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High-pressure behaviour of GeO₂: a simulation study

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Online at stacks.iop.org/JPhysCM/22/152102**Abstract**

In this work we study the high-pressure behaviour of liquid and glassy GeO₂ by means of molecular dynamics simulations. The interaction potential, which includes dipole polarization effects, was parametrized using first-principles calculations. Our simulations reproduce the most recent experimental structural data very well. The character of the pressure-induced structural transition in the glassy system has been a matter of controversy. We show that our simulations and the experimental data are consistent with a smooth transition from a tetrahedral to an octahedral network with a significant number of pentacoordinated germanium ions appearing over an extended pressure range. Finally, the study of high-pressure, liquid germania confirms that this material presents an anomalous behaviour of the diffusivity as observed in analogous systems such as silica and water. The importance of pentacoordinated germanium ions for such behaviour is stressed.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Germania (GeO₂), along with silica and beryllium fluoride, is a 'strong' glass-former [1] characterized by a tetrahedral network structure at ambient conditions in the amorphous phase [2]. Its structure is based on corner-sharing Ge(O_{1/2})₄ tetrahedra (the 1/2 index means that each O²⁻ ion is shared by two Ge⁴⁺), with a Ge–O average distance of 1.73 Å and a mean inter-tetrahedral Ge–O–Ge angle of 132° [3, 4]. There is considerable interest in the behaviour of such tetrahedrally coordinated glasses under pressure. In the associated crystalline materials high-pressure transitions are observed between four- and six-coordinate structures. Pressure-induced structural changes in the amorphous phases have been linked to anomalous behaviour in the elastic, viscous and thermal properties and to the phenomenon of polyamorphism [5]. In amorphous silica itself, the major structural transition occurs

at relatively high pressures (~25 GPa) where direct structural studies remain difficult [6]. However, because of the larger cation/anion radius ratio in germania relative to silica, the transition occurs in a pressure domain now accessible to structural studies. Despite this, a clear picture of the nature of the pressure-induced structural changes in germania has only recently started to emerge. We have therefore performed computer simulations in an attempt to clarify the relationship of the information emerging from the different experiments.

High-pressure structural studies have been made using EXAFS spectroscopy [7–10] and x-ray and neutron diffraction experiments [4, 11, 12]. All the experimental studies agreed on the existence of a structural change in the pressure range 3–15 GPa, associated with an increase in the Ge–O separation which is broadly consistent with an increase in coordination number. Vaccari *et al* [8], for example, showed, from EXAFS studies, that this distance switched from 1.74 Å (at 0 GPa) to 1.82 Å (at 13 GPa). On the other hand, the literature has long been very contradictory about the character of the change in

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coordination number. The first study to address this issue is that of Itie *et al* [7] who performed x-ray absorption measurements up to 23.2 GPa and reported that the Ge coordination changes from four-fold to six-fold at pressure between 7 and 9 GPa. Vaccari *et al*, on the other hand, proposed a progressive shift in the coordination number, and found no evidence of a fully six-coordinate structure, even at the highest pressure of their study (~ 13 GPa). Very recent XAFS and EXAFS studies [9, 10] extended the studied pressure range to 53 and 44 GPa respectively and it was postulated that a complete six-fold coordination of the Ge ions is only reached at pressures as high as 25–30 GPa. The ability of EXAFS to provide very accurate first-neighbour distances is well established, but so is its limitation for the determination of coordination numbers in amorphous materials [13–15]. Only an average coordination number can be extracted, with an important error bar which depends crucially on assumptions about the shape of the radial distribution functions at larger separations, and to estimate proportions of different coordination polyhedra in a material from EXAFS alone is not normally considered reliable.

In principle neutron diffraction, when employing the isotopic substitution method, gives access to all the partial structure factors, and hence to the corresponding partial radial distribution functions (RDF) which contain all the structural information. In the case of GeO₂, this programme has been fulfilled only at ambient pressure by Salmon *et al* [16]: at elevated pressures only total x-ray and neutron diffraction patterns are available. A first attempt to study the high-pressure system by these means was reported by Guthrie *et al* [11]: unfortunately, the data were too noisy to extract good RDFs. However, a very sharp transition from a tetrahedral to an octahedral structure was proposed, with a small range of pressure in which the system is characterized by five-fold coordination around Ge⁴⁺ ions. Very recently, Drewitt *et al* have performed new neutron diffraction measurements up to 8.6 GPa and obtained data of very high quality [12]. Their results show a gradual change of the intermediate range order with increasing density as manifested by an increase in position and reduction in height of the first sharp diffraction peak in the total structure factor. From their data there is no evidence in support of an abrupt transformation of the network structure over the investigated pressure range, in agreement with the most recent EXAFS experiments [8, 9, 12].

