



# Molecular dynamics simulations of bio-active phosphate-based glass surfaces

Sergio E. Ruiz Hernandez<sup>a,\*</sup>, Richard I. Ainsworth<sup>b</sup>, Nora H. de Leeuw<sup>a</sup>

<sup>a</sup> School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff CF10 3AT, UK

<sup>b</sup> Department of Chemistry and Biochemistry, University of California, San Diego 9500, La Jolla, California 920093-0359, USA

## ARTICLE INFO

### Article history:

Received 2 February 2016

Received in revised form 24 May 2016

Accepted 5 June 2016

Available online xxxxx

### Keywords:

Molecular dynamics

Dissolution

Phosphate

Bioactive glass

## ABSTRACT

Classical molecular dynamics (MD) simulations were used to study the structural changes in the surfaces of bio-compatible phosphate glasses with compositions  $(P_2O_5)_{0.45}(CaO)_x(Na_2O)_{0.55-x}$  ( $x = 30, 35, 40$ ) to evaluate their effect on the solubility of the material. Direct comparison of the data for the three compositions highlighted the critical role that an enhancement in  $Na^+$  concentration plays in the hydrolysis of the material, which is responsible for the release of network components into solution. The calculations also confirm that the most soluble material is  $(P_2O_5)_{0.45}(CaO)_{0.30}(Na_2O)_{0.25}$ , has the lowest calcium coordination number, thereby causing fewer cross links to phosphate chains.

© 2016 Published by Elsevier B.V.

## 1. Introduction

Phosphate-based glasses (PBGs) in the  $CaO-Na_2O-P_2O_5$  system have a number of biomedical applications [1,2]. Their ionic compositions mimic the mineral constituent of hard tissue, and they can therefore act as a template to repair soft tissue [3]. Based on their controlled ion release capabilities, they can also temporarily replace hard tissues whereas metal-doped PBGs are used in veterinary medicine to treat trace element deficiencies [1,4,5]. PBGs can also be employed to deliver drugs, from simple antibacterial ions such as Ag or Cu [1,6,7] or radioisotopes [8] to potentially more complex organic molecules for chemotherapy applications [9].

The success in medicinal utilization of this unique group of materials is closely related to their ability to dissolve completely *in vivo* in aqueous media, where the solubility rate can be tuned by altering the  $Ca^{2+}/Na^+$  ratio. It is known that the solubility of these ternary phosphate-based bioglasses decreases with an increase in the  $Ca^{2+}/Na^+$  ratio in the composition [10,11]. Much of our recent computational work has been dedicated to improving our understanding of glass dissolution processes and the structural and compositional features that affect them [12–14]. For example, previous theoretical studies of the bulk glass have shown that the mentioned change in solubility is caused by  $Ca^{2+}$  binding more phosphate chains than  $Na^+$ , thereby satisfying its bonding preference for non-bridging oxygen neighbours at the expense of sodium [12]. Also  $Ca^{2+}$  binds to more  $PO_4^{3-}$  tetrahedra and has a lower concentration of intra-tetrahedral phosphate bonds than  $Na^+$ ,

where both features help to enhance the glass's durability as more  $Ca^{2+}$  is included [12]. The same authors proposed that the clustering of modifier cations, which affect the solubility of these bioactive glasses by strengthening the glass network, should also be considered [14].

Thus far, theoretical studies on PBGs have been limited to the bulk material, but further detailed investigations must directly focus on the interface between the glass and the physiological environment, considering that it is at the surface that the bioactive processes occur. Moreover, among the wide range of factors affecting the solubility of the ternary phosphate-based bioglasses are the ion exchange between the surface and environment and variations in the glass surface structure. Classical molecular dynamics simulations (MD) with an accurate force field [13–19] have proven to be a highly suitable computational tool to obtain atomistic models of melt-derived glasses. They can provide a precise representation of the bonding and coordination environments found in the PBG surfaces, thus enabling the generation of larger statistical samples [15] than would be available from *ab initio* methods.

