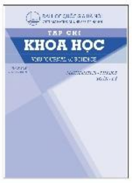
VNU Journal of Science: Mathematics – Physics, Vol. 37, No. 4 (2021) 31-37

VNU Journal of Science: Mathematics - Physics

Journal homepage: https://js.vnu.edu.vn/MaP



Original Article

A Simulation Study of the Amorphous Germania Structure up to 70 GPa

Mai Thi Lan[1,*], Nguyen Thu Nhan[1], Nguyen Thi Thao[2], Pham Tri Dung[3]

[1]School of Engineering Physics, Hanoi University of Science and Technology,
1 Dai Co Viet, Hai Ba Trung, Hanoi, Vietnam
[2]Hong Duc University, 565 Quang Trung, Thanh Hoa, Vietnam
[3]Naval Academy, 30 Tran Phu, Vinh Nguyen, Nha Trang, Vietnam

Received 01 December 2020
Revised 06 February 2021; Accepted 19 February 2021

Abstract: This work presents the effect of pressure on the local microstructure of amorphous Germania (GeO_2). The Molecular Dynamics simulation was performed on systems at 900 K and high pressure up to 70 GPa. The structural properties have been analyzed through the pair correlation function, coordination number distribution, and structure factors. The structural phase transition process starts occurring at 30 GPa. At above 30 GPa, the degree of structural order increases and the intermediate-range order structure depends strongly on pressure. Correlation between the peaks in the plot of structure factor and the topology of basic structural units GeO_n ($n = 4$-6) is also discussed in detail in this paper.

Keywords: Germania, MD, structure.

1. Introduction

Germanium oxide with GeO_2 chemical formula, also called Germania, is the main component in many important applications, such as semiconductor devices, piezoelectric materials, optical fiber, glass,… Like SiO_2, GeO_2 also has the tetrahedral local structure under ambient conditions. When GeO_2 is under compression, there also occurs structural phase transition. However, it occurs at lower pressures than the one in the case of SiO_2. Many works indicated that the structure of GeO_2 strongly depends on pressure. It changes from GeO_4 to GeO_6 structural phase under compression [1-5]. The Ge-O bond

---

[*] Corresponding author.
E-mail address: lan.maithi@hust.edu.vn

https//doi.org/10.25073/2588-1124/vnumap.4625

length and coordination number increase under compression. Specifically, the Ge-O bond length increases from 1.74 Å at 0 GPa to 1.82 Å at 13 GPa [1]. Recently, the extended X-Ray Absorption Fine Structure (EXAFS) and XAFS spectra experiment [2, 6] for GeO_2 was carried out at pressure up to 44 and 53 GPa, respectively. The results show that the six-fold coordination of Ge only exhibits in the pressure range of 25-30 GPa. The bond distance of Ge-Ge pair has two values of 2.79 Å and 3.20 Å at high pressure [6]. Under normal conditions, the mean bond length of Ge-O is about 1.73 Å and Ge-O-Ge bond angle in GeO_4 units is 1320. The influence of high pressure on the structure of GeO_2 is also interesting for researching by experiment [5, 7-8]. The results show that the structure of GeO_2 changes strongly in the pressure range from 3 to 15 GPa. The coordination number increases from 4 to 6 in the pressure range of 7-9 GPa. However, Vaccari et al. indicated that there was no exhibition of six-fold coordination at pressure up to 13 GPa. By using Neutron diffraction, at above 8.6 GPa, Drewitt et al. [7] showed a change in the intermediate-range order structure of GeO_2 that related to increasing position and decreasing height of the first peak in the structure factor. GeO_2 was also investigated intensively by simulation [3, 9-11]. The simulated results indicate the influence of pressure on the structure of GeO_2. Under compression, there is a structural phase transition from GeO_4 to GeO_6 via GeO_5. The proportion of GeO_x units depends strongly on pressure. Although GeO_2 system has been studied extensively by both experiment and simulation, the results of the structure of GeO_2 are still debatable and need to be further investigated.

This paper presents a Molecular Dynamics simulation of amorphous GeO_2 structure at high pressure up to 70 GPa. The structure of GeO_2 system is clarified via analyzing the structure factors, distribution of coordination number and the pair correlation function at different pressures.

