Structure of densified amorphous germanium dioxide

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Classical molecular dynamics simulations are used to study the structure of densified germanium dioxide (GeO$_2$). It is found that the coordination number of germanium changes with increasing density (pressure) while pressure released systems do not exhibit a marked change in local structure as compared to the virgin system. The structural modification with pressure appears to be stepwise and gradually affects long range (through the reduction of the long-range correlations as seen from the shift of the first sharp diffraction peak), intermediate range (by angular reduction) and finally short range structure (by tetrahedron distortion).

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Structural transitions in minerals are known to take place under various geological conditions [1,2]. In the Earth’s interior, silicate and alumino-silicate melts change their local structure causing strong density and viscosity modifications in magmas [3] and silicon exhibits at high pressure a change of its coordination number [4]. These results have been mostly obtained with high pressure-temperature experiments [5] but also with computer simulations [6] reproducing extreme conditions. Both have inferred the nature of these structural transitions, the structure and the phase portrait of the liquid state. However, while a majority of studies have been devoted to the silica and silicate chemistry, little has been done to elucidate the corresponding behavior in germanium dioxide (GeO$_2$) even though this material is a structural analog of silica in many respects: both materials exhibit at ordinary conditions a tetrahedral local structure, they can also exist in $\alpha$ as well as $\beta$ quartz phases [7] and the change of germanium coordination from four to six also occurs at high pressure [8]. The structure of in situ densified or permanently densified GeO$_2$ remains however controversial. While the global increase with pressure of the germanium-oxygen distance in GeO$_2$ has been related from x-ray diffraction [8] with the conversion of tetrahedral Ge(4) into octahedral Ge(6), it seems that this structural change is reversible as no Ge(6) is found in decompressed samples [9], a situation which does not occur [8] in the decompressed rutilelike $c$-GeO$_2$ The interest in germanium coordination change has been also motivated by the observation of the so-called “germanate anomaly” which corresponds to a maximum in density and refractive index when 15 – 16 mol% Na$_2$O are added into the basic GeO$_2$ network former [10]. These binary systems have been investigated by various spectroscopic tools [11]-[12] and it is suggested that the increasing presence of GeO$_6$ octahedra (Ge(6)) within the network is responsible of the anomaly. On the other hand, micro-Raman [13] applied on the same systems suggests that the anomaly is due to a massive conversion of 4-membered rings into more close-packed ones such as 3-membered rings, with no, or at least very few, Ge(6) present.

A preliminary task if one wishes to describe density induced structural changes in germanates, is first to understand how the basic network former GeO$_2$ changes with densification. While crystalline phases of GeO$_2$ have been studied from numerical calculations [14,15], we are not aware of any published result on simulated liquid and amorphous GeO$_2$. It is therefore of striking interest to see what Molecular Dynamics (MD) can tell about a certain number of experimental open questions which remain at this stage. How does densification affect the local structure in the amorphous material? Which thermodynamical quantity (temperature, Pressure) controls mostly the existence of a 6-fold coordinated germanium? Does octahedral germanium exists in pressure released (permanently densified) GeO$_2$? This Letter attempts to address some of these basic issues by providing the first MD study of amorphous germania. The results show several main features. They demonstrate the reversible nature of pressure induced changes and no major difference with the virgin structure is found upon pressure release, while the local coordination number of the germanium increases smoothly from 4 to 5.5 with applied pressure, a result that would be accessible from in situ experiments as already realized for silica [16]. Furthermore, several régimes of densification can be clearly identified: a first régime [$P \leq 1.8$ GPa] during which no global change in the local structure is found to occur whereas the increase in the position of the first sharp diffraction peak (FSDP) suggests a global reduction of the longer range correlations. In the window $1.8 \text{ GPa} \leq P \leq 2.8 \text{ GPa}$, a sharp decrease of the intertetrahedral bond angle permits to densify the structure with no distorsion of the basic GeO$_{3/2}$ tetrahedron. This leads to the buckling of the network connected tetrahedra. Finally, for larger pressures, distorsion of the tetrahedron sets in. As a consequence, additional constraints appear for $P > 3 \text{ GPa}$ which produce a global stiffening of the network [17,18]

The system consists of 256 germanium and 512 oxy-
gen atoms interacting via a Born-Huggins-Mayer type potential which has been fitted in the case of GeO$_2$ by Oeffner and Elliot to recover the crystalline phases of GeO$_2$ and its vibrational spectra [14]. The atoms have been first confined in a cubic box of length $L = 23.044\,\text{Å}$ in order to recover the experimental value of the density ($\rho_g = 3.66\,\text{g.cm}^{-3}$). After having thermalized the system at 3000 $K$ for 20000 time steps (20 ps) the system has been cooled to 300 $K$ with a linear cooling schedule at a quench rate of $2.5 \times 10^{12}\,\text{K.s}^{-1}$. Integration has been done using a leap-frog Verlet algorithm. Various configurations (positions and velocities) have been saved at different temperatures which have been used as starting configurations for production runs of $10^5$ steps.