In this work we have therefore used MD to explore structural changes in the glass surfaces of compositions  $(P_2O_5)_{0.45}(CaO)_x(Na_2O)_{0.55-x}$  ( $x = 30, 35, 40$ ) and their influence on the material's bioactivity and solubility.

## 2. Methods

### 2.1. Structural models

The composition of the glasses and the notation used in this work are shown in Table 1 and the protocol for obtaining the models is described in details in Ainsworth et al. [1]. Starting from the volume-

\* Corresponding author.

E-mail address: RuizHernandezS@cardiff.ac.uk (S.E. Ruiz Hernandez).

**Table 1**  
Composition of the glass studied.

Notation	Composition	$\rho$ (g/cm <sup>3</sup> )	Number of atoms	Box size
N25	(P <sub>2</sub> O <sub>5</sub> ) <sub>0.45</sub> (CaO) <sub>0.30</sub> (Na <sub>2</sub> O) <sub>0.25</sub>	2.56	3001	34.65
N20	(P <sub>2</sub> O <sub>5</sub> ) <sub>0.45</sub> (CaO) <sub>0.35</sub> (Na <sub>2</sub> O) <sub>0.20</sub>	2.57	2998	34.69
N15	(P <sub>2</sub> O <sub>5</sub> ) <sub>0.45</sub> (CaO) <sub>0.40</sub> (Na <sub>2</sub> O) <sub>0.15</sub>	2.59	3001	34.71

optimized bulk supercell, two slab geometries with 3D periodicity, but with the top and bottom faces exposed to vacuum (Fig. 1), were obtained by elongating the c vector of the simulation cell by ~30 Å, producing four surface samples by exposing different sections of the bulk glass.

## 2.2. Evaluation of interatomic potential energies

Our simulations are based on the Born model of solids [21], where ions are assumed to interact via long-range Coulomb forces and additional short-range forces given by simple parametric functions which represent electron-mediated interactions, e.g. Pauli repulsions and Van der Waals dispersion attractions between neighbouring electron charge clouds. The electronic polarizability of the ions is also accounted for via the model by Dick and Overhauser [22], in which each polarizable ion is represented by a core and a massless shell, connected by a spring. The spring constant and the distribution of the ion charge between the

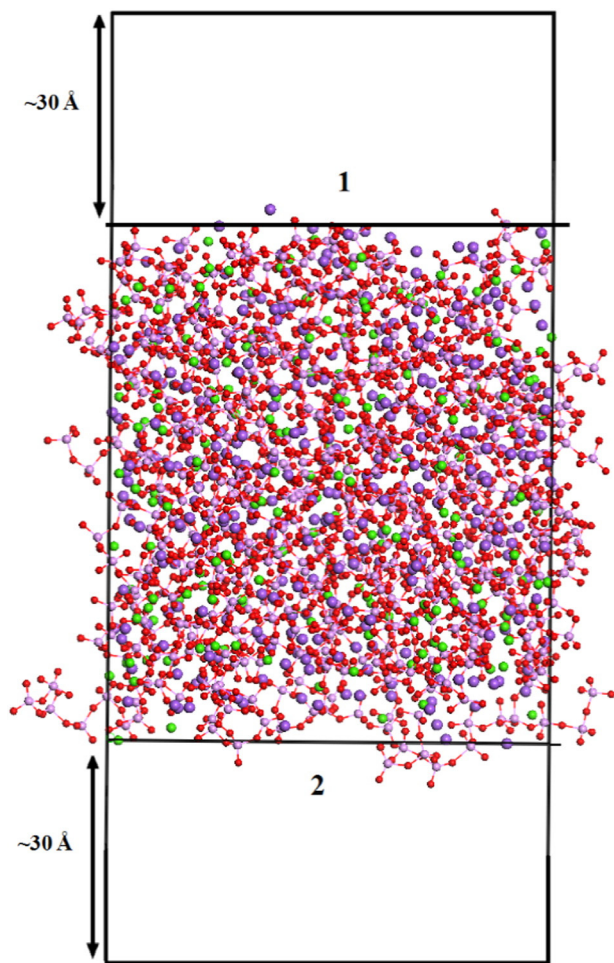
**Table 2**  
Potential parameters used in this work.

