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The first peak splitting of the Ge—Ge pair RDF in the correlation to network structure of GeO_2 under compression

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ABSTRACT

The network structure of GeO_2 at 3500 K and under pressure of 0–100 GPa is investigated in terms of the short range order (SRO) and intermediate range order (IRO) by molecular dynamics simulation. The results show that the structure of GeO_2 consists of GeO_4 tetrahedra that link to each other, forming a tetrahedral network. Under compression, there is a gradual transition from tetrahedral network to octahedral network (GeO_6-network) via GeO_5 polyhedra. At a certain pressure, the structure of GeO_2 comprises three kinds of basic structural polyhedra: GeO_4, GeO_5 and GeO_6. The spatial distribution of the basic structural polyhedra is not uniform, but they form clusters of GeO_4-, GeO_5- and GeO_6-polyhedra. The size of the GeO_5-cluster reaches the maximum at pressure of approximately 15–20 GPa (at density of approximately 4.95–5.25 g/cm^3). The GeO_5 cluster exists as an immediate configuration in the structural transition. At low pressure, most GeO_x polyhedra ($x = 4, 5, 6$) link to each other by one common oxygen (corner-sharing bond). At high pressure, GeO_x polyhedra link to each other by a corner-sharing, edge-sharing (two common oxygens) or/and face-sharing bond (three common oxygens). The Ge—Ge bond length in a corner-sharing bond is much longer than that in edge-sharing and face-sharing bonds, and this is the origin of the first peak splitting of the Ge—Ge pair RDF (Radial Distribution Function) under compression. At high pressure, the GeO_5- and GeO_6-polyhedra are dominant and tend to link each other through edge-sharing and face-sharing bonds, forming edge-sharing and face-sharing clusters. The size of edge-sharing and face-sharing clusters increases with increasing pressure, and this can be seen via the degree of the first peak splitting of the Ge—Ge pair RDF.

1. Introduction

Germania (GeO_2) and silica (SiO_2) are typical “strong” network glass-forming materials [1–3]. They are characterized by a tetrahedral network structure at ambient conditions in crystalline, amorphous and liquid states. Germania is considered as a chemical and structural analogue of silica with a similar pressure response at lower pressures due to the larger ionic radius of Ge^{4+} ions [9]. Its structure is based on corner-sharing GeO_4 polyhedra considered as basic structural polyhedra with average Ge—O bond length of approximately 1.74 Å. The mean intra-polyhedral O—Ge—O and inter-tetrahedral Ge—O—Ge bond angles are approximately 109° and 130°, respectively [4–9]. Pressure-induced structural changes of amorphous and liquid GeO_2 have been extensively studied due to their importance in high technology materials (optical, electron and ceramic materials) [8–10] and geological sciences. Structural changes under compression in GeO_2 have been linked to anomalous behavior in transport and thermal properties as well as polyamorphism [10–13]. Many works in both experimentation and simulation have been conducted to clarify the relationship between densification and structure and the physicochemical properties of GeO_2. EXAFS spectroscopy, X-ray and neutron diffraction experiments and calculation results in [5–14] have shown that the Ge—O bond length and Ge—O coordination number increase with increasing pressure. The Ge—O bond length increases from 1.74 Å (at ambient pressure) to 1.82 Å (at 13 GPa) [8,9,14]. Under compression, the structure of amorphous and liquid GeO_2 undergoes a transformation from a tetrahedral network (GeO_4-network) to a dense octahedral network (GeO_6-network) via GeO_5 polyhedra. The GeO_5 polyhedra are considered as an intermediate state in the structural phase transition that is formed at 6–10 GPa [15]. A sharp first-order-like transition from a tetrahedral to octahedral network in GeO_2 glass was also proposed based on the rapid change of Ge—O bond length at the 7–9 GPa pressure range in X-ray-absorption spectra experiments [10]. X-ray and neutron-diffraction measurements in [16] show that a complete octahedral network occurs at approximately 15 GPa. However, no abrupt change of Ge—O bond length or Ge—O coordination number is revealed in recent

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works (either experimentation or simulation) [17–23]. Regarding polyamorphism, in our previous work [22], we have shown that at certain pressure, the structure of amorphous and liquid GeO_2 comprises GeO_4, GeO_5 and GeO_6 polyhedra. The spatial distribution of GeO_x-polyhedra is not uniform but forms GeO_4-, GeO_5- and GeO_6-clusters. Under compression, the size of GeO_5- and GeO_6-clusters increases, while the size of GeO_4- clusters decreases. However, the information on the spatial distribution of GeO_x has not been calculated quantitatively but mainly based on visualization (qualitative evaluation). In a very recent work [6], by using X-ray total scattering and X-ray absorption (XAFS) techniques, the authors showed that at high pressure, the Ge—Ge bond length comprises two values: 2.79 and 3.20 Å. The authors explained that rutile-structured crystalline GeO_2 is regarded as an analogue of octahedral GeO_2 glass composed of two Ge—Ge bond lengths: 2.83 and 3.35 Å. This intuitive explanation will be developed, in this article, more precisely and quantitatively. In a very recent work [23], Yoshio Kono and co-authors also showed that the Ge—Ge bond length comprises two values (double-peak feature): approximately 2.82 and 3.21 Å at 22.6 GPa; 2.79 and 3.24 Å at 37.9 GPa; 2.73 and 3.15 Å at 49.4 GPa; and 2.73 and 3.13 Å at 61.4 GPa. However, the double peak tends to merge into a single peak as pressure increases. At pressure beyond 72.5 GPa, the double peak becomes a single peak. It is explained that the structure of GeO_2 glass is sixfold coordinated similar to $CaCl_2$-type crystalline GeO_2 (the Ge—Ge pair RDF has two distinct peaks) in the 22.6–37.9 GPa pressure range. At pressure beyond 70 GPa, the structure of GeO_2 glass with sixfold is similar to the pyrite-type GeO_2. It would be very interesting to compare the structural transformations of glasses and crystallines under compression as performed in the literature [6,23]. Crystalline GeO_2 at ambient temperature and pressure is α-quartz-like phase. In this phase, the Ge—O coordination number is fourfold (GeO_4) with a corner-sharing bond between GeO_4 tetrahedra. Under compression, the phase transformation sequence of α-quartz-like GeO_2 → (10 GPa) rutile-like GeO_2 → (25 GPa) $CaCl_2$-type → (44 GPa) α-PbO_2-type → (70–90 GPa) pyrite-type structures [8]. In rutile-like GeO_2, $CaCl_2$-type structured GeO_2, α-PbO_2-type structured GeO_2, the Ge—O coordination number is sixfold (GeO_6) with corner-sharing and edge-sharing bonds between GeO_6 octahedra. The structural change in crystalline GeO_2 under compression results in local- and intermediate-structure change ($GeO_4 \rightarrow GeO_6$ and corner-sharing → edge-sharing bond). This is also similar to the structural change of amorphous and liquid GeO_2 under compression. The double-peak feature at high pressure can be related to edge-sharing bonds.