Densification has been realized reproducing experimental conditions, i.e. starting from an initial configuration at $T = 300\,K$ and $\rho_g$ and increasing the density during $10^4$ time steps. At the density $\rho_g$, the glass transition temperature was about 1660 $K$, and as expected, the $T_g$ shifts to the higher temperatures with increasing density ($1894\,K$ at $\rho = 1.1\rho_g$). The sample data of Price and co-workers [12] has been almost recovered, i.e. after MD pressure release from 15.16GPa determined from the virial [19]. The final density of the decompressed system at zero pressure was $\rho = 4.5\,\text{g.cm}^{-3} = 1.25\rho_g$. The corresponding configuration (termed in the following as “permanently densified system”) was taken for comparison with the experimental study [20] of permanently densified GeO$_2$

The results for the partial structure factors $S_{ij}(Q)$ are displayed in Fig. 1 at $\rho_g = 3.66\,\text{g.cm}^{-3}$ which show a fair agreement with the experimental results obtained from a combination of x-ray data [12].

One has however to note that these measurements have been refined but without any complete resolution of all the partials [20]. The principal features in the structure factors of GeO$_2$ are the peaks occurring at $Q_P = 1.5 - 2\,\text{Å}^{-1}$ (the first sharp diffraction peak, FSDP, corresponding to a correlation length $L_1 = 2\pi/Q_P \simeq 4.1\,\text{Å}$). Peaks at $2.6\,\text{Å}^{-1}$ and $4\,\text{Å}^{-1}$ appearing in the partial structure factors of the Ge-O and O-O can be associated with chemical short range order (CRSO) and topological short-range order as derived from scaling considerations [21]. For the former, the similar height in $g_{\text{GeGe}}$ and $g_{\text{OO}}$ but with opposite sign suggests the CRSO nature of the

![FIG. 1. Partial structure factors $S_{ij}(Q)$ of vitreous germania at 300 K from MD simulations (solid line) at $\rho = \rho_g$ compared to experimental results (circles) from [11].](image)

![FIG. 2. Calculated partial pair correlation functions in vitreous germania at 300K at ordinary density $\rho_g = 3.66\,\text{g.cm}^{-3}$ (solid line) and in a permanently densified system ($\rho = 4.5\,\text{g.cm}^{-3}$, dashed line). The insert represent the corresponding running coordination number $n_{ij}(R)$ together with results from a system under 16.6 GPa pressure (dots).](image)
network. The evolution of the total scattering function and the position of the FSDP with respect to pressure is discussed below.

The calculation of the pair correlation functions permits to extract the simulated bond lengths which also agree with experimental findings: $d_{Ge-Ge} = 3.32\text{Å}$, $d_{Ge-O} = 1.72\text{Å}$ and $d_{O-O} = 2.81\text{Å}$ (to be respectively compared to the experimental values $3.16\pm0.03\text{Å}$, $1.73\pm0.03\text{Å}$ and $2.83\pm0.05\text{Å}$). Weak changes are found when comparing the virgin and the permanently densified systems. The most striking difference is found in the Ge-Ge correlator which differs even at low distances whereas the loss of peak heights in $g_{OO}$ produces a slight shift in the corresponding running coordination number $n_{OO}$. The number of oxygen neighbours around an germanium atom remains however unaffected by pressure release. More dramatic is the change in structure in the pressurized system at $16.6\text{ GPa}$ (dots in the inserts of Fig. 2) which show substantial differences in the bond distances ($d_{Ge-Ge} = 3.25\text{Å}$, $d_{Ge-O} = 1.75\text{Å}$ and $d_{O-O} = 2.56\text{Å}$) and an increase of the number of oxygen neighbours in the vicinity of a Ge atom (about 5 in the insert representing $n_{GeO}$, see also Fig. 3). Evidence of supplementary atoms in the first shell surrounding a central $GeO_4/2$ unit is also provided by the increase of $n_{GeGe}$.

