STRUCTURAL PROPERTIES OF AMORPHOUS GEO2: A MOLECULAR DYNAMICS SIMULATION STUDIES

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ABSTRACT

Understanding the structural properties of network-forming glasses is of great interest not only in condensed matter physics, geoscience, and materials science, but also in engineering and industry. Experimental results suggest that amorphous germanium oxide have a tetrahedral local structure that serves as a corner-sharing building block to produce a three-dimensional network. However, it is very challenging to experimentally deduce the medium (or intermediate) range order. In this study, the structural properties of amorphous germanium oxide was investigated by means of the classical molecular dynamics technique. The simulations were done in the microcanonical ensemble, with a system at a density of 3.7 g cm^{-3}, using a pairwise potential. The pair correlation functions, bond angle and coordination numbers are computed. The simulation results show that there exists a short range order, defined by the nearest neighborhood of a Ge atom, which consists of a $Ge(O_{1/2})_4$ tetrahedron, with a Ge–O bond length of 1.75 A, longer than the Si–O bond length (1.62 A). Beyond this basic unit, the tetrahedra are linked to each other by their vertices, forming an angle Ge–O–Ge of ~130°, but randomly distributed in the space.

Keywords: Germanium dioxide (GeO$_2$), molecular dynamics, Pair correlation function, network oxides

INTRODUCTION

Amorphous germania (GeO$_2$) is regarded as one of the "strong" network-forming glasses which have been extensively studied due to their importance in industry, geophysical and material sciences. GeO$_2$ glass like silica glass is a prototypical oxide glass that form the basis for large families of noncrystalline materials. The structure of GeO$_2$ glass has generally been considered to be comparable to that of silica glass despite differences in bond lengths, angles and the relative size of Ge versus Si. They share several physical behavior, including a structural transition from a network of corner-sharing tetrahedra under ambient conditions to a dense octahedral material at high pressure (Micoulaut, Cormier, & Henderson, 2006; Polsky, Smith, & Wolf, 1999). This results to a large change in the short and medium range order (Salmon et al., 2012). However, the structural changes occur at much lower accessible pressures in the case of GeO$_2$ which makes them more amenable to study. In spite of the similarities between GeO$_2$ and SiO$_2$, a number of differences exist. For example, the GeO$_2$ phase diagram exhibits a smaller number of polymorphs, and all three GeO$_2$ phases (crystalline, glass, liquid) have an increased sensitivity to pressure, i.e. undergoing pressure-induced changes at much lower pressures than their equivalent SiO2 analogues. In addition, differences exist in GeO2 glass in the medium-range order, resulting in the glass transition temperature of germania being much lower than for silica. (Micoulaut, Cormier, & Henderson, 2006).

Experimental studies of amorphous GeO$_2$ have generally involved either x-ray or neutron scattering and spectroscopic techniques such as x-ray absorption spectroscopy (EXAFS/XANES) and Raman spectroscopy (Guthrie et al., 2004; Henderson & Fleet, 1991; Zeidler et al., 2014). On the other hand, theoretical studies have generally employed classical or ab initio molecular dynamics calculations to gain insight into the structure of these materials (Micoulaut, Cormier, & Henderson, 2006; Oeffner & Elliott, 1998). In both approaches, the results of the studies show that the tetrahedral structure of GeO$_2$ glass are randomly oriented, linked by their vertices with a broad distribution of A–O–A

angles, resulting in a three-dimensional structure possessing a medium range order (Brazhkin, Lyapin, & Trachenko, 2011). In the crystalline state, germanium oxide exists in two polymorphic forms: one low density phase (4.28 g cm-3) with an quartz structure, where each Ge is coordinated with four oxygen and a high density phase (6.25 g cm-3) with rutile structure, where each Ge is coordinated with six oxygen, which is the stable structure at room conditions (Hong, Newville, Duffy, Sutton, & Rivers, 2014). The difference in density arises mostly from the local environment of the germanium atom, which is, respectively, fourfold tetrahedral and sixfold octahedrald coordinated.

In recent years the molecular dynamics (MD) method has been used to simulate glass structures (Brazhkin, Lyapin, & Trachenko, 2011; Igwe & Batsari, 2022). The advantage of MD simulation is that one can calculate almost the properties previously determined experimentally. Germanium dioxide has been mostly studied in its crystalline form by several ab initio methods. Oeffner and Elliott (Oeffner & Elliott, 1998), have fitted an empirical interatomic potential to an ab initio energy surface to account for the structure and the vibrational spectra of the a-quartz and rutile-like phases of GeO$_2$ and related issues have been investigated by means of an equation of state. Several authors have used the same kind of approach i.e., by fitting interatomic potential or by performing density functional calculations, to account for the structural change of the GeO$_2$ crystalline polymorphs.

