-strain curve measured for the pristine (black line) and disordered (grey line) SBN14 glasses](image-url)
The stress/strain curves exhibit a usual shape, with a linear stress increase versus strain for small deformations (the “elastic phase”), followed by a plateau in which the stress varies little while the strain continues to increase, and a decreasing leg where the stress diminishes until structural decohesion (the “plastic phase”).

Young’s modulus is estimated for the SBN14 glass from the mean slope of the initial linear portion of the stress-strain curve. The values determined for Young’s modulus in the pristine glass is 74.0 GPa while the corresponding experimental value is 82 GPa (+10%) [18].

Interestingly, a small number of bond breaking is observed during the “elastic phase”. This means that the term “elastic phase” used to refer to the linear part of the stress – strain curve is not rigorously exact at the atomistic level.

Concerning the microscopic mechanisms that appear during strain deformation, a detailed description is proposed in the following reference [9]. Only the most significant processes are summarized here.

The observation of the dynamical fracturing of simulation cells reveals four stages in the process: nucleation of cavities, growth of cavities, coalescence of cavities, and final decohesion. As already observed during earlier studies, cavity nucleation does not occur systematically near the tip of the notch: some cavities can appear at a distance. The cavity formation is enhanced when the amount of free volume inside the glass is large. In consequence, more cavities are counted in the disordered glass compared to the pristine one.

In the SBN14 glass, cavities tend to form in areas initially enriched in Na atoms. These regions can be deformed easily because the bonds between Na and O atoms are relatively weak and the Na atoms can move easily under the effect of an external perturbation [19].

To analyze the structural changes that accompany glass fracture, the partial radial distribution functions are plotted at different moments of the sample deformation. The B-O radial distribution function is plotted in Figure 2. Only the first peak of the function is shown; the subsequent peaks do not show any significant changes.

![Figure 2. B-O radial distribution function at different moments (a. between 0ps and 24ps, b. between 24ps and 40ps) in the SBN14 pristine glass](image)

The distances between tri-coordinated boron and oxygen atoms are shorter on average than the distances between tetra-coordinated boron and oxygen atoms, a fact which explains the two clearly separated sub-peaks (the calculations are performed at low temperature, which also limits fluctuations in the first-neighbor distances).
A difference is visible in the behavior of B-O bonds depending on the boron coordination number. The [4]B-O bonds stretch initially because of the local stress concentration, then return to their original state following the creation of new free surfaces during the cavity coalescence phase, allowing stress relaxation.

The [3]B-O bonds behave differently. No significant bond stretching occurs during the time interval between 0 and 40 ps. The height of the first maximum of the peak corresponding to the [3]B-O bonds at the end of fracture is simply observed to increase, reflecting the conversion of some tetra-coordinated boron atoms to tri-coordinated boron atoms during fracture. The tri-coordinated boron atom environment thus remains more stable than the one around tetra-coordinated boron atoms. This suggests that local stresses are not concentrated on BO4 entities to the same extent as BO3 entities. A possible explanation is that the local degrees of freedom are greater around BO3 entities because of the smaller number of chemical bonds that bind them to the polymerized network. They are thus freer to rotate or reorient. Presumably these entities, by easily adapting their local conformation to the external stress, participate to a greater extent in the plastic deformation process than the entities with more limited degrees of freedom, whose internal organization is deformed by external stress.

The SiO4 entities are observed to behave in the same manner as the BO4 entities (the radial distribution functions are shown in [9]). On the contrary, the local entities around the Na atoms are observed to behave in the same manner as the BO3 entities. So the local environments around the tri-coordinated B atoms and the Na atoms adapt themselves easily to the applied external tensile stress.

Experimentally, it has been observed that the SBN14 fracture toughness increases by 16% when it is subjected to an external irradiation by thermal neutrons for a deposited nuclear energy corresponding to an internal dose of 6.1 $10^{19}$ $\alpha$/g [20]. An explanation for this fact can be proposed on the basis of the atomistic simulations. The irradiated structure is more disordered and depolymerised than the pristine one, and its density decreases. The density decrease induces an easier cavity formation and hence, an easier fracturing. On the other hand, the more depolymerised structure leads to a greater amount of plastic processes, which delays the glass fracturing. In the SBN14 case, it seems that this second process is dominant and results in a fracture toughness increase.

4. Effect of thermal quenching on the hardness

4.1 Hardness simulation details

Prior to performing the nanoindentation simulations, the surfaces of the glass were relaxed for 50 ps, while keeping the bottom atoms fixed. Afterwards, they were indented using a Vickers diamond tip sized 9.8 nm x 9.8 nm x 3.05 nm with a 136° apex angle, displaced in steps of 0.1 Å with a constant speed of 10 m/sec. At the point of full loading a 50 ps holding period was introduced in order to cancel a large number of structural collective motions, while at the end of each simulation a final 20 ps relaxation step was performed. In this way the pristine glasses were indented up to a total displacement of approximately 3.0 nm and then the simulations were repeated for the disordered glasses to the point that the two maximum loads almost matched.

To model the interactions between the diamond tip and the glass structure, ZBL potentials were used [21]. These potentials were able to reproduce the short range repulsion when the tip penetrated the glass. The hardness values presented here have been calculated by employing the Oliver-Pharr method [22,23].

4.2 Results

The nanoindentation profiles (shown in reference [10]) clearly suggest that the hardness of the SBN14 disordered structure is lower to that of the pristine one since for an identical applied load, the penetration depth is larger. Quantitatively, hardness values of 5.5±0.6 GPa and 3.9±0.6 GPa are respectively measured in the pristine and disordered SBN14 glass, corresponding to a 29.1% decrease.

