Iron phosphate glasses: Structure determination and displacement energy thresholds, using a fixed charge potential model

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A B S T R A C T

Iron phosphate glass is a versatile matrix for the immobilisation of various radioactive elements found in high-level nuclear waste (HLW). Quenched glass structures of iron phosphate glasses with Fe/P ratios of 0.33, 0.67 and 0.75 and with a composition of 40 mol% Fe_2O_3 and 60 mol% P_2O_5, with 4% and 17% Fe^{2+} ion concentrations were generated using molecular dynamics and the threshold displacement energies calculated. In the minimum energy structures, we found that in nearly all cases the P atoms were 4-fold coordinated. The potential energy per atom increased with increasing concentration of Fe^{2+} ions with similar Fe/P ratio, suggesting that decreasing the Fe^{2+} content is a stabilising factor. The average bond distances between Fe^{2+}–O, Fe^{3+}–O, P–O and O–O were calculated as 2.12, 1.88, 1.5 and 2.5 Å respectively. The threshold displacement energy (E_d) was found to be dependent upon the ion specie, less for Fe^{2+} ions compared to Fe^{3+} ions, and was overall slightly lower than that determined for borosilicate glass.

1. Introduction

Phosphate glasses, due to their favourable properties such as: reasonably low liquid and glass transition temperatures, low viscosity, high thermal expansion coefficient, high electrical conductivity and high ultraviolet transmission, find application in a wide range of fields. For example, phosphate glasses are used in lasers [1], solid electrolytes [2], bio-medical devices [3] and nuclear waste immobilisation [4]. A good review up to the year 2000 is given in [5]. According to the literature [6], in spite of the good glass forming characteristics of phosphate glasses, their relatively poor chemical durability limits their application, especially in the field of nuclear waste immobilisation. However, a new group of phosphate glasses, iron phosphate glass, is being considered as a promising matrix for the immobilisation of high-level waste rich in alkali oxides, sulphates and chrome oxides [7–10]. Iron phosphate glass and its waste form containing simulated fast reactor waste were synthesised, characterised and reported by us earlier [11,12]. Higher waste loading, better chemical durability and better corrosion resistance [13,14] are certain promising features of iron phosphate glass compared to other phosphate glasses. Among the various compositions of iron phosphate glass, the one with 40 mol% Fe_2O_3–60 mol% P_2O_5 (referred as IPG in the present paper) is found to be more chemically durable [15–17]. It also has the ability to accommodate large amounts of certain nuclear

wastes, especially those that are not well suited for borosilicate glasses [16]. The better chemical durability of iron phosphate glass is attributed to the presence of more hydration resistant Fe–O–P bonds compared to P–O–P bonds available in other phosphate glasses [16]. The synthesis, characterisation and experimental determination to elucidate the structure of a wide variety of iron phosphate glasses are available in the literature [7,17–20]. However, the available literature on the structural modelling of iron phosphate glasses is limited [21,22]. This is because, the structure of iron phosphate glasses, not only depends on composition, quenching temperature of the melt and quenching technique [23], it depends also on the concentration of Fe^{2+} and Fe^{3+} ions in the glass.

The iron phosphate glass with the composition 40 mol% Fe_2O_3–60 mol% P_2O_5, has been reported by various researchers to have different ratios of Fe^{2+}/Fe [7,12,24,25]. The concentration of Fe^{2+}/Fe in glass with the same atomic composition varies from 4 to 20%, while the density varies between 2.9 and 3.0 g cm^{-3} with the uncertainty in density ranging from ±0.005 to 0.02 g cm^{-3} [7,24]. The concentrations of Fe^{2+}/Fe and density of IPG reported by us [12] were 4% and 2.9 g cm^{-3} respectively. The promising composition of 40 mol% Fe_2O_3–60 mol% P_2O_5 (IPG) is found with the varying density depending on the concentration of Fe^{2+} in the glass. It is evident from the literature [7,24,25] that as the concentration of Fe^{2+} in IPG increases, the density also increases for the same atomic composition. It has been shown experimentally by Mössbauer spectroscopy [24], that as the melting temperature of IPG increased from 1423 to 1673 K, the density of the glass increased along with the increase in concentration of Fe^{2+}. Thus, it becomes essential to model the structure of iron phosphate glasses specific to the composition and Fe^{2+}/Fe ratio.