Computer simulations could help in resolving these differences since they can provide a detailed picture of the structure of a system. Unfortunately, to date, all the molecular dynamics (MD) calculations involving pressurized germania have been performed with pair potentials of limited accuracy [17–25]. For example, for the most commonly used potential, developed by Oeffner and Elliot [26], two different parameter sets were proposed: an original one, which was fitted from an *ab initio* energy surface, and a so-called rescaled one, which was developed from the previous one in order to give a better reproduction of the vibrational properties. For this reason, some apparent inconsistencies have arisen in the literature because different classical potentials were being used [17, 23, 27, 28]. Finally, since the OE potential is not able to reproduce with a single set of parameters all

the ambient pressure properties of amorphous germania, it is also reasonable to suspect that it might fail when studying the pressure behaviour of this material. This might explain the disagreement with the experimental trends found in some papers in the literature. For instance, in [25], the Ge–O bond distance is found to remain constant in the 3–25 GPa pressure interval, whilst in [20] the Ge–O coordination number is found to increase continuously from the lowest pressure (1 GPa), both trends being in strong contrast with the experimental evidence [7, 8, 11].

Recently, first-principles molecular dynamics (FPMD) studies of glassy GeO₂ have also been reported [23, 29–31]. In principle, the amount of empirical information needed to set up a first-principles calculation is minimal and it would normally be the method of choice to study the physico-chemical properties of condensed-phase systems. However, it is computationally very expensive compared with classical molecular dynamics, which is a major drawback when dealing with glassy systems, where the structural relaxation times are necessarily long. These studies have therefore focused on the study of the structural and vibrational properties of the glass; only one of them included results for high-pressure systems [31].

We recently introduced a new interaction potential, which includes many-body polarization effects, and succeeded in reproducing the structural and vibrational properties of glassy germania at ambient pressure as well as the dynamical properties of liquid germania in the 3600–5000 K temperature range [28], with a *single* set of parameters. This potential was parametrized with reference to extensive density functional theory (DFT) electronic structure calculations on disordered condensed-phase configurations. Also, similarly constructed potentials have been shown to provide an excellent, transferable description of a number of complex oxides [32, 33]. The aim of this paper is to show how the use of this potential together with a direct comparison with the available experimental data, can improve our understanding of the behaviour of glassy germania at high pressure. In the end, we will emphasize that the various experimental studies are in accord, even if the initial interpretations that were made of them did not.

Once the question of structure is resolved, it is of interest to study the influence of structural changes on the physical properties of the system. A well-known effect is the existence of dynamical anomaly in silica-based systems when the pressure increases [5]. Unlike most other systems which, under compression, tend to show a decreasing mobility of the species, in liquid silica the diffusion coefficients increase until they reach a maximum for a given pressure, and then decrease. This anomaly was linked to the existence of pentacoordinated species [34]. The only evidence for such a behaviour in liquid germania was provided by Sharma *et al* who showed a decrease of the viscosity with pressure, though the pressure range of this study was very limited (0–1 GPa) [35]. There are also some simulation studies on high-pressure liquid germania but, unfortunately, the results are contradictory. Hoang *et al* [19] do indeed observe an anomalous behaviour of the diffusivity in GeO₂. However, Hung *et al* [21], who also studied this system

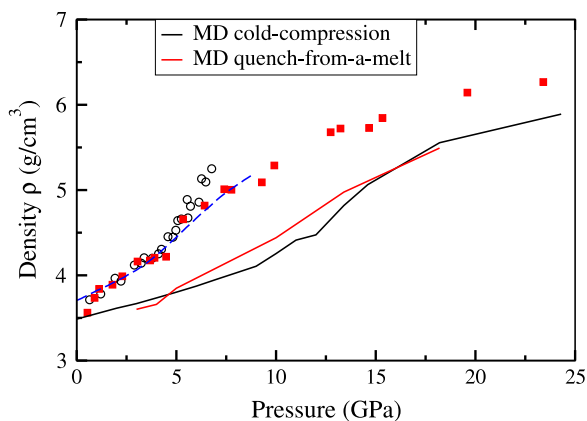


Figure 1. The mass density ρ for GeO_2 glass as a function of pressure for cold compression and quench-from-a-melt procedures. Experimental data are from the *in situ* compression studies of Hong *et al* [41] (red squares), Smith *et al* [42] (empty circles) and Tsiok *et al* [43] (blue broken curve).

by means of classical molecular dynamics, found no evidence of such a phenomenon, but again both of these studies involved classical pairwise additive interaction potentials of limited accuracy. To address this issue we have therefore studied the structural and dynamical properties of liquid germania, at a temperature of 4000 K and over a wide range of pressures.

2. Simulation details

The interaction potential used in this study has already been described elsewhere [28]. The ionic species carry their valence charges (Ge^{4+} and O^{2-}), and the polarization effects that result from the induction of dipoles on the oxide ions are accounted for. The parameters of the interaction potential for germania were obtained from the application of a force- and dipole-matching procedure aimed at reproducing a large set of first-principles (DFT) reference data [36] on the condensed phase.

To obtain structural properties in the glassy state, we performed MD simulations in the *NPT* ensemble using the method introduced by Martyna *et al* [37]. Details on the generation of a compressed glassy state will be reported below. When dynamical properties were computed, the system was simulated in the *NVT* ensemble using the Nosé–Hoover chain thermostat method [38]. A relaxation time of 10 ps was used for the thermostats and the barostats. The simulations on glassy GeO_2 ($T = 300$ K) were performed on a simulation cell containing 432 atoms whereas the *NVT* simulation cells on liquid germania ($T = 4000$ K) contained 600 atoms. We used a time step of 1 fs to integrate the equations of motion, and minimization of the polarization energy was carried out at each time step using a conjugate gradient method. All simulations were equilibrated for at least 0.5 ns and then a subsequent run of 0.5 ns was made to accumulate enough statistics.