In this study, the nature of structural properties in glassy GeO$_2$ was investigated, in order to provide insight into the atomic motions in this glass material. MD simulation was conducted through the large-scale atomic/molecular massively parallel simulator LAMMPS (Thompson et al., 2022) and OVITO (Stukowski, 2010) was adopted to visualise and analyse the results.

MATERIALS AND METHODS

Interatomic Potential

In molecular dynamics techniques a key issue is the choice of the interatomic potential. For this simulation we have adopted the potential developed by Oeffner and Elliot (Oeffner & Elliott, 1998) for the crystalline phase. This potential is still

simple and has been demonstrated to reproduce a number of experimental properties not only in the solid phase, but also in the liquid as well as in the amorphous state. The potential employs pairwise additive Buckingham type interatomic terms of the form:

$$V(r_{ij}) = \frac{q_i q_j}{r_{ij}} + A_{ij}e^{-r_{ij}/B_{ij}} - \frac{C_{ij}}{r_{ij}^6} \qquad (1)$$

where the terms represent Coulomb, van der Waals and repulsion energy, respectively. Here r_{ij} is the interatomic distance between atoms i and j. The effective charge q, the van der Waals coefficients A_{ij}, the softness parameter B_{ij} and the repulsive radius C_{ij}, are the energy parameters. Oeffner and Elliot presented two set of parameters, one corresponding to the so-called 'original potential', and the other one corresponding to the rescaled potential. The long range Coulomb interactions are calculated with the standard Ewald summation technique. The equations of motion are integrated with a modification of the Beeman algorithm, as is implemented in the LAMMPS program (Thompson et al., 2022), with a time step of $1t = 1 \times 10\text{-}15s$

Simulation details

Molecular dynamics simulations are carried out in the microcanonical ensemble (NVE) for Ge (192) and O (384) units, in a cubic cell system at mass density, $\rho = 3.7$ g cm-3, using periodic boundary conditions. The amorphous state system was prepared by starting at the temperature 5000K, with a cubic lattice which corresponds to an artificial cristobalite structure with a density of 2.9 g cm-3 in order to have a liquid at 5000K at zero pressure. Then, the sample is cooled to 3000 K by using a velocity scaling procedure at a rate of 0.02 K/1t.Next, the system is allowed to reach equilibrium for over 50 0001t. With this well-equilibrated GeO_2 liquid at 3000 K we prepare our system at a density of $\rho = 3.7$ gcm-3, by reducing simultaneously the lengths of the MD cell and the positions of all the atoms, in seven steps, from the initial low density of 2.9 gcm-3 to the final at 3.7 g cm-3, having in between systems at 3.16, 3.22, 3.31, 3.40, 3.50 and 3.60 g cm-3. After each shrink of the simulation cell, we thermalized the system at 3000 K for over 50 0001t. Then, we lowered the temperature to 1500 K at a rate of 0.0075 K/1t, and ran the system for over 50 000 time steps with temperature control, and others 50 000 steps without any disturbance. Finally, using a cooling rate of 0.0024 K/1t, the system at 300 K was obtained. Then it was kept at constant temperature for 75 0001t and ran another 75 000 steps without any temperature control.

RESULTS AND DISCUSSION

Figure 1 shows a typical structure found in the simulation box. As in the case of silica glass, here also there is a short range order defined by a basic tetrahedron, and beyond that there is an intermediate range order, composed of a tetrahedron at the center, surrounded by four tetrahedra, linked by the vertex, each of them forming an angle Ge–O–Ge of approximately 130◦
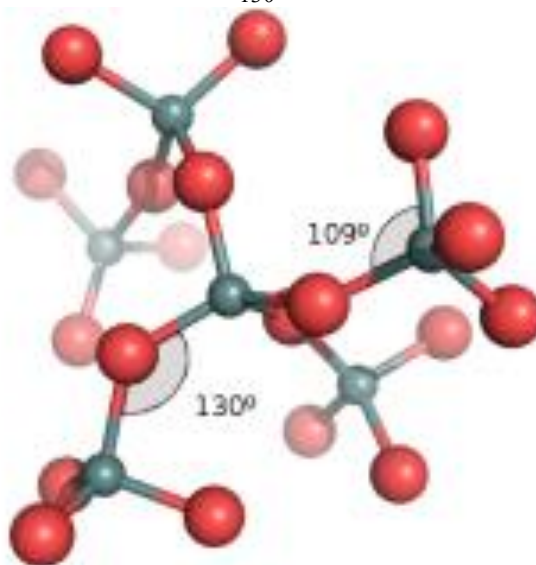