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Table 1
Three-body potential terms used in the present study.

Parameter	O–P–O	P–O–P
λ_i (eV)	5.3516	8.2997
$\gamma_{ij} = \gamma_{ik}$ (Å)	0.5	0.5
θ_0	109.47°	135.5°
r_c (Å)	2.5	2.5

It is well known that amorphous structures are more difficult to handle computationally than crystalline lattices since many different atomic configurations are possible. Therefore averaging over many different structures is very important. It is also essential to have good inter-atomic potentials that describe the amorphous systems. A recent paper [21] reported one of the first studies of iron phosphate glasses using fixed charge potentials.

Other authors have also developed potentials of a form that could be used to model phosphate glasses. However potentials that involve shell models such as that by Ainsworth et al. [26] are not really suitable for radiation cascade studies and a previous potential formulation by Pedone et al. [27], which also included the capability to model Fe–P–O systems had not been explicitly tested on these glasses. Since a key aim of our research programme is to investigate radiation effects in phosphate glasses, the potential developed in [21] was chosen as the underlying model for the work.

Thus we modify the potential in [21] so that it is suitable for radiation studies, compare the results with the previous work, and then test other compositional structures with various Fe/P ratio and Fe^{2+}/Fe ratios that we have produced experimentally. Furthermore, we determine the threshold displacement energies as the first step towards the investigation of collision cascades in these systems.

2. Methodology

Molecular dynamics simulation studies were carried out to model the structure of iron phosphate glasses. The code (LBOMD) has been used over many years for radiation damage studies, see e.g. [28] for work involving radiation damage in spinels. The two body interactions, i.e. Fe–O, P–O and O–O were modelled using a Buckingham rigid ion potential (Eq. (1)), together with a Coulomb term to model the long-range interactions between ionic charges.

$$V\left(r_{ij}\right) = \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} + A_{ij}\ \exp\left[\frac{-r_{ij}}{\rho_{ij}}\right] - \frac{C_{ij}}{r_{ij}^6}. \quad (1)$$

The subscripts, i and j, refer to each ion; q_i and q_j are the ion charges, r_{ij} is the inter-ionic distance and ε_0 is the permittivity of free space. The parameters: A_{ij}, ρ_{ij} and C_{ij} for each ionic bond are given in reference [21].

In addition to the two-body terms, three body terms were also used to control the local bond angles. This three-body potential is especially very important for P–O bonds due to their ionic–covalent nature similar to that of Si–O bonds found in silicate glasses [29].

The original authors [21] used a harmonic three-body potential, $V(\theta_{ijk}) = 1/2\ k(\theta_{ijk} - \theta_0)^2$, where k = 3.5 eV and θ_0 = 109.47° for O–P–O, and k = 3.0 eV and θ_0 = 135.5° for P–O–P. This function presents some computational difficulties for radiation damage studies, as it requires the computation of the derivative of arccos(θ) to obtain the forces. This derivative is infinite when θ = 180°. Furthermore, there is no smooth cut-off to zero as the atomic separation increases.

Among the various analytical forms of three-body potentials listed in the literature [30–32], the three-body Stillinger–Weber potential [31] (Eq. (2)) was chosen instead to model the three body terms. This is more suitable to use in radiation damage simulations and the construction of a potential that can be used in such simulations is also a key aim of the work.

$$\phi_3\left(r_{ij}, r_{ik}, \theta_{jik}\right) = \lambda\ \exp\left[\left(\frac{\gamma}{r_{ij}-r_c} + \frac{\gamma}{r_{ik}-r_c}\right)\left(\cos\theta_{jik} - \cos\theta_0\right)^2\right]. \quad (2)$$

For an atom triplet (j–i–k), r_{ij} and r_{ik}, are the two internal atomic separations, and θ_{jik}, is the bond angle at the central atom 'i'. θ_0 represents the angle towards which the angle θ_{jik} is constrained and r_c is the cut-off radius beyond which the three-body terms do not apply. λ, γ and θ_0 are adjustable parameters.