3. Compressing a glass: some limitations

Generating a glassy state by means of computer simulations is a challenging operation. Indeed the relatively short timescales

available (a few nanosecond in our case) force us to use unrealistically fast cooling rates. This implies that sometimes the glass we obtained is further away from equilibrium than the experimental one. In fact, even experimentally, glasses prepared in different ways show different properties, implying that even on a timescale of hours (i.e. 12 orders of magnitude higher than what we can afford with MD simulations) there are still some relaxation effects. This problem becomes even more significant when one tries to compress a glass. To this end, Scandolo *et al* described two different compression methodologies for SiO_2 [39]. The first one is a cold compression route consisting of increasing pressure slowly at ambient temperature while the second one, which they called a ‘quench-from-the-melt’ procedure, consists of obtaining the compressed glass by a slow cooling of a compressed sample from a temperature where atomic diffusion is observable on the timescale of the MD simulation. By comparing their results with the available experimental data on compressed glass, they showed that the samples obtained with the two procedures are representative of the experimental *in situ* compressed (as, for example, in [8, 9]) and densified forms of glass [40], respectively. They found that structural differences between annealed and cold-compressed forms were most noticeable at distances of 3.5–4 Å.

In the case of GeO_2 there has been little effort so far in this direction. Most of the previous work on this system used the cold compression route but a direct quantitative comparison with experimental data was never attempted. In this work we tried both routes used by Scandolo *et al* and compared the results with the experimental density versus pressure data. This is shown in figure 1. It can be appreciated that neither of the two routes reproduces quantitatively the experimental data. In both cases the simulated glass seems to be less responsive to compression, which we attribute to the limited simulation times (see below). It seems, however, that the quench-from-a-melt procedure gives a closer agreement with the experimental data than the cold-compressed route, once again indicating that a certain degree of diffusion helps the glass relaxation. It has to be remembered, however, that Scandolo *et al* showed how the quench-from-a-melt route is more representative of the densified forms of the glass, so that a comparison with the experimental data on *in situ* compressed glass, such as in [11, 16] might not work as well.

It should be evident from the above discussion that we are unable to reproduce quantitatively the equation of state of glassy germania. This should not necessarily be taken as a limitation of our potential but as a consequence of the relatively short timescales available in computer simulations. For this reason, in the remainder of this paper, we will simulate cold-compressed GeO_2 and report our data as a function of *density*, instead of pressure. When a comparison with experimental data is required, we will convert the experimental pressures into densities by using the data in figure 1 from [43, 41]. In the case of liquid germania, since the system is very diffusive and reaches equilibrium in a few picoseconds, we do not anticipate any problem with the equation of state and we will therefore report our data as a function of pressure.

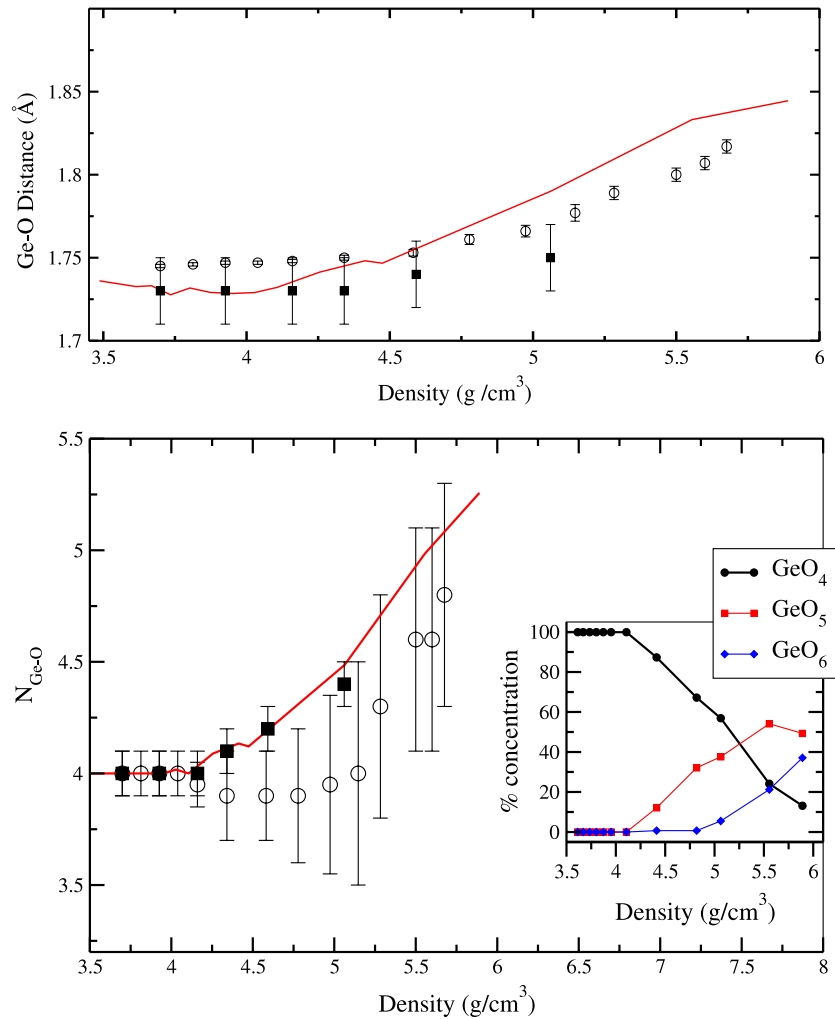


Figure 2. Top panel: comparison between the simulated (solid line) and experimental Ge–O bond distance from Vaccari [8] (black empty dots) and Drewitt [12] (black filled squares) as a function of increasing density. Bottom panel: comparison between the simulated (solid line) and experimental, (black empty dots) Vaccari [8] and (black filled squares) Drewitt [12], first shell Ge–O coordination number. The inset in the bottom panel shows the density dependence of the percentage concentration of GeO₄, GeO₅, GeO₆ units.

