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Interstitial sites for He incorporation in nuclear glasses and links to the structure: Results from numerical investigation

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ABSTRACT

To investigate rare gases incorporation in glasses in relation with nuclear waste confinement, a wide range of borosilicate glasses have been studied by means of molecular dynamics simulations. The rare gases solubility is related to the number of interstitial sites accessible for these gases. To elucidate any relation between the number of interstitial sites and the glass composition, a large set of glass compositions that contain the most representative components in nuclear glasses is considered. We are mainly interested in SBN glasses (SiO_2–B_2O_3–Na_2O). A composition dependent force field was used to model the interactions between the atoms. Delaunay tessellation method was used to characterize the different topologies accessible for rare gases and analyze the interstitial sites distribution. In order to investigate irradiation effects by nuclear energy deposition on the number of interstitial sites accessible for He, disordered glasses representative of structures submitted to series of displacement cascades, were prepared by modifying the preparation procedure and the number of interstitial site changes were analyzed.

1. Introduction

Borosilicate glasses are widely used, nowadays, in different domains ranging from industrial to optical applications. In particular, they are used for nuclear waste confinement. For this purpose, more complex glasses were developed. One of them is the French nuclear glass known as R7T7, which has been developed for several years in order to optimize its properties [1–3]. This glass contains more than 30 different oxides leading to a more complex structure that is very difficult to study numerically. It is not an easy task to fit a potential that can reproduce accurately the structure of such complex glasses. As a first approach to simulate complex glasses, one can consider simplified glasses with three oxides as in our case. This choice is limited by the simulation tools and mainly the empirical potentials that can reproduce accurately the structure of these glasses.

The long term behavior of nuclear waste glasses (alteration under water [4,5], under irradiation [6–12]) have been studied by many authors. Due to the α disintegrations, He ions accumulate in the glassy network. The rare gas solubility [13–16] in glasses is related to the number of interstitial sites accessible for these gases. This number can be determined using Delaunay tessellation method [17].

The main components of the glasses used for nuclear waste confinement are: SiO_2, B_2O_3, Na_2O, Al_2O_3 and CaO. They represent 80% of the total mass of the R7T7 glass [1]. Even if these constituents form a large fraction in the glass composition, one has to keep in mind that the rest of the oxides, even at small fractions, could have an effect on the glass structure or at least on some of its properties. For simplicity, glasses with three oxides known as SBN glasses are considered. These glasses have been studied experimentally [20,21] and by molecular dynamics simulations [8,10,12]. In this paper, a large set of SBN glasses (see Table 1) is used to determine the number of interstitial sites accessible for He and establish the links with the glass composition. Delaunay tessellation method [17] is employed to determine the distribution and the number of interstitial sites that He can occupy.

This paper is organized as follow: first, the different borosilicate glasses investigated are presented. The next section is devoted to the simulation results. Our main concluding remarks are summarized in the last section.

2. Borosilicate glasses

Generally, SBN glasses [22] are characterized by two parameters: the ratio $K = [SiO_2]/[B_2O_3]$, between silicon dioxide (SiO_2) and boron trioxide (B_2O_3) in molar fractions [%], and the ratio $R = [Na_2O]/[B_2O_3]$, between sodium oxide (Na_2O) and boron trioxide (B_2O_3) in molar fractions [%]. Two series of SBN glasses were considered: the first corresponds to a K ratio of 2.12 and different values of the ratio R (0.43, 0.56, 0.79, 1.06, 1.36, 1.71 and 2.12). The

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Table 1
Compositions of SBN glasses: the compositions are reported in molar fractions [%]. The experimental densities are also reported.

Glass	SiO_2	B_2O_3	Na_2O	K	R	ρ_{Exp}
SBN-12	59.66	28.14	12.20	2.12	0.43	2.378
SBN-15	57.63	27.13	15.24	2.12	0.56	2.380
SBN-20	54.19	25.51	20.30	2.12	0.79	2.497
SBN-25	50.76	23.89	25.35	2.12	1.06	2.521
SBN-30	47.33	22.28	30.39	2.12	1.36	2.518
SBN-35	43.95	20.63	35.42	2.12	1.71	2.540
SBN-40	40.47	19.08	40.45	2.12	2.12	2.510
SBN-55.3	55.30	14.71	29.99	3.76	2.03	2.540
SBN-59.2	59.24	15.76	25.0	3.76	1.58	2.540
SBN-63.2	63.20	16.80	20.0	3.76	1.19	2.481
SBN-67.1	67.10	17.90	15.0	3.76	0.83	2.450
SBN-CJ1	67.73	18.04	14.23	3.76	0.78	2.450

second corresponds to a ratio K of 3.76 and different values of the ratio R (0.78, 0.83, 1.19, 1.58 and 2.03). In total, we have investigated 12 SBN glasses.

These glasses were investigated by means of molecular dynamics simulations using the DL_POLY molecular simulation package [23]. A composition dependent force field [24] was used to model the interactions between the atoms. This potential is based on Buckingham potential type and includes Coulomb interaction treated via Ewald summation [25]. The parameters for Si–O, Na–O and O–O have been taken from the work of B. Guillot et al. [26]. The B–O parameters and the atomic charges have been adjusted to reproduce the complex environment around boron atoms [24].