The Stillinger–Weber potential was chosen because the cos(θ) term is obtainable directly from the atomic separations via the dot product (also, the derivatives are a function of cos(θ)). The Stillinger–Weber potential has continuous derivatives and a built-in smooth cut-off to zero at r = r_c. We fit the Stillinger–Weber potential to the original authors' function by computing the parameter λ. We do this by computing the Taylor series expansion of Eq. (2) at $\theta = \theta_0$ to the second order. For this calculation we set γ = 0.5 eV and $r_{ij} = r_{ik}$ = 1.5 Å (the equilibrium bond length).

For both triplets (P–O–P and O–P–O), we set this equal to the original authors' function and rearrange to find λ. These parameter values (λ, γ and θ_0) for both triplets are summarised in Table 1.

For radiation damage studies, the two-body potential cannot model the repulsion between nuclei when the inter-particle separation is small. A screened Coulomb potential is normally used to model such interactions and the ZBL model [33] is the commonly used model when the separation is small. As a result we have joined the two-body potential given in Eq. (1) to the ZBL potential using a splining function. The details and parameters for the splining function are given in Table 2.

Each of the glass structures was prepared by distributing the required number of atoms of each species randomly within a cubic box. We then use a simple temperature-rescaling algorithm [34] to quench the system. This works by measuring the temperature at each time-step. If the temperature exceeds the desired value by 7%, then, the velocities of all the atoms are rescaled, such that, the temperature is the desired value. We quench the system from 6000 K to 10 K at a rate of

Table 2
The splining parameters for joining the Buckingham + Coulomb potential to the ZBL potential. The splining function is of the form $\exp(f_0 + f_1 x + f_2 x^2 + f_3 x^3 + f_4 x^4 + f_5 x^5)$ joined to the ZBL potential at x = a and to the Buckingham + Coulomb at x = b so that the function and its first 2 derivatives are continuous. The units of f_i are $Å^{-i}$. In the case of Fe^{3+}–O and O–P, there were offsets of 13 and 50 eV respectively added to the potential (and later subtracted) to make the potential positive at x = b.

Interaction	a (Å)	b (Å)	f_0	f_1	f_2	f_3	f_4	f_5
Fe^{2+}–Fe^{2+}	1.1	1.9	38.456891	−115.889467	166.591541	−122.352450	44.173231	−6.208431
Fe^{2+}–Fe^{3+}	0.9	1.9	11.672255	−14.893823	17.600151	−15.321189	6.858104	−1.147068
Fe^{2+}–O	0.2	0.85	11.274280	−21.233242	44.802056	−69.570862	60.519843	−21.948215
Fe^{2+}–P	0.7	1.45	13.486801	−28.411131	49.982100	−53.364231	28.581882	−5.844285
Fe^{3+}–Fe^{3+}	0.9	1.9	3.289491	20.674793	−40.640856	30.334182	−10.171431	1.285723
Fe^{3+}–O	0.5	1.25	13.468756	−36.254018	82.390627	−109.951757	74.401925	−20.216820
Fe^{3+}–P	0.4	1.45	11.230029	−14.585045	17.056385	−15.965608	8.848866	−1.935188
O_-–O	0.35	1.8	9.273627	−11.588100	8.398709	−2.456703	−0.030643	0.093801
O_-–P	0.25	1.03	11.166080	−26.912807	75.616106	−136.453869	116.256770	−36.456113
P_-–P	0.24	1.26	11.028636	−16.858035	23.118958	−21.054756	11.153372	−2.472515