Figure 1: A typical representative polyhedron found in the simulation model of amorphous GeO2. The small spheres correspond to germanium atoms and the big spheres to oxygen atoms.

Structural properties

The structural properties are inferred by means of atomic correlations. The partial and total pair distribution functions $g(r)_{ij}$ are shown in Fig. 2., to determine the short-range order in the glass, out of which the bond distances can be extracted. The first and second peak of g(r) in GeO2 glass is generally considered to represent Ge–O and Ge–Ge distance, respectively. The Ge–O bond length is determined by the sharp peak observed at $g(r)_{Ge-O} = 1.75$ Å . This peak has been observed in previous experimental result (Hong et al., 2014; Micoulaut, Cormier, & Henderson, 2006; Price, Saboungi, & Barnes, 1998), as $g(r)_{Ge-O} = 1.73 \pm 0.03$ A and the previous MD simulation (Matthieu, 2004) found $g(r)_{Ge-O} = 1.72$ Å. As one can see, the second oxygen nearest neighbors (NN) of Ge are around the distance of 4.5 Å, after a spherical shell of radius 1 Å without any oxygen atom. Thus, meaning that each germanium atom is surrounded by somewhat more than four germanium atoms. The nearest neighbor distance for O–O peaks at 2.84 Å and for Ge–Ge at 3.26 Å. The corresponding experimental results are 2.83±0.05 Å and 3.16 Å ±0.03 Å respectively. Notice that the Ge–O, O–O and Ge–Ge NN distances are all greater than silica.
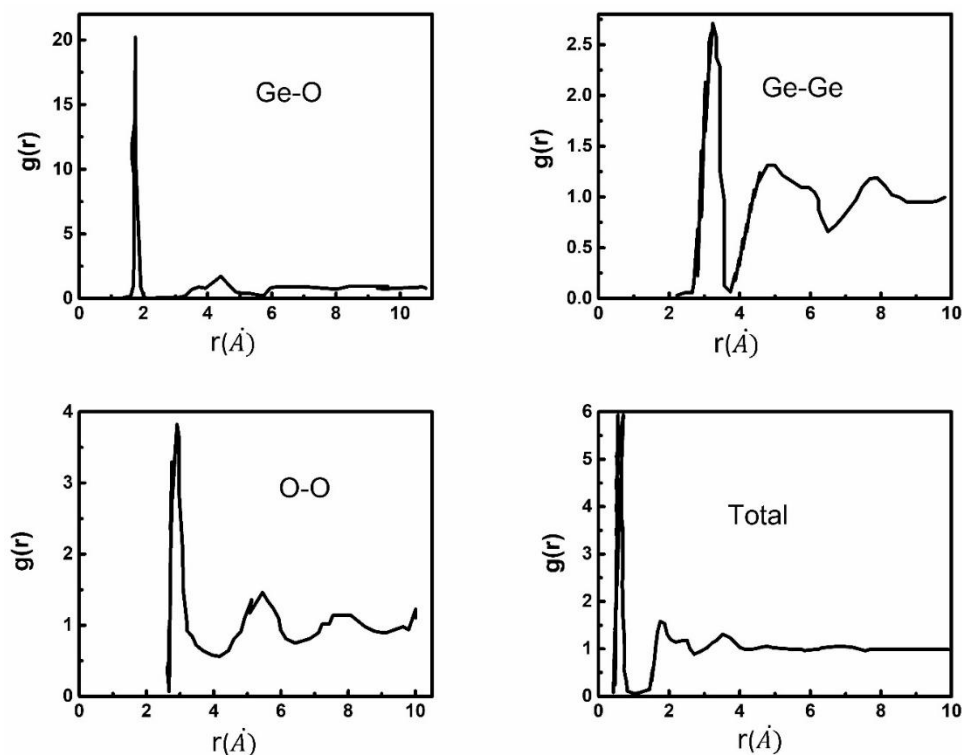
Figure 2: Partial and total pair distribution functions for amorphous GeO2.