Species	Charge		Spring constant (eV Å <sup>-2</sup> )
	Core	Shell	
P	+5.0		
Ca	+2.0		
Na	+1.0		
O	+0.85	-2.85	74.92
Buckingham potential			
$A \exp(-r/\rho) - C/r^6$			
	A (eV)	$\rho$ (Å)	C (eV Å <sup>6</sup> )
P–Os	1020.0	0.34322	0.03
Os–Os	22,764.3	0.149	27.88
Ca–Os	56,465.3453	0.193931	0.0
Na–Os	2152.3566	0.309227	0.09944
Three-body potential			
$(1/2)k_{3b}(\theta - \theta_0)^2$			
	$k_{3b}$ (eV rad <sup>-2</sup> )		$\theta_0$
Os–P–Os	3.3588		109.47
P–Os–P	7.6346		141.1793

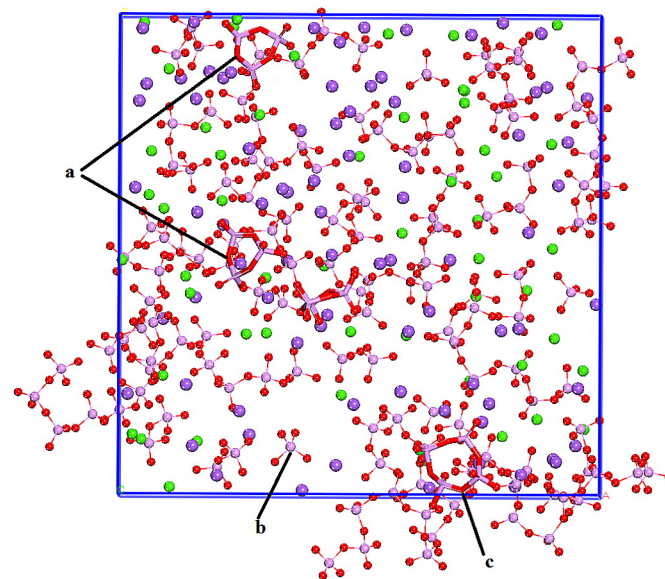
core and shell determine the polarizability of the ion. In our case, only the oxygen anion was considered polarizable, while cations were modelled as rigid ions. The potential model used here for the PBGs, shown in Table 2, is the formal-charge, polarizable force field to describe inter-atomic forces, which has previously been shown to accurately reproduce the structures and properties of glasses in the system P<sub>2</sub>O<sub>5</sub>–CaO–Na<sub>2</sub>O, compared to experiment and ab initio methods. [1,10,12].

## 2.3. Molecular dynamics simulations

The MD runs were performed in the constant volume and temperature (NVT) canonical ensemble at 300 K using the DL\_POLY code (version 2.20) [23], where all atoms were allowed to move during the simulations. An Evans thermostat [24] was used and the timestep between successive integrations of the Newtonian equation of motion was set to 0.1 fs. The motion of oxygen shells was treated by assigning



**Fig. 1.** Representation of the simulation cell exposing different surfaces, here labelled 1 and 2. P (pink), O (red), Ca (green) and Na (violet). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



**Fig. 2.** Top view of a sample surface in N25 showing some features observed after relaxation. Only the top 10 Å of the slab are displayed. (a) 3 M ring (b) Q<sup>0</sup> phosphates (c) 4 M ring. Color code: P (pink), O (red), Ca (green) and Na (violet). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Download English Version:

<https://daneshyari.com/en/article/5441471>

Download Persian Version:

<https://daneshyari.com/article/5441471>

[Daneshyari.com](https://daneshyari.com)