2. Calculation Method

The paper used Molecular dynamics simulation method for constructing models of Germania system. The models applied the pair interatomic potentials of BKS type [12]: $U(r_{ij}) = q_i q_j e^2/r_{ij} + A_{ij} exp(-B_{ij} r_{ij}) - C_{ij} r_{ij}^{-6}$. The first term $(q_i q_j e^2/r_{ij})$ relates to the long-range coulombic interactions that are calculated with the standard Ewald summation technique. The other terms consist of repulsion and attractive interaction; where r_{ij} is the interatomic distance between i^{th} and j^{th} atoms; q_i and q_j are the charges of i^{th} and j^{th} atoms; A_{ij}, B_{ij} and C_{ij} are the parameters accounting for the repulsion terms. The values $q_1 = +1.5$ and $q_2 = -0.75$ are the charges of Ge and O atoms. The other values are $A_{11} = 0$, $A_{12}=208008.8549$, $A_{22}=7693.3496$ *eV*; $B_{11}=0$, $B_{12}=6.1293$, $B_{22}=3.2851$ $Å^{-1}$; $C_{11}=0$, $C_{12}=236.6475$, $C_{22}=131.0874$ *eV* $Å^6$. We used the Verlet algorithm to integrate Newton's motion equation with a time step of $4.7x10^{-16}$ *s*. The initial configuration of the system was obtained by randomly placing 1998 Ge, O atoms in simulation box with periodic boundary conditions. Then it was heated to 6,000 K to remove memory effect and treated over 50,000 steps. Next, the sample was cooled down to 900 K within 100,000 steps at constant ambient pressure to reach equilibrium state. From this well-equilibrated GeO_2 amorphous, six amorphous samples were constructed by compressing at different pressures of 10, 15, 20, 30, 50 and 70 GPa. The structural properties of the considered models were calculated by averaging over 1,000 configurations separated by 100 time steps during 100,000 last MD steps.

3. Results and Discussion

Before studying the structure of the amorphous Germania, we calculated the total structure factor $S_N(Q)$ of GeO_2 under ambient conditions and compared with the Neutron diffraction experiment [7] to test the reliability of our model. Figure 1 shows the structure factor of GeO_2 that has the curves fit well with the experimental data. In this work, the diffraction peaks give 1.65, 2.65, and 4.6 Å that are comparable with the Neutron diffraction values of 1.55, 2.65, 4.65 Å, respectively. The position of the first diffraction peak is higher than the experimental data. However, in general, the simulated results are in agreement with experiment data. Therefore, the constructed models are valid.

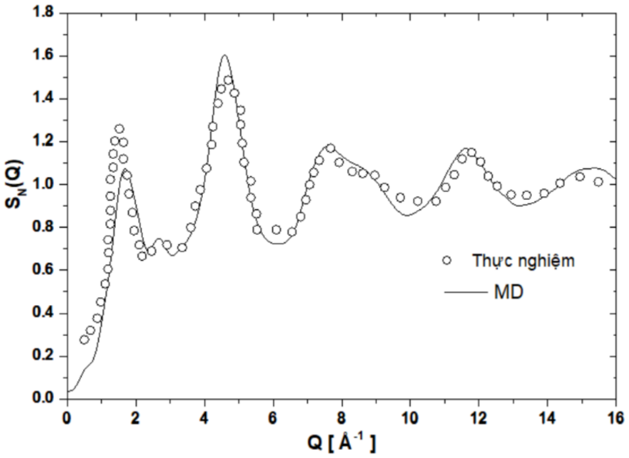


Figure 1. The total structure factor $S_N(Q)$ of GeO_2 under ambient conditions.

Now, we focus on investigating the structure of GeO_2 at different pressures via analyzing the Ge-Ge, Ge-O, and O-O pair correlation functions $g_{ij}(r)$ that is displayed in Figures 2, 3, and 4. For the Ge-Ge pair, at 0 GPa, the function $g_{Ge\text{-}Ge}(r)$ in Figure 2 has the first peak at 3.20 Å, but this peak is slightly concave at a distance of 3.38 Å. However, at high pressure up to 70 GPa, the first peak of $g_{Ge\text{-}Ge}(r)$ is split into two distinct peaks at positions of 2.64 Å and 3.32 Å. Furthermore, it also has a left shoulder at about 2.34 Å. For the function $g_{Ge\text{-}O}(r)$ (see Figure 3), we observed an increase in the position of the first peak with pressure.

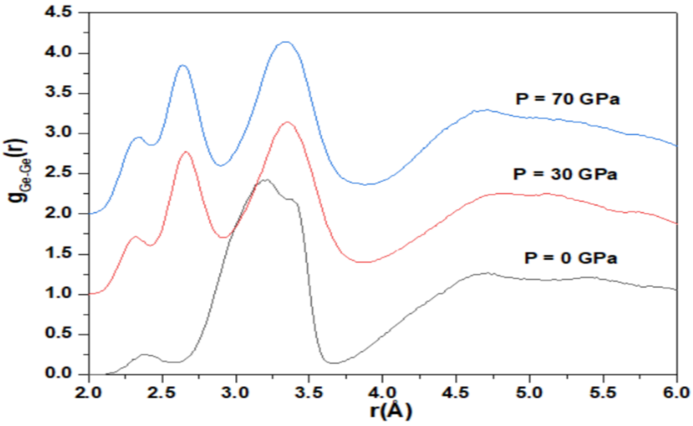


Figure 2. The Ge-Ge pair correlation functions $g_{ij}(r)$ at different pressures.