4. Glassy germania

In the top panel of figure 2 we report the average Ge–O distance⁶ as a function of increasing density. It is compared to the values obtained by Vaccari *et al* [8] and Drewitt *et al* [12] via EXAFS and neutron diffraction measurements. The agreement is quite good, considering the scatter of the experimental data and the intrinsic error associated with the pressure-to-density conversion. The simulations, like the experiments, show first a Ge–O bond distance which is fairly constant in the 3.66–4.5 g cm^{−3} density range (corresponding to an experimental pressure range of 0–5 GPa) and then a gradual increase in the Ge–O bond distance, starting at a density of 4.5 g cm^{−3}.

We can interpret that data in terms of compression mechanisms. When a tetrahedral system like GeO₂ is compressed, three types of structural change could occur.

⁶ This distance was defined as $d_{\text{GeO}} = \frac{\int_0^{r_{\text{cut}}} r^3 g(r) dr}{\int_0^{r_{\text{cut}}} r^2 g(r) dr}$ where $g(r)$ is the Ge–O radial distribution function and r_{cut} is the position of the first minimum in the $g(r)$.

Firstly, the system could keep exactly the same structure, but adapt by allowing the bond lengths to decrease: obviously this is not the case here. Secondly, the tetrahedral units could be kept unmodified, in which case the decrease of accessible volume would imply a rearrangement of the network structure, progressively minimizing the size of the voids [44, 40] and resulting in changes in the first sharp diffraction peak. Finally the tetrahedral structure could be lost, and higher coordinated structural units could be formed. Such an evolution may induce an increase of the Ge–O bond length in order to allow more than four oxide ions into the germanium first coordination shell. The analysis of bond length data gives evidence of a succession of the two latter mechanisms, at low and high pressures. This was also confirmed by an analysis of the bond angle distributions (not shown).

To verify this, we have determined the germanium coordination number. The cut-off used for the coordination number calculation was 2.38 Å, which corresponds to the first minimum of the Ge–O partial RDF. Again we compare these values with the ones obtained by Vaccari *et al* [8] and Drewitt *et al* [12]. Good agreement is found, especially

with the neutron data. The simulated coordination number remains constant, at a value of 4, until a density of 4.5 g cm^{-3} . In this first régime, germania is therefore keeping its tetrahedral structure under compression, but the tetrahedra reorient themselves. Then, in a second régime, more highly coordinated germanium ions begin to be observed. In the inset of the figure, the percentage of GeO_4 , GeO_5 and GeO_6 units are given as a function of density. Once again, at a density of 4.5 g cm^{-3} , some Ge^{4+} ions start to accept 5 O^{2-} ions in their vicinity. Then, at $\rho \sim 5.0 \text{ g cm}^{-3}$ (corresponding to an experimental pressure of about 7–8 GPa), GeO_6 units begin to be formed. At the highest density studied experimentally, $\rho \sim 5.85 \text{ g cm}^{-3}$ (corresponding to approximately 15 GPa), a non-negligible proportion of GeO_4 units is still observed. We find no evidence of a state in which there are only five-fold coordinated Ge ions in the studied pressure range. These five-fold coordinated units play an important role in liquid germania as we shall show in the next section. Our results can also be compared to the recent FPMD simulations on the same system [31]. In the latter, a much sharper change in the first-neighbour distances is observed upon compression: at a density of 5.4 g cm^{-3} , the Ge–O distance already reaches a value of 1.89 \AA , showing important differences with experimental data. This is very likely due to the small size of the samples (108 atoms) and to the higher quenching rates that have to be involved in FPMD simulations.

At first sight, our results differ significantly from the conclusions of Guthrie *et al* from their combined x-ray and neutron diffraction study of glassy germania [11]. Qualitatively, they observed an analogous mechanism, but with a much sharper increase in the coordination number. They proposed a complete transition to a GeO_5 units based structure for pressures ranging from 6 to 10 GPa, and a final completely octahedral structure at a pressure of 15 GPa. These values were extracted from a Fourier transform of the x-ray diffraction *total* structure factor (their neutron data being too noisy to allow an attempt to extract partials). To show that the discrepancy observed is due to the analysis of the x-ray data, rather than a deficiency of the representation of the structure in the simulations, we have computed the x-ray structure factor. This was obtained using the following relationship

$$S(q) = c_{\text{Ge}}^2 f_{\text{Ge}}(q)^2 [S_{\text{Ge-Ge}}(q) - 1] + 2c_{\text{Ge}}c_{\text{O}} f_{\text{Ge}}(q) f_{\text{O}}(q) \times [S_{\text{Ge-O}}(q)] + c_{\text{O}}^2 f_{\text{O}}(q)^2 [S_{\text{O-O}}(q) - 1] \quad (1)$$

where c_{α} and $f_{\alpha}(q)$ represent respectively the atomic fraction and x-ray form factor of element α . $S_{\alpha\beta}(q)$ is the partial structure factor which can be obtained via a Fourier transform of the partial radial distribution functions:

$$S(q)_{\alpha\beta} = \delta_{\alpha\beta} + \int_0^{\infty} 4\pi r^2 \frac{\sin(qr)}{qr} [g_{\alpha\beta}(r) - 1] dr. \quad (2)$$