Angular distribution

Further information about the local structural units is provided by the angular distribution. Figure 3 displays the angular distribution. There is a short range order defined by a basic tetrahedron GeO4, which is characterized by the angle O–Ge–O, with a clear peak at 109∘, and the angle O–O, with a main peak at 60∘. These basic tetrahedral are mainly linked to each other through the vertex, forming a broad angular distribution Ge–O–Ge, centered approximately at 130∘, close to the experimental value of 130∘. This distribution also presents a small peak at around 90∘, which corresponds to an edge-sharing tetrahedral forming a few twofold rings.
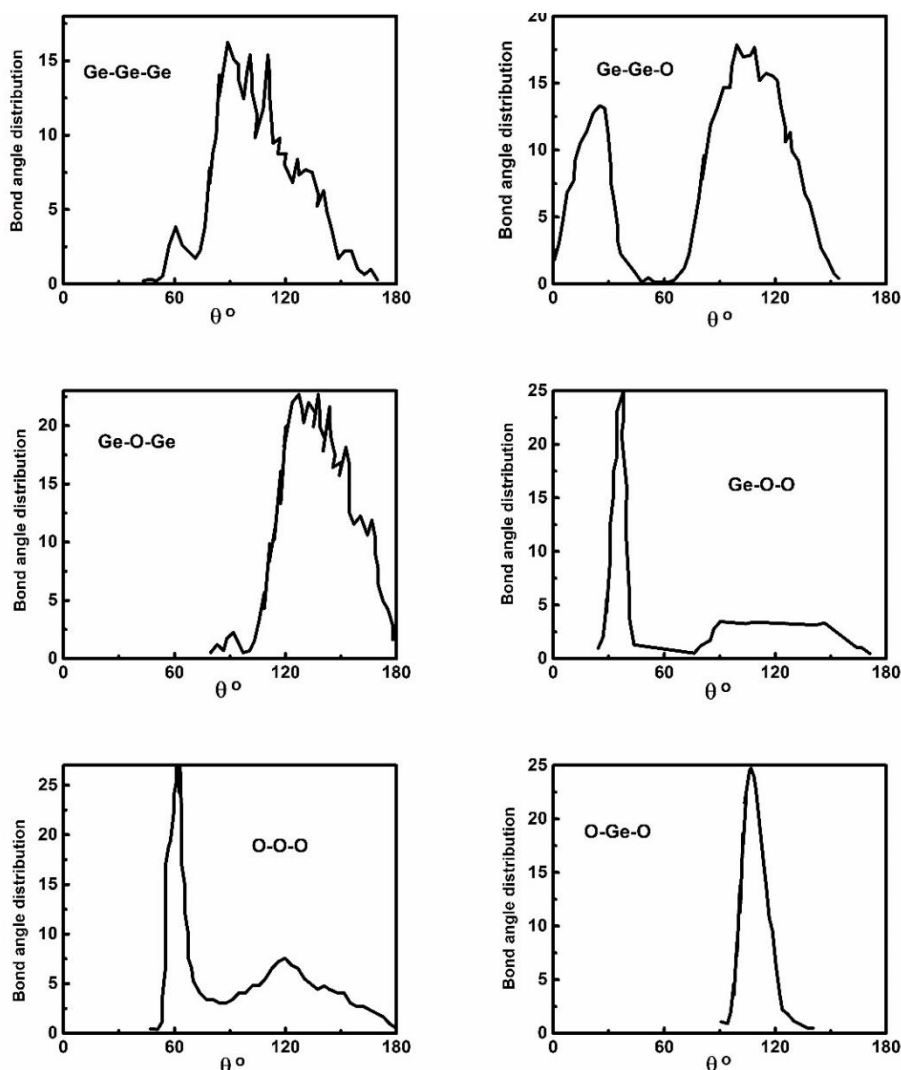
Figure 3: Distribution of bond angles for amorphous GeO_2.