3. Simulation results and discussion

3.1. Glass preparation

The glasses were prepared as follow: a random configuration of 10000 particles is generated and equilibrated at high temperature (5000 K) during 1 ns then quenched to room temperature with cooling rates of the order of 10^{12} to 10^{13} K/s. At room temperature, simulations at constant pressure ($p = 0$) were performed to determine the equilibrium glass density. The last step consists in simulation in micro-canonical ensemble for at least 1 ns using a time step of 1 fs to produce a set of configurations that are used to analyze the interstitial sites. For better statistics, the results are averaged over 100 configurations stored at fixed time intervals during 1 ns from the simulations in microcanonical ensemble (NVE).

3.2. Delaunay tessellation

Starting from a given atomic configuration, one can use Delaunay tessellation to compute the volume of interstitial sites between atoms. More details about this method and the algorithm can be found in the work of Malavasi et al. [17]. To apply the algorithm, the following atomic radii are used: 0.41 Åfor Si atoms [18], 0.27 Åfor B atoms [19], 0.95 Åfor Na atoms [18] and 1.10 Åfor O atoms. The Si, B and Na radii correspond to the values proposed by R.D. Shannon or L. Pauling [18,19]. The O radius corresponds to the half distance between atoms in O_2 molecule. This value is chosen in order to guarantee that, for two neighboring atoms, the value of their radii remains lower than the distance between them. In the rest of the paper, we will present the interstitial site radius distribution, considering each interstitial site as a sphere, and calculating its radius.

3.3. Distribution of interstitial sites

Using the Delaunay tessellation method [17], the distribution of the number of interstitial sites is determined as a function of the interstitial radius for all the glass compositions considered in the present study. Fig. 1 represents the distribution of interstitial sites in SBN glasses. For the clarity of the figure, only the distributions corresponding to the first serie ($K = 3.76$) of SBN glasses (SBN-55.3, SBN-59.2, SBN-63.2, SBN-67.1 and SBN-CJ1) and silica are shown. The distribution of interstitial sites in silica was obtained following the same method as in borosilicate glasses. A system of 10200 particles is used. The distributions corresponding to the second serie ($K = 2.12$) of SBN glasses are not shown in this figure since they follow the same trend as the distributions of SBN glasses shown in the Fig. 1.

The results show that the distribution of interstitial sites follow the same behaviour for all borosilicate glasses. However, these distributions differ slightly from that of pure silica. This later is shifted to highest interstitial radius and shows four different peaks while in the case of borosilicate glasses, only two main peaks were found. The height of these two peaks changes as a function of the glass composition. In the case of SBN glasses, the first peak decreases while the second increases with increasing the ratio R. Even if these distributions present some differences in the height of the peaks, they exhibit a similar behaviour for higher interstitial radius value. All the distributions go to zero. However, the radius value where the distribution goes to zero depends strongly on the glass composition. For all borosilicate glasses and considered box simulation sizes used here, we found interstitial sites accessible for He (1.28 Å) atoms but no sites for Xe (radius 1.96 Å). From the Fig. 1, one can see clearly that the number of interstitial sites accessible for a given rare gas is higher in silica then in borosilicate glasses. This is related to the fact that some components in borosilicate glasses – like sodium – have a tendency to occupy the interstitial sites. The number of interstitial sites, depend strongly on the glass composition as one can see from the inset of Fig. 1 where the region between 1.2 and 1.8 Å is enlarged.

3.4. Number of interstitial sites

In pure silica, the number of interstitial sites accessible for He is 2.57×10^{27} sites/m^3. This value is in good agreement with the experimental value found in the literature (2.13×10^{27} sites/m^3) [27]. There is a difference of about 20.0% between the estimated value and the experimental one. This difference can be related to the atomic radii used or to a shift in the density. As the densities

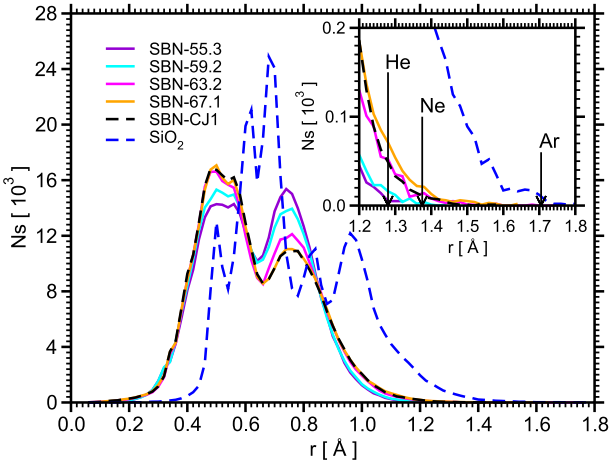

Fig. 1. Number of interstitial sites distribution in borosilicate glasses and silica at 300 K. The region between 1.2 and 1.8 Åwas enlarged and the arrows show He, Ne and Ar radii. Systems of 10000 atoms were used to determine the number of interstitial sites for SBN glasses (10200 for silica). The results were averaged over 100 configurations.