The q -dependent x-ray form factors are calculated from

$$f_{\alpha}(q) = \sum_{i=1}^4 a_{\alpha,i} \exp[-b_{\alpha,i}(q/4\pi)^2] + d_{\alpha}. \quad (3)$$

The parameters we used for the calculation of these form factors are reported in table 1; note they are consistent with an

Table 1. Parameters used for the form factors [45, 46].

	a_1	b_1	a_2	b_2	a_3	b_3	a_4	b_4	d
O^{2-}	4.174	1.938	3.387	4.145	1.202	0.228	0.528	8.285	0.706
Ge^{4+}	4.758	7.831	3.637	30.05	0	0	0	0	1.594

ionic representation of the distribution of electrons (i.e. Ge^{4+} and O^{2-}). Figure 3 has been organized in a similar way to figure 1 in [11] in order to facilitate a comparison; in particular, $S(q)$ has been normalized by:

$$\left(\sum_{\alpha=1}^2 c_{\alpha} f_{\alpha}(q) \right)^2. \quad (4)$$

The six patterns are reported at the densities corresponding approximately to the following experimental pressures: 0, 3, 5, 7, 10, 15 GPa. In the right-hand panel of figure 3 we report the calculated neutron diffraction patterns at the same densities; these are obtained from the same expressions but with $f_{\alpha}(q)$ replaced with b_{α} , the neutron diffraction length [4]. In this figure we also show some experimental data from the recent study by Drewitt *et al* [12] at densities close to the simulation ones. These data were collected at the following pressures: 2.2, 4.9 and 8.0 GPa.

By comparing figure 3 with figure 1 in [11], it can be readily appreciated that the agreement with the experimental x-ray structure factors is excellent at all pressures. Our data show that the first sharp diffraction peak position (FSDP) shifts toward higher wavenumbers upon pressure increase until it merges with the principal peak, in agreement with the data in [11]. From the fact that our simulations are in good agreement with the x-ray structure factors from [11] as well as the more recent neutron data [12] and the bond lengths from the most recent EXAFS [8] we conclude that the different sets of experimental data themselves are mutually consistent (see also discussion below). The difference in the *interpretation* of the x-ray data by Guthrie *et al* [11] (i.e. sharp versus smooth tetrahedral to octahedral structure) is therefore likely to be due to the difficulty of extracting good coordination numbers from noisy data.

The comparison with the neutron data from Guthrie *et al* [11] is inhibited by the noisiness of the experimental data but the data of Drewitt *et al* [12] is of higher quality. For densities above $\rho \sim 5.0 \text{ g cm}^{-3}$, corresponding to an experimental pressure of 8–9 GPa, there are, to the best of the authors' knowledge, no available neutron data. Our simulations are consistent with the main trends observed in the neutron work, namely a diminution in the height and a shift to higher q of the FSDP with increasing pressure. However, the agreement between simulations and experiment is less good than in the x-ray case. The simulations appear to overestimate the height of the FSDP, especially at low pressure, and also to underestimate the amplitude and sharpness of the principal peak at about 2.5 \AA^{-1} . In the total neutron structure factor of GeO_2 there is a near-total cancellation between the different partial structure factors in the vicinity of the principal peak, so that the 'principal' peak in the total $S(q)$ is of much

