Raman scattering and molecular dynamics investigation of lead metasilicate glass and supercooled liquid structures

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ABSTRACT

In this research we correlate the structural parameters obtained from molecular dynamics (MD) simulations and Raman scattering to construct a self-consistent picture of the glass structure, and its variation from ambient temperature to the supercooled liquid above the glass transition temperature (Tg). The MD results show that the glass structure is composed of SiO_4 tetrahedra and PbO_x (x = 4, 5) polyhedra. To correlate the Q^n population obtained from the MD and Raman a second type of Q^3 species is required. The two types of Q^3 species are interpreted as being associated with the bimodal distribution displayed by the Pb—Si pair correlation function. From a MD snapshot is also shown that the second Q^3 species can have a bridging oxygen bound to a Pb ion. As the temperature increases, depolymerization of the Q^n speciation is observed and confirmed by the oxygen speciation determined from both Raman and MD. The depolymerization of the silica network is consistent with the non-Arrhenian (fragile) viscosity decrease with temperature and may explain this viscosity behavior.

1. Introduction

Investigation of glass and supercooled liquid structures at high temperatures is of prime importance to understand glass properties, to tailor the composition of new functional glasses, and to describe natural phenomena, such as igneous processes [1, 2]. Silicate glass structures can be described in terms of building blocks having well-established short-range order, the silica tetrahedron (SiO_4) [2]. In pure silica glass, each SiO_4 is corner linked to four other SiO_4 (Q^4 units), forming a tri-dimensional "molecular" network where bridging-oxygen anions (BO) are bound to adjacent Si cations, −Si−O−Si−. The addition of modifier cations (M), such as Na or Pb, induces depolymerization of the silica network through the breakdown of −Si−O−Si− linkages, forming non-bridging oxygen anions (NBO), −Si−O−M. This depolymerization process creates tetrahedra that have different proportions of BOs and NBOs. These units are called Q^n species, where *n* represents the average number of BO per tetrahedron. Therefore, the Q^n species distribution yields insights into the connectivity of the silica network.

The PbO·SiO_2 (PS) is an important model for the glass community and its isochemical crystal phase melts congruently [3]. Moreover, lead silicate glasses are of considerable scientific interest because they have an outstanding glass forming ability despite having equal or less than 50 mol% of SiO_2 [4], so-called inverted glasses. Several investigations have reported the Q^n species of lead silicate glasses (Table 1). For

example, the MD simulations of Cormier et al. [5] calculated the dominant Q^n species as being Q^2, at 41%. Using nuclear magnetic resonance (NMR) experiments, Fayon et al. [6] found that Q^2 is 51% of the total Q^n, while Feller et al. [7] obtained 38% Q^2, and Schneider 47% (± 8%) [8]. More recently, Kacem et al. [9] obtained a population of 59% of Q^2 using Raman spectroscopy. Despite some numerical differences (Table 1), all these studies show that the PS glass at room temperature has a Q^n distribution centered on the Q^2 species, similar to its isochemical crystal.

In addition to the NBO and BO, some oxygen atoms may not be bound to Si atoms at all, the so-called free oxygens (O^{-2}) [10–12]. These particular oxygen atoms are referred here to as non-network oxygen (NNO); they are not bound to any Si atom but can be bound to M cations [13]. For example, an oxygen atom may be bound to two M cations via M-O-M linkages. For PS glass, Cormier et al. [5], using MD simulations, computed 36.6% of BOs, 60.0% of NBOs and 3.4% of NNOs. Based on the NMR experiments of Lee et al. [14], 36% of the total oxygen atoms are estimated to be BO, 62% are NBO and 2% are NNO, whereas Dalby et al. [15] obtained 42.6% of BOs from X-ray photoelectron spectroscopy experiments. Additionally, X-ray scattering, neutron scattering and computer simulations have also been used to study other structural parameters, e.g., first neighbor distances, co-ordination numbers and bond-angle distributions [4, 5, 16, 17]. Based on these parameters, it has been suggested that PS is composed by two

Table 1
Q^n distributions (%) of PS glass from previous studies.

Reference	Method	Q^0	Q^1	Q^2	Q^3	Q^4
Cormier et al. [5]	MD	2	19	42	30	7
Fayon et al. [6]	NMR	0	13	51	30	6
Schneider et al. [8]	NMR	0	21	47	26	6
Feller et al. [7]	NMR	6	25	38	25	6
Kacem et al. [9]	Raman	2	24	59	12	3

*These variations are partially due to the use of different techniques and fitting procedures, and also due to the glass samples being made (quenched) at different cooling rates.

subnetworks, one formed by the SiO_4 and the other formed by PbO_x (x = 3 to 5) polyhedra [16, 17].

Despite the numerous studies on PS glass structure, there is a lack of knowledge about the structural modifications that take place at high temperatures above Tg. Recently, Rodrigues et al. [18] showed that a combination of Raman spectroscopy and molecular dynamics simulations (MD) are a particularly good method for investigating the variation of glass structure with temperature. The Raman technique accesses the vibrational modes of the material, which for glasses are often very similar to the vibrational density of states calculated by MD. On the other hand, MD make use of the Raman spectrum to calibrate the energy scale to describe the structural properties [18]. Moreover, Raman spectroscopy permits the determination of the Q^n distribution [9], while the MD, can also describe the atomic structure via calculation of the pair correlation functions and bond-angle distributions, in addition to the Q^n population [5, 17]. As a result, it is possible to describe an insightful picture of a given glass structure and its temperature dependence.