In this work, we investigate the effect of pressure on the structure of GeO_2 at 3500 K and in the 0–100 GPa pressure range. The network structure and polyamorphism are analyzed in detail and visualized in 3D space. The network topology is analyzed via corner-sharing, edge-sharing and face-sharing bonds and their clustering. The polyamorphism is clarified via clustering of GeOx polyhedra and their size distribution. Specially, the first peak splitting of the Ge—Ge pair RDF is investigated and explained in detail. The structure of the immediate structural phase and structural heterogeneity are also discussed here.

2. Computational procedure

A large-scale molecular dynamics simulation is performed for a GeO_2 system consisting of 5499 atoms (1833 Ge and 3666 O atoms) at 3500 K and in the 0–100 GPa pressure range. A model with a larger number of atoms in this investigation should provide more reliable results for structures at high temperature and pressure than earlier studies [24–26]. The Oeffner–Elliott potentials and periodic boundary conditions are used to construct the models [27]. To integrate the equation of motion, the Verlet algorithm is used with time steps of 0.8 fs. The initial configuration is generated by placing all atoms randomly in a simulation box and heating it to 6000 K to remove the initial configuration. After that, the sample is cooled to 5000, 4000, and finally 3500 K. Next, a long relaxation (10^7 time steps) is allowed to achieve equilibrium using an isothermal–isobaric (NPT) ensemble. The structural data of the considered models are determined by averaging over 1000 configurations during the last 10^4 time steps.

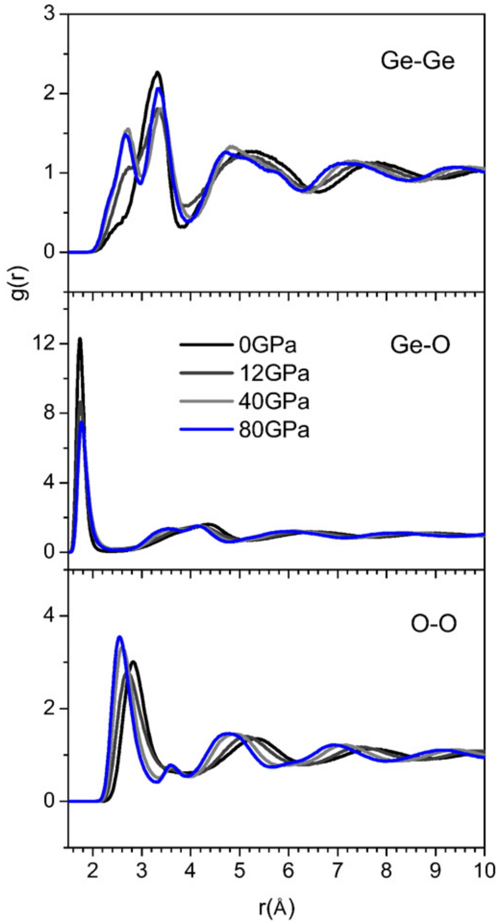

Fig. 1. Radial distribution function for Ge—Ge, Ge—O, O—O pairs at different pressures.

The size distribution of GeO_4-, GeO_5- and GeO_6-clusters is calculated using the following algorithm: 1/ the GeO_x polyhedra in the model are classified into three sets: GeO_4-, GeO_5- and GeO_6-ones; 2/ in the set of GeO_4 polyhedra, all atoms are labeled from 1 to n (n is the number of atoms in the set). After that, if two Ge ions have at least one common O atom, they will belong to the same cluster and have the same label (the value of this common label is the label of the Ge atom with the smaller value). Four O^{2-} ions that bind with the Ge^{4+} ion will share its

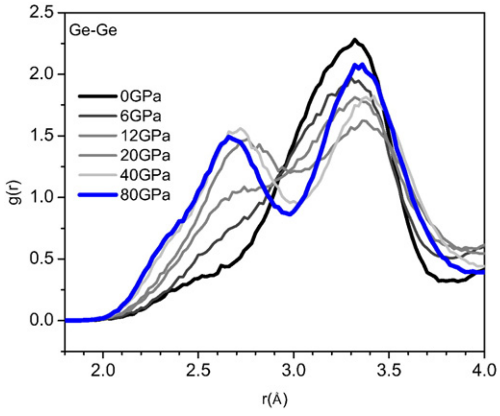

Fig. 2. Radial distribution function for Ge—Ge pairs.