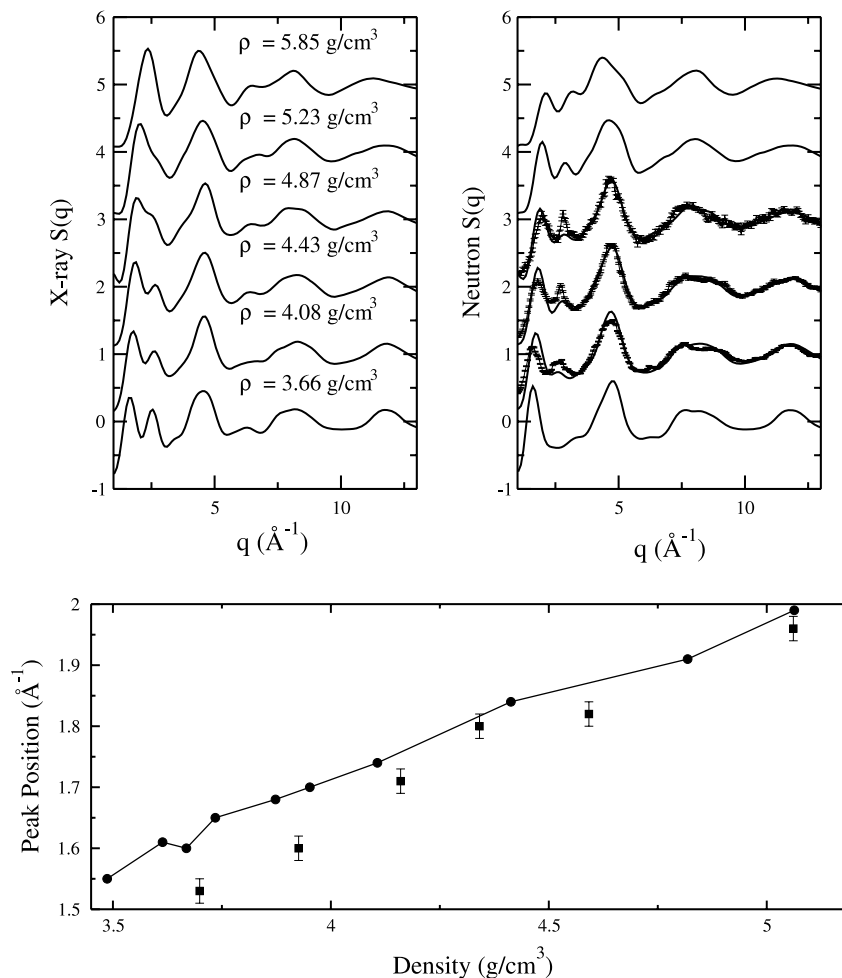


Figure 3. Top: simulated x-ray and neutron diffraction patterns as a function of increasing density. The experimental data in the right-hand panel (line with error bar) are from [12]. Bottom: pressure dependence of the FSDP as extracted from the neutron patterns. The experimental data (filled black squares) are from [12].

lower amplitude than in the individual Ge or O partials. The discrepancy we noted above presumably reflects a small error in position or width of the principal peak in these partials. The FSDP on the other hand reflects the intermediate range order in the glass and the implication of a disagreement in this domain is that the quenching method we have used to prepare the glass does not allow this structure to develop in the same way as in the experimental material. In support of this contention, we note that the $S(q)$ s calculated from the cold-compressed and densified samples differed most in this region of q -space. The position of the FSDP obtained from the neutron structure factors is shown in the bottom part of figure 3 and increases linearly with density. The corresponding values from the Drewitt *et al* work are also shown.

Overall then, our simulations agree well with the available pressure-dependent diffraction data when we compare directly with the experimentally measured quantity, $S(q)$. There is also good agreement with the density dependence of the nearest-neighbour separation obtained from analysis of the EXAFS data. The examination of the local structure in the simulations supports the conclusion that the transition from a tetrahedral to an octahedral glass is smooth and gradual and probably not completed even at pressures as high as 15 GPa.

5. Liquid germania

The high-pressure behaviour of liquid germania presents some differences compared with the glassy case. Although a similar increase in mean coordination number is observed, both the Ge–O coordination number and Ge–O distances (not shown) increase more smoothly as pressure is raised. The increase in coordination number begins as soon as the pressure is increased. In figure 4 we show the oxygen and germanium self-diffusion coefficients as a function of increasing pressure for liquid germania at 4000 K. It can be seen that the diffusion coefficient exhibits the same anomalous maximum in the $P = 15$ – 25 GPa range as observed in other tetrahedral network materials (like silica and water [5, 47]). In the case of liquid silicates, it was unambiguously shown by Angell *et al* that such a pressure enhancement of ion mobilities was linked to the formation of five-fold coordinated silicon ions, which act as defects in the original tetrahedral network structure [34]. The proportion of GeO_5 polyhedra with each coordination number is shown on figure 4, and we can see that its variation with pressure matches exactly the variation of the diffusion coefficients, in agreement with the silica situation.

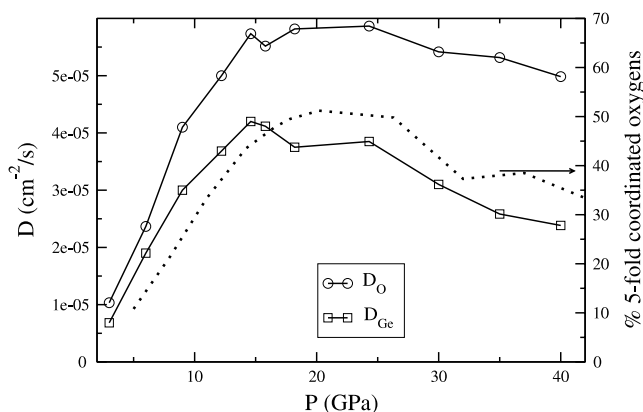


Figure 4. Simulated diffusion coefficients on liquid ($T = 4000$ K) germania and percentage of GeO_5 units as a function of increasing pressure.