In the present research, we determine the structural evolution with temperature of the PS glass and supercooled liquid. We stress the connection between Raman spectroscopy and MD simulation as a powerful combination to investigate glass properties and the development of structural models.

2. Materials and methods

2.1. Molecular dynamics simulation

The effective interaction potential proposed to describe the PS system has the same functional form as those used to study other oxide systems, like $BaSi_2O_5$ and $Ba_{1-x}K_xBiO_3$ [18–20]. It consists of a steric repulsion due to size effects, Coulomb interactions due to charge transfer between ions, charge-induced dipole due to the electronic polarizability of ions, and the van der Waals attraction. The interatomic potential reads

$$V(r) = A\left(\frac{\sigma_i + \sigma_j}{r}\right)^{\eta_{ij}} + \frac{Z_i Z_j}{r}\exp\left(-\frac{r}{\lambda}\right) - \left(\frac{\alpha_i Z_j^2 + \alpha_j Z_i^2}{2r^4}\right)\exp\left(-\frac{r}{\xi}\right) - \frac{W_{ij}}{r^6}. \quad (1)$$

here, A is the strength of the steric repulsion, σ is the ionic radii of the ions i and j, η_{ij} the exponent of the repulsion term, Z the effective charge of ions, α the electronic polarizability, and W_{ij} the van der Waals intensity. λ and ξ are the screening lengths for Coulomb and charge-dipole interactions, respectively. A cutoff distance, r_c, was introduced and the potential was shifted, therefore the potential itself and its first derivative were null at the cutoff distance.

The parameters shown in Table 2 were fit to reproduce the correct energy and length scales at the experimental density and zero pressure. The length scale was verified by comparing the simulated static structure factor with reported results from neutron diffraction experiments, while Raman scattering provided the energy scale necessary to determine the effective charges.

We report here a system with 15,000 particles (3000 Pb + 3000 Si + 9000 O atoms). All simulations were done in a NPT ensemble

Table 2
Set of the two-body potential parameters used in the MD simulation.

	Pb	Si	O
Z (e)	0.81570	1.63140	−0.81570
σ (Å)	1.22	0.45	1.44
α (Å³)	1.0	0.0	3.0

	Pb–Pb	Pb–Si	Pb–O	Si–Si	Si–O	O–O
A (eV)	0.63346	0.63346	0.63346	0.63346	0.63346	0.63346
W (eVÅ⁶)	0	0	243.689	0	0	0
η	11	9	7	11	9	7

λ = 6.0 Å, ξ = 3.0 Å, r_c = 10.0 Å.

using the LAMMPS program assuming time steps of 1.0 fs. Starting from a very hot liquid, which was thermalized by 100,000 time steps, the system was cooled down at a rate of $6.66 \cdot 10^{12}$ K/s to the desired temperature where the properties were analyzed. At each temperature, the system was thermalized by 20,000 time steps, and the results were obtained from an additional 20,000 time steps.

The structural properties were analyzed for their two- and three-body correlations. The pair distribution function, coordination numbers, static structure factor, and bond-angle distribution are discussed below; please check [18] for the definition of these quantities. The vibrational density of states was obtained from a Fourier transformation of the velocity-velocity auto-correlation function, whereas the Q^n distribution as a function of temperature was calculated from the phase space trajectories. The estimated molecular dynamics glass transition temperature, T_g^{MD}, is around 950 K $\pm$ 50 K. This value was obtained by comparing the structural relaxation time (τ) at different temperatures and the experimental observation time, t_{obs}. The observation time was determined by $t_{obs} = (dlogt/dt)^{-1}$, and the relaxation time was determined through a non-exponential fit of the incoherent intermediate scattering function $F_s(q,t)$ [21, 22]. T_g^{MD} was defined as the temperature where $\tau \sim t_{obs}$.

2.2. Experimental procedure

A 100 g PbO·SiO₂ glass sample was made by mixing ground quartz SiO₂ (Vitrovita, Brazil) and Pb₃O₄ (Sigma-Aldrich, USA) in the stoichiometric ratio. Afterwards, the mixture was melted in a platinum crucible for two hours and then quenched between two steel plates. The glass used in this study is that of batch 2 from Cassar et al. [3]. The Raman measurements were done using a Horiba-Jobin-Yvon HR800 Evolution micro-Raman spectrometer using a 532 nm wavelength laser as the excitation source and a 50× long work distance objective. All measurements were taken in-situ, using a 1 mm sized sample mounted in a Linkam TS1500 micro-furnace. The spectra were collected using the 1800 slits/mm grating between 600 and 1300 cm⁻¹ with a laser power of 1 mW at the sample. Each spectrum is an average of five 60 s measurements. Before each measurement we waited 5 min for temperature stabilization, taking 10 min at each temperature step in total. Wavenumbers were calibrated against the position of the silicon peak (520.7 cm⁻¹), and the experimental results were normalized by the experimental T_g^{DSC} = 687 K.

For the Raman curve fitting, we used the Fityk (0.9.8) software [23]. The high-frequency bands are assumed to have Gaussian lineshapes. The first step was to fit the baseline using a cubic function, where only the intensities of the Gaussians were left free, the Levemberg-Marquardt fitting algorihm was used. Then, the band center positions, and later the full-width at half-maximum (FWHM) were permitted to vary freely, where the Nelder-Mead Simplex fitting algorihm was used to fit them. As a result, at the last step of the curve fitting, no constraints in the Gaussians or the baseline were imposed, and all parameters were let free. However, this procedure does not mean that