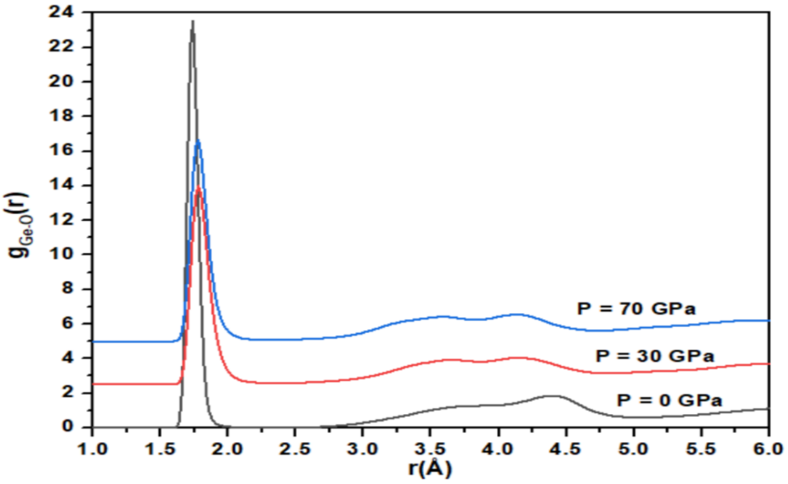


Figure 3. The Ge-O pair correlation functions $g_{ij}(r)$ at different pressures.

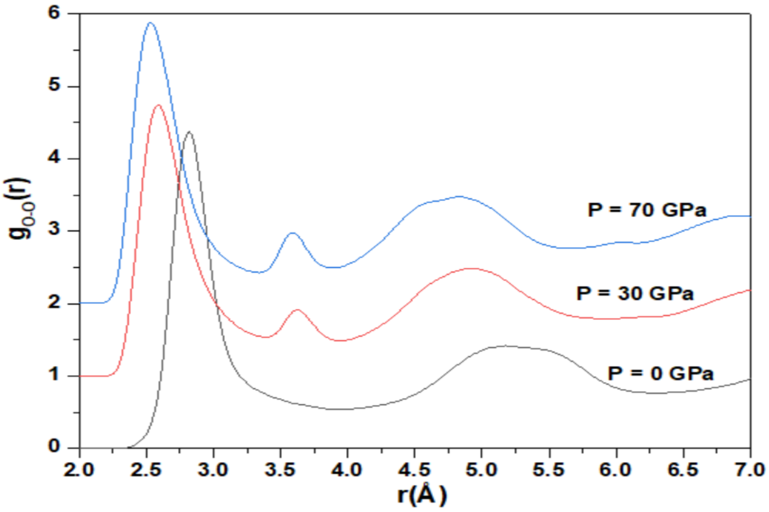


Figure 4. The O-O pair correlation functions $g_{ij}(r)$ at different pressures.

The bond distance of Ge-O pair at 0 GPa increases from 1.74 Å to 1.78 Å at 70 GPa. In the case of the O-O pair correlation function in Figure 4, the $g_{O\text{-}O}(r)$ function shows that the position of the first peak shifts to the left under compression. Specifically, the distance between two O atoms decreases from 2.82 Å at 0 GPa to 2.54 Å at 70 GPa. Besides, at compressed pressure up to 30 GPa, there appears the second peak at a position of 3.64 Å. The results demonstrate that the bond distance between two Oxygen atoms in GeO_2 changed significantly under compression. It is well assumed that the short-range order structure in amorphous GeO_2 changes slightly, meanwhile the intermediate-range order structure tends to become more orderly, especially in the considered 30-70 GPa pressure range. The coordination number is determined by integrating the first peak of the pair correlation function $g_{ij}(r)$: $Z_{ij} = 4\pi\rho \int_0^{r_c} g_{ij}(r) r^2 dr$; where rc is the cut-off distance, which was the chosen position of minimum after fist peak of the gij(r) function; ρ is density of the sample. The Ge-O coordination number at different pressures is indicated in Figure 5.

