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Nanoindentation studies of simplified nuclear glasses using molecular dynamics

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ABSTRACT

Indentation experiments on complex borosilicate glass used for the immobilization of long-lived radionuclides have demonstrated that its hardness is decreased up to a specific value after being subjected to alpha disintegrations. In this study we have performed multi-million atom nanoindentation simulations using molecular dynamics in order to better understand the atomic mechanisms that produce this decrease. The glasses we selected to simulate are three simplified sodium borosilicates in a pristine form, as well as a "disordered" form, which is analogous to the real irradiated glass. The profiles obtained after the end of the nanoindentation simulations exhibit sink-in for all cases. The calculated hardness values agree with those previously published and were found to follow the decreasing trend which has been experimentally observed after irradiation. These values were found to depend on the composition and more specifically on silica, three-coordinated boron and non-bridging oxygen content. During nanoindentation, silicon atoms retain their coordination numbers, while there is an increase in boron and sodium coordination during loading and a partial reversal during unloading. Finally, nanoindentation induced an increased number of small rings and a decrease of larger ones, the effect being more notable in the case of disordered glasses.

1. Introduction

Complex borosilicate glasses are of interest in the nuclear industry because they are used for the immobilization of high activity waste i.e. long life and highly radioactive actinides and fission products. Since these glasses are being subjected to irradiation it is important to follow the evolution of their properties with time, in order to ensure their satisfying long-term behavior. In France the borosilicate based R7T7 glass is currently being used for the containment of high activity waste [1]. For this complex oxide glass it is now established that collisions by heavy recoil nuclei are mainly responsible for the variation of its mechanical properties up to a dose of approximately 2×10^{18} α/g [2,3], after which a plateau is reached. At the same time the complexity of this glass, due to the high number of its constituents, often forces us to consider more basic systems that contain the most important components. In this direction work has been carried out on simplified oxide glasses that contain the basic components of R7T7, demonstrating that alpha disintegrations result in the swelling of the glass matrix, the increase of fracture toughness and the decrease of Young's modulus, as well as hardness up to a saturation point [4–7]. More specifically, as far as the evolution of hardness is concerned, the study of De Bonfils et al. for boron, silicon, and sodium oxide based simplified nuclear glasses of the CJ series under Au irradiation showed that it generally decreases between 30%–35% without reporting a particular dependence on composition [5].

Sodium borosilicates are an important group of simplified oxide glasses that can aid us towards the complete understanding of the mechanical properties of nuclear glass under irradiation. Their microstructure has been adequately described by the Yun-Dell-Bray model [8–10] which relates the observed nonlinearity of boron coordination with the ratios $R = [Na_2O]/[B_2O_3]$ and $K = [SiO_2]/[B_2O_3]$. For the hardness of sodium borosilicate glasses with a high SiO_2 content, previous studies have shown that it reaches a maximum close to $R = 0.5$ because at this value the percentage of four-coordinated boron reaches its highest value [11,12]. Nonetheless, we also have to consider the effect of non-bridging oxygen atoms, which start to make their appearance at lower values of R and could affect the mechanical properties.

In this study we focus on the microstructural alterations that produce the observed decrease of hardness after irradiation. For this reason we have performed large-scale molecular dynamics (MD) simulations of Vickers nanoindentation for three sodium borosilicate glasses. The simulations have been performed on the pristine form of the glasses alongside a disordered state which exhibits similar structural characteristics to the true irradiated glass.

2. Method

2.1. Computational details

As mentioned in the Introduction section, we have focused on three sodium borosilicate glasses, whose compositions can be seen in Table 1.

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SBN14, also known as CJ1, is the one closest to the composition of the actual R7T7 glass.

For the calculation of the interactions between the atoms of the borosilicate glass, we have used the potential that was recently developed by Kieu et al. [13], which uses adjustable charges depending on chemical composition, in order to accurately describe boron coordination in the matrix and has been previously used for the study of mechanical properties of sodium borosilicate glasses [7]. For the interaction between the glass and the carbon atoms of the indenter we chose the short-ranged Ziegler–Biersack–Littmark (ZBL) potential [14], while Ewald summation was used to treat the Coulombic terms. For all atomic pairs, we set the potential cutoff to 8.0 Å, Newton's equations of motion were integrated using the leapfrog algorithm with a timestep of 1 fs, while the Berendsen thermostats and barostats were used, as will be described below.

The non-irradiated structures were created by melting random configurations of the desired atomic composition at 5000 K for 100 ps and afterwards cooling to 300 K with a rate of $5 * 10^{12}$ K/s in 100 K steps using the constant volume-isothermal (NVT) ensemble, followed by a 20 ps equilibration using the isothermal-isobaric (NPT) ensemble and 5 ps using the constant volume-constant energy one (NVE). In order to simulate the glassy structure after the effects of ballistic damage one has to initiate a series of displacement cascades inside the matrix. For systems as large as the ones in this study this would require an excessive amount of computational time. Instead, we have used the fast quenching method that has been previously shown to predict well the swelling of the glasses and increase of $^{[3]}$B with respect to the effect of displacement cascades [7]. According to this method, the structures were heated to a specific temperature and then a progressive cooling was performed, this time using a rate of 10^{14} K/s and the NPT ensemble. This way we can achieve a different fictive temperature and vary the $^{[3]}$B content in the glass, as it has been previously experimentally shown for sodium borate glasses [15]. The heating temperatures used were 3000 K for the SBN12 and SBN14 glasses and 1600 K for SBN55. This way the glass structure that we obtain is not the real irradiated one but an analogous that displays similar structural characteristics. In the following parts of this work the term “pristine” will be used to indicate the non-irradiated glasses and the term “disordered” for the ones obtained by fast quenching.