Concerning previous experimental results, our calculated values for the pristine glasses are comparable to the ones found by Kato et al. [24] and Yoshida et al. [25] for sodium borosilicate glasses of similar compositions using Vickers indentation. Furthermore, when compared to the 5.79 GPa and 4.05 GPa hardness values obtained by de
Bonfils et al. for pristine and Au irradiated SBN14 glass [6], our results show very good agreement. The reported 30%-35% decrease in hardness is also correctly reproduced.

The same procedure is applied for the glasses called SBN12 and SBN55, to complete our understanding about the correlations between glass compositions and hardness. Systematically a hardness decrease is observed in the disordered structures compared to the pristine ones.

When the three glassy compositions are considered together in their pristine forms, correlations between local entities and hardness can be evidenced. First, it appears that the increase of the SiO$_2$ content results in a noticeable increase of the hardness. This is a consequence of the content increase of the very stable SiO$_4$ tetrahedra, a result which is in agreement with previous works [19]. Secondly, when the hardness values of the pristine glasses are plotted together with the [3]B coordination and non-bridging oxygen percentages (Figure 3.), it appears that a decrease of the [3]B percentage leads to a hardness increase, while an increase of the non-bridging oxygen percentage leads to a hardness decrease. This result is quite logical because [3]B and non-bridging oxygen lead to a weakening of the structure in a similar way as was described for the effects of fast quenching on fracture toughness.

For the three disordered glasses, the hardness change is plotted alongside the [3]B change (Figure 4). In this figure, the horizontal axis corresponds to the [3]B number of the disordered structures expressed relatively to the total number of formers (i.e. Si+B). It appears that the larger the number of tri-coordinated boron atoms created among the formers, the larger the hardness decrease. So, a high [3]B concentration facilitates the network deformation, in agreement with what has been observed previously concerning the fracture behaviour.

![Graph](image_url)  

**Fig. 3.** Hardness value and [3]B and non-bridging oxygen concentrations for three pristine SiO$_2$–B$_2$O$_3$–Na$_2$O glasses. The glass compositions are given in Table 1.
Finally, in the disordered glasses, there is a systematic decrease of the density due to the swelling of the structure and as a result free volume is created. This fact can also contribute to the hardness decrease since it is expected that the indentation tip will be able to move more easily into a more open structure.

5. Discussion

Radiation effects were simulated indirectly by accelerating the quench rate during the glass elaboration. This leads to structural modifications of the glassy structure: increase of the $[3]B$ concentration relative to the $[4]B$ concentration and increase of the non-bridging oxygen concentration. In parallel, the disorder level increases corresponding to a systematic widening of the structural distributions (first neighbour distance, angular, and ring size distribution).

These structural modifications are at the origin of mechanical property changes in the SBN14 glass: fracture toughness increase and hardness decrease. Concerning the fracture toughness, the change can be explained by the $[3]B$ content increase leading to more plastic events during the fracture of the glass. This effect is dominant compared to the opposite effect associated to the free volume increase inside the glass structure, which facilitated the cavitation.

In Kieu’s work [9,20], two other glasses, SBN12 and SBN55, were considered. In the case of the SBN12 glass (containing a low Na$_2$O concentration), a fracture toughness decrease is measured in the disordered glass compared to the pristine one. In this glass, the effect associated to the free volume increase is dominant compared to the competitive effect associated to the boron coordination decrease. Concerning the SBN55 glass, a quasi stability of the fracture toughness is measured.

Hence, it seems that, depending on the glass composition, the dominant effect can evolve, leading to an increase or a decrease of the fracture toughness.

The situation is different for the hardness. In this case, both free volume accumulation and $[3]B$ concentration increase in parallel with the formation of non-bridging oxygen induce a decrease of the hardness. Indeed, if free volume accumulates in a glass network, it will be easier for the indentation tip to penetrate the material. Moreover, the average boron coordination decrease and the formation of non-bridging oxygen allowing more plastic
deformation, will also lead to a hardness decrease. In consequence, for the SBN14, but also for the SBN12 and SBN55 glasses [10], a hardness decrease is systematically observed, in agreement with experimental findings [6].

One point that is difficult to accurately estimate is the amount of artefacts introduced by the thermal treatment method used to prepare the disordered glasses, compared to a real irradiation by displacement cascade accumulation. Indeed, accelerating the quench rate mimics the radiation effects up to a certain point, but some differences remain [26]. In particular, it has been shown that a displacement cascade accumulation provokes a larger disordering and the formation of larger open spaces compared to structures prepared at different quench rates. For this reason, it is difficult to estimate the consequences of replacing displacement cascades by a simple thermal treatment. Only by simulating larger systems irradiated by displacement cascades will we be able to definitely answer this question.

6. Conclusion

Understanding radiation effects in nuclear glasses is important in order to assess their long term behaviour in a geological repository. In this paper, the results obtained by classical molecular dynamics about the mechanical properties of a simplified SiO$_2$–B$_2$O$_3$–Na$_2$O glass with the same molar proportions as in the real French nuclear glass were reviewed. A pristine and a disordered structure, representative of the irradiated one, were prepared in order to address the question of the radiation effects on the fracture toughness and hardness.

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Concerning the hardness, both the decrease of the boron coordination in parallel with non-bridging oxygen formation and free volume accumulation lead to a hardness decrease because of a more disordered and open structure that facilitate the tip penetration.

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