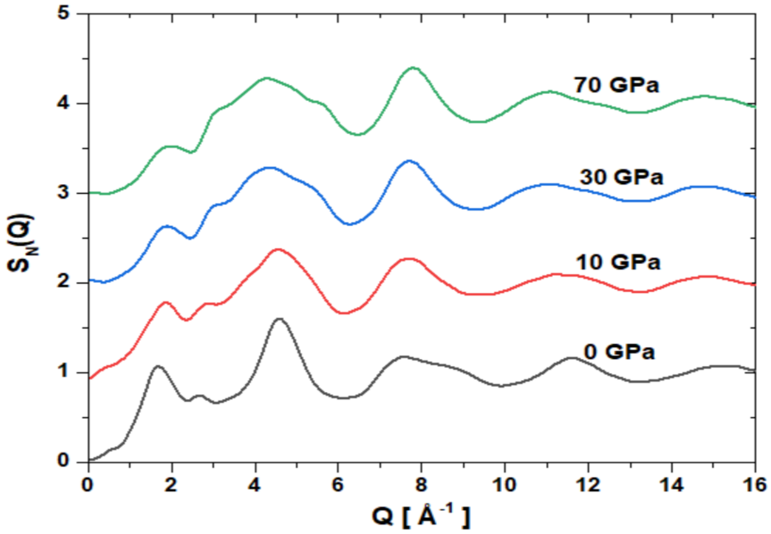


Figure 5. The total structure factor $S_N(Q)$ of GeO_2 at different pressures.

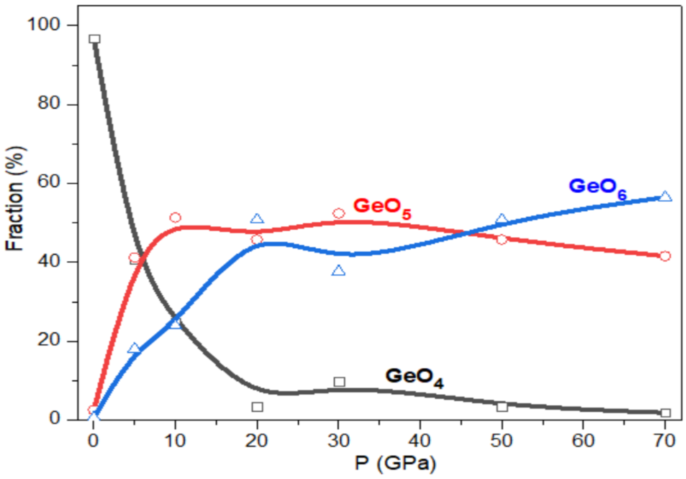


Figure 6. The Ge-O coordination number at different pressures.

At 0 GPa, the basic structural units in amorphous GeO_2 are the polyhedron GeO_4 with the proportion of 96.78% and a small fraction of 3.22% GeO_5 and GeO_6. When pressure increases, the fraction of GeO_4 drops rapidly, whereas the rate of GeO_5 and GeO_6 increases sharply. The percentage of GeO_5 reaches a peak is 52.43% at 30 GPa and goes down gradually. The proportion of GeO_6 increases and gets a maximum peak of 50.81% at 20 GPa. Then it continues falling to 37.68% at 30 GPa and above 30 GPa this fraction increases to 59% at 70 GPa. We can conclude that the structure of amorphous GeO_2 consists of the basic structural units GeO_n (n = 4-6). The amorphous-amorphous phase shifts from GeO_4 network to GeO_5 and GeO_6 network under compression. The GeO_4 tetrahedral network is the main network in amorphous GeO_2 at ambient pressure. Meanwhile, the GeO_5 and GeO_6 networks are the main networks in amorphous GeO_2 at above 30 GPa.

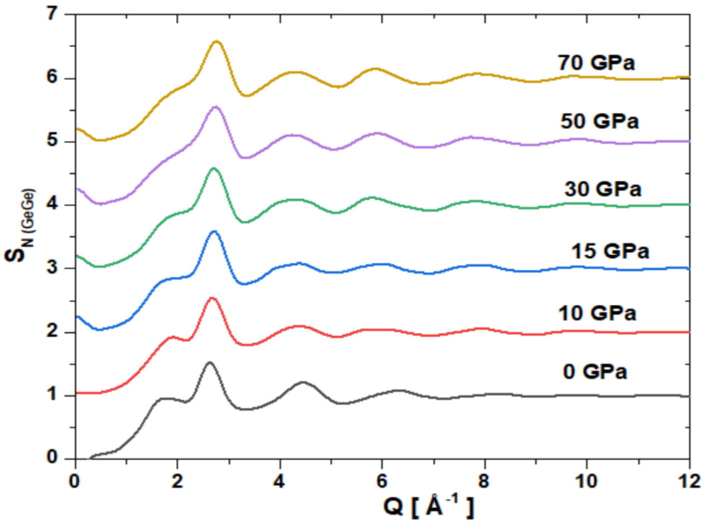


Figure 7. The Ge-Ge structure factor at