6. Conclusions

In this work we used a new polarizable interaction potential to study the high-pressure behaviour of glassy and liquid germania. For glassy germania, we were able to reproduce all the experimental structural information by making comparisons at the same density. The density evolution of the Ge–O coordination number, bond distance, x-ray and neutron structure factors was in good agreement with the data from [8, 11, 12]. The only observed shortcoming was the inability of our simulations to properly reproduce the equation of state for glassy germania. This is most likely due to the relatively short timescale available to computer simulations. From our data and from a comparison with the available experimental evidence, it can be concluded that the transition from a tetrahedral to an octahedral glass is smooth and gradual and probably not completed at pressures as high as 15 GPa. In view of our results, it seems likely that the differences between the mechanisms which have been proposed to interpret this data (such as sharp versus smooth tetrahedral to octahedral transitions) is due to the difficulty of extracting reliable coordination number from noisy data. Finally, a study of the percentage concentration of GeO_4 , GeO_5 , GeO_6 units shows that as density is increased, these are present in different proportions but a state with GeO_5 units only was not observed.

As for liquid germania, our results are mainly predictive due to the lack of experimental data, and of interest for the comparison with the behaviour of other systems which are tetrahedrally coordinated at ambient pressure. We find that liquid germania undergoes a transition from a four-fold to a six-fold coordinated phase and that this transition is smoother than the one observed in the glassy phase. Most importantly, we find that the diffusivity in germania behaves anomalously as a function of pressure, showing a maximum in the $P = 15$ – 25 GPa range, as found in other tetrahedral network liquid such as silica and water. The cause of this behaviour is traced back to the presence of pentahedrally coordinated Ge ions.

Acknowledgments

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References

- [1] Angell C A 1995 Formation of glasses from liquids and biopolymers *Science* **267** 1924–35
- [2] Galeener F L, Leadbetter A J and Stringfellow M W 1983 Comparison of the neutron, Raman, and infrared vibrational spectra of vitreous SiO_2 , GeO_2 and BeF_2 *Phys. Rev. B* **27** 1052–78
- [3] Micoulaut M, Cormier L and Henderson G S 2006 The structure of amorphous, crystalline and liquid GeO_2 *J. Phys.: Condens. Matter* **18** R753–84
- [4] Salmon P S, Barnes A C, Martin R A and Cuello G J 2007 Structure of glassy GeO_2 *J. Phys.: Condens. Matter* **19** 415110
- [5] McMillan P F and Wilding M C 2009 High pressure effects on liquid viscosity and glass transition behaviour, polyamorphic phase transitions and structural properties of glasses and liquids *J. Non-Cryst. Solids* **355** 722–32
- [6] Wilding M, Guthrie M, Bull C L, Tucker M G and McMillan P F 2008 Feasibility of *in situ* neutron diffraction studies of non-crystalline silicates up to pressures of 25 GPa *J. Phys.: Condens. Matter* **20** 244122
- [7] Itie J P, Polian A, Calas G, Petiau J, Fontaine A and Tolentino H 1989 Pressure-induced coordination changes in crystalline and vitreous GeO_2 *Phys. Rev. Lett.* **63** 398–401
- [8] Vaccari M, Aquilanti G, Pascarelli S and Mathon O 2009 A new EXAFS investigation of local structural changes in amorphous and crystalline GeO_2 at high pressure *J. Phys.: Condens. Matter* **21** 145403
- [9] Hong X, Newville M, Prakapenka V B, Rivers M L and Sutton S R 2009 High quality x-ray absorption spectroscopy measurements with long energy range at high pressure using diamond anvil cell *Rev. Sci. Instrum.* **80** 073908
- [10] Baldini M, Aquilanti G, Mao H k, Yang W, Shen G, Pascarelli S and Mao W L 2010 High-pressure EXAFS study of vitreous GeO_2 up to 44 GPa *Phys. Rev. B* **81** 024201
- [11] Guthrie M, Tulk C A, Benmore C J, Xu J, Yarger J L, Klug D D, Tse J S, Mao H k and Hemley R J 2004 Formation and structure of a dense octahedral glass *Phys. Rev. Lett.* **93** 115502
- [12] Drewitt J W E, Salmon P S, Barnes A C, Klotz S, Fischer H E and Crichton W A 2010 Structure of GeO_2 glass at pressures up to 8.6 GPa *Phys. Rev. B* **81** 014202
- [13] Filipponi A and Di Cicco A 1995 X-ray-absorption spectroscopy and n -body distribution functions in condensed matter. II. Data analysis and applications *Phys. Rev. B* **52** 15135–49
- [14] Filipponi A 2001 EXAFS for liquids *J. Phys.: Condens. Matter* **13** R23–60
- [15] Okamoto Y 2004 XAFS simulation of highly disordered materials *Nucl. Instrum. Methods Phys. Res. A* **526** 572–83