Static structure factor

Further structural correlations in amorphous GeO_2 can be extracted from the partial scattering functions. Which was calculated by the Fourier transform of the partial pair distribution functions. If adequately weighted by neutron and/or x-ray factors can be compared directly to the experiments. The partial static structure factors Sij(q) are given by (Peralta, Gutiérrez, & Rogan, 2008):

$$S_{ij}(q) = \delta_{ij} + 4\pi\rho\sqrt{c_i c_j} \int_0^R r^2 [g_{ij}(r) -$$

$$1]\frac{\sin(qr)}{qr}\frac{\sin(\frac{\pi r}{R})}{\pi r/R}dr \qquad (2)$$

Where $c_{i(j)} = N_{i(j)}/N$ is the concentration of $i(j)$ species. The window function $\frac{\sin(\frac{\pi r}{R})}{\pi r/R}$ was introduced to reduce the termination effects resulting from the finite upper limit (Lorch, 1969). The cut-off length, R, is chosen to be half the length of the simulation box.

This will lead to the total scattering static structure factor as:

$$S_q(q) = \sum_{ij}\sqrt{(c_i c_j)}S_{ij}(q) \qquad (3)$$

Figure 4 shows the neutron and the x-ray structure factors *S(q)* for amorphous GeO_2. It can be seen that the agreement of the calculated and experimental neutron *S(q)* is quite good, being a small difference at the first peak, whereas the calculated one is slightly shifted to the right. In both figures, corresponding to *S(N)(q)* and *SX(q)*, for $q \leq 5$ Å^{-1} three main peaks are observed, the first one at $q \sim 1.65$ Å^{-1}, a second one at $q \sim 2.7$ Å^{-1} and a third one at $q \sim 4.5$ Å^{-1} . The second peak has a rather small intensity in comparison to the other two peaks.
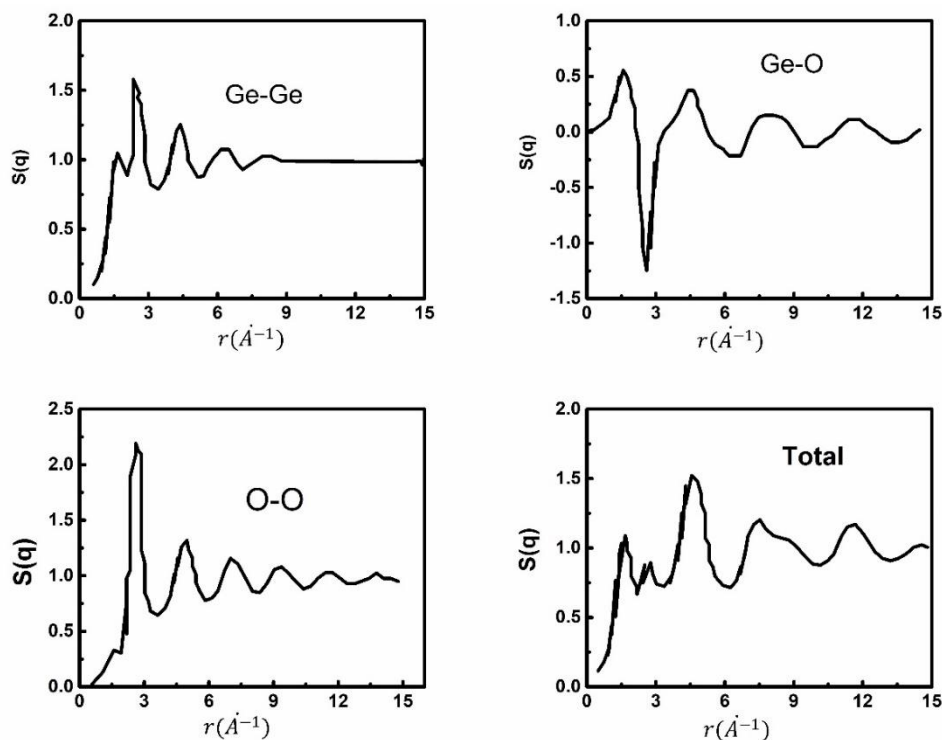
Figure 6: Structure factors for amorphous GeO2.

CONCLUSION

In summary, we have presented a computer model of amorphous GeO2, based on an empirical pairwise interatomic potential. According to this model, there exists a short range order, defined by the nearest neighborhood of a Ge atom, which consists of a Ge$(O_{1/2})_4$ tetrahedron, with a Ge–O bond length of 1.75 Å , longer than the Si–O bond length (1.62 Å). Beyond this basic unit, the tetrahedra are linked to each other by their vertices, forming an angle Ge–O–Ge of ~130°, but randomly distributed in the space. Note that its counterpart network oxide (SiO2), has a similar structure, but the Si–O–Si angle is about 142°.

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