![Diagram](image1)

**FIG. 3.** Left axis: The distortion parameter of a regular $GeO_4/2$ as a function of applied pressure(open circles). For comparison, the same parameter for $SiO_2$ (filled circles). The dashed horizontal line represents the value $\sqrt{3/8}$. The right axis represents the Ge-O coordination number (solid line).

Using the present simulation, it is now possible to analyze in more depth the low pressure behaviour. Focus is made on the distortion of the tetrahedron parameter defined by $\delta = d_{X-O}/d_{O-O}$ [$X=Si,Ge$] which provides a direct measure of the effect of the pressure on the local structure of the network. For an ideal tetrahedron, $\delta = \sqrt{3/8}$. The latter quantity is of central interest when studying the flexibility of the glass under pressure [18] and the rigid unit modes in the context of pressure induced rigidity [22,23]. In Fig. 3 (left axis) are represented the variation of the tetrahedron parameter $\delta$ with pressure for both silica [24] and germania. At low pressure, $\delta$ remains almost constant suggesting that the tetrahedral environment is preserved, slightly higher however than the value of a perfect tetrahedron. For $P \geq 2.8\text{ GPa}$, there is increasing distorsion of the tetrahedron in germania. The way of distorsion appears however to be radically different as compared to the silica system. In the former it is found a stepwise increase (most noticable from the jump of $\delta$ at around $3\text{ GPa}$), in contrast with the more or less smooth increase of $\delta$ for the latter. In the insert of Fig. 3 are shown the variation of the mean bond angles O-Ge-O and Ge-O-Ge with respect to pressure. For both the virgin and the permanently densified system, the O-Ge-O bond angle peaks at around $109^\circ$. As pressure is increased, the intratetrahedral bond angle decreases since the Ge-O bond distances increases. The constant value of the O-Ge-O bond angle at low pressure correlates of course with the absence of distorsion of the basic tetrahedron. The main feature provided by the angular analysis comes from the variation of the intertetrahedral mean bond angle Ge-O-Ge with pressure, which exhibits a sharp drop at around $1.8\text{ GPa}$, from $158^\circ$ to $135^\circ$ followed by a stabilization at around $140^\circ$. Densification first applies on the angles connecting the tetrahedra and preserves the latter. If pressure keeps increasing, the distorsion of the tetrahedra sets in, which in turn stabilizes more or less the Ge-O-Ge bond angle.

![Diagram](image2)

**FIG. 4.** Scattering factor $S(Q)$ for different applied pressures: 0,3.0, 5.76, 8.92 and $16.6\text{GPa}$. The lower curve is the virgin system at 0$\text{GPa}$, compared to experiments [11]. The insert shows the simulated position in $Q_P$ of the FSDP with pressure (solid line). Experimental data are from [23](open circles) and [9](filled circles).

Further interpretation is provided from the variation of the position of the FSDP with respect to pressure. In Fig. 4 are represented the scattering functions for different applied pressures which show a global broadening
of the peak at 4 Å⁻¹ whereas the position of the FSDP at 1.5 Å⁻¹ is shifted to the higher values in Q, already at very low pressure and even before the angular drop at P = 1.8 GPa. With increasing pressure, the calculated FSDP broadens and becomes less intense, as currently observed from X-ray or neutron diffraction [11]. It is worth to note that the peak at 2.5 Å⁻¹ obtained in the present simulation is only weakly observable in the experiments from neutron diffraction [9] displayed in Fig. 4. However, the simulated double peak distribution between 1.5 and 2.5 Å⁻¹ has been observed by different authors [26] (see also discussion in [12]). The evolution with pressure of the position Qₚ of the FSDP is represented in the insert of Fig. 4. Both experiments and simulation show that Qₚ already increases at low pressures and then stabilizes at around Q = 1.7 Å⁻¹ (∼2 Å⁻¹ in the simulation). This suggests that intermediate range order is immediately affected by the densification and then remain unaffected with further densification.

In conclusion, we have shown that simulated GeO₂ under pressure shows several main features with applied pressure and pressure release: i) a global increase of the number of oxygen neighbours in the vicinity of a germanium atom, ii) a stepwise change in the local structure with applied pressure, made of a reduction of long range correlation (seen from the position of the FSDP), a sharp reduction of the intertetrahedral bond angle and then a progressive distortion of the GeO₄/3 tetrahedron and iii) no noticeable change in local structure between a virgin and a permanently densified system. This clearly draws the following picture: Pressure applies on different length scales. With increasing magnitude, densification is realized by a successive deformation of long range structure, intermediate (angular) and finally short range structure (tetrahedral).

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