- [16] Salmon P S 2006 Decay of the pair correlations and small-angle scattering for binary liquids and glasses *J. Phys.: Condens. Matter* **18** 11433–44
- [17] Micoulaut M 2004 Structure of densified amorphous germanium dioxide *J. Phys.: Condens. Matter* **16** L131–8
- [18] Gutiérrez G and Rogan J 2004 Structure of liquid GeO₂ from a computer simulation model *Phys. Rev. E* **69** 031201
- [19] Hoang V V 2006 Static and dynamic properties of simulated liquid and amorphous GeO₂ *J. Phys.: Condens. Matter* **18** 777–86
- [20] Shanavas K V, Garg N and Sharma S M 2006 Classical molecular dynamics simulations of behavior of GeO₂ under high pressures and at high temperatures *Phys. Rev. B* **73** 094120
- [21] Hung P K, Vinh L T and Nghiep D M 2007 Computer simulation of GeO₂ liquid *J. Non-Cryst. Solids* **353** 2163–70
- [22] Hoang V V, Anh N H T and Zung H 2007 Diffusion in simulated liquid GeO₂ under pressure *Physica B* **394** 39–45
- [23] Peralta J, Gutiérrez G and Rogan J 2008 Structural and vibrational properties of amorphous GeO₂: a molecular dynamics study *J. Phys.: Condens. Matter* **20** 145215
- [24] Hung P K, Vinh L T, Nhan N T, Hong N V and Mung T V 2008 Local structure of liquids Al₂O₃ and GeO₂ under densification *J. Non-Cryst. Solids* **354** 3093–7
- [25] Li T, Huang S and Zhu J 2009 The structure and void analysis of pressure-induced amorphous GeO₂: molecular dynamics simulation *Chem. Phys. Lett.* **471** 253–7
- [26] Oeffner R D and Elliott S R 1998 Interatomic potential for germanium dioxide empirically fitted to an *ab initio* energy surface *Phys. Rev. B* **58** 14791–803
- [27] Hawlitzky M, Horbach J, Ispas S, Krack M and Binder K 2008 Comparative classical and *ab initio* molecular dynamics study of molten and glassy germanium dioxide *J. Phys.: Condens. Matter* **20** 285106
- [28] Marrocchelli D, Salanne M, Madden P A, Simon C and Turq P 2009 The construction of a reliable potential for GeO₂ from first principles *Mol. Phys.* **107** 443–52
- [29] Giacomazzi L, Umari P and Pasquarello A 2005 Medium-range structural properties of vitreous germania obtained through first-principles analysis of vibrational spectra *Phys. Rev. Lett.* **95** 075505
- [30] Giacomazzi L, Umari P and Pasquarello A 2006 Vibrational spectra of vitreous germania from first-principles *Phys. Rev. B* **74** 155208
- [31] Zhu X F and Chen L F 2009 First-principles molecular dynamics simulations of the structure of germanium dioxide under pressures *Physica B* **404** 4178–84
- [32] Norberg S T, Ahmed I, Hull S, Marrocchelli D and Madden P A 2009 Local structure and ionic conductivity in the Zr₂Y₂O₇–Y₃NbO₇ system *J. Phys.: Condens. Matter* **21** 215401
- [33] Jahn S and Madden P A 2007 Modeling Earth materials from crustal to lower mantle conditions: a transferable set of interaction potentials for the CMAS system *Phys. Earth Planet. Inter.* **162** 129–39
- [34] Angell C A, Cheeseman P A and Tamaddon S 1982 Pressure enhancement of ion mobilities in liquid silicates from computer simulation studies to 800 kilobars *Science* **218** 885–7
- [35] Sharma S K, Virgo D and Kushiro I 1979 Relationship between density, viscosity and structure of GeO₂ melts at low and high-pressures *J. Non-Cryst. Solids* **33** 235–48
- [36] Madden P A, Heaton R, Aguado A and Jahn S 2006 From first-principles to material properties *J. Mol. Struct.: THEOCHEM* **771** 9–18
- [37] Martyna G J, Tobias D and Klein M L 1994 Constant pressure molecular dynamics algorithms *J. Chem. Phys.* **101** 4177–89
- [38] Martyna G J, Klein M L and Tuckerman M 1992 Nosé–Hoover chains: the canonical ensemble via continuous dynamics *J. Chem. Phys.* **97** 2635–43
- [39] Liang Y, Miranda C R and Scandolo S 2008 Temperature-induced densification of compressed SiO₂ glass: a molecular dynamics study *High Pressure Res.* **28** 35–44
- [40] Stone C E, Hannon A C, Ishihara T, Kitamura N, Shirakawa Y, Sinclair R, Umesaki N and Wright A C 2001 The structure of pressure-compacted vitreous germania *J. Non-Cryst. Solids* **293** 769–75
- [41] Hong X G, Shen G Y, Prakapenka V B, Newville M, Rivers M L and Sutton S R 2007 Intermediate states of GeO₂ glass under pressures up to 35 GPa *Phys. Rev. B* **75** 104201
- [42] Smith K H, Shero E, Chizmeshya A and Wolf G H 1995 The equation of state of polyamorphic germania glass: a two-domain description of the viscoelastic response *J. Chem. Phys.* **102** 6851–7
- [43] Tsiok O B, Brazhkin V V, Lyapin A G and Khvostantsev L G 1998 Logarithmic kinetics of the amorphous–amorphous transformation in SiO₂ and GeO₂ glasses under high pressure *Phys. Rev. Lett.* **80** 999–1002
- [44] Wilson M, Madden P A, Medvedev N N, Geiger A and Appellagen A 1998 Voids in network-forming liquids and their influence on the structure and dynamics *J. Chem. Soc. Faraday Trans.* **94** 1221–8
- [45] Cromer D T and Waber J T 1974 *International Tables for X-Ray Crystallography* ed J A Ibers and W C Hamilton (Birmingham: Kynoch Press) p 71
- [46] Tokonami M 1965 Atomic structure factor for O²⁻ *Acta Crystallogr.* **19** 486
- [47] Sciortino F, Geiger A and Stanley H E 1991 Effect of defects on molecular mobility in liquid water *Nature* **354** 218