Prior to performing the nanoindentation simulations the surfaces of all structures were relaxed for 50 ps, while keeping the bottom atoms fixed. Afterwards, they were indented using a Vickers diamond tip sized 9.8 nm × 9.8 nm × 3.05 nm with a 136° apex angle, displaced in steps of 0.1 Å with a constant speed of 10 m/s. At the point of full loading we introduced a 50 ps holding period in order to cancel a large part of collective motion in the structure, while at the end of each simulation a final 20 ps relaxation step was performed. In this way the three pristine glasses were indented up to a total displacement of approximately 3.0 nm and then we repeated the simulations for the disordered glasses to the point that the two maximum loads almost matched. A typical system setup for nanoindentation is shown in Fig. 1. Compared to an experimental nanoindentation setup, our system has a smaller size and penetration depth but nonetheless we can extract valuable information about the microstructural behavior of these glasses under stress, being close to the limit of what can be achieved this day with the use of MD simulations.

Table 1
Percent molar composition and total number of atoms for the glasses under study.

	SiO_2 (mol.%)	B_2O_3 (mol.%)	Na_2O (mol.%)	N_{at} ($\times 10^6$ atoms)
SBN12	59.66	28.14	12.20	2.1
SBN14 (CJ1)	67.73	18.04	14.23	2.1
SBN55	55.30	14.71	29.99	2.2

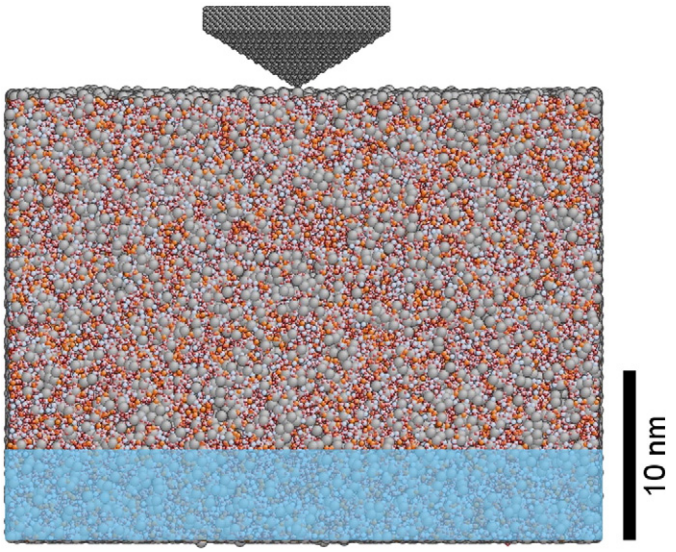

Fig. 1. Simulation cell prior to nanoindentation for the disordered SBN14 glass. The light-colored area indicates the fixed bottom layer. Color version: Dark gray, light gray, orange and red spheres are Na, Si, B and O atoms, respectively.

All the calculations in this work have been performed using the DL_POLY MD code [16] on 128 2.7 GHz cores at the TGCC supercomputing center of CEA.

2.2. Structural characterization

As described in the computational details, before performing the nanoindentation simulations for each glass, we canceled the periodic boundary conditions on the z-axis in order to allow any atomic rearrangements in the surface layers to take place. To quantify the relaxation of each surface, we used the formula:

$$\Delta z = \frac{z_{fin} - z_{ini}}{z_{ini}} \quad (1)$$

where z_{ini} is the height of the simulation cell before the cancelation of boundary conditions and z_{fin} is the surface level after the surface relaxation. The surface level was defined by dividing the cell into 5 Å boxes, finding the atom with the highest z-coordinate in each one and then averaging.

Regarding the surface deformation after nanoindentation, we calculated the profiles on a line that passes through the center of the imprint mark in order to detect any possible sink-in or pileup of the material. These profiles have been calculated by defining a series of parallelepipeds sized 10.0 Å × 5.0 Å × L_z (where L_z is the height of the simulation box) on a line which vertically intercepts the imprint mark and finding the atom with the highest z-coordinate in each one.

The hardness values presented in the results were calculated by employing the Oliver–Pharr method [17,18]. This method is frequently used in nanoindentation experiments and makes use of the loading–unloading curve. According to it we fit to the unloading part the function:

$$P = a\left(h - h_f\right)^m. \quad (2)$$

This way it is possible to calculate the contact stiffness S, defined as dP/dh at maximum loading P_{max}. We can then calculate the value of the contact depth h_c:

$$h_c = h_{max} - 0.75\frac{P_{max}}{S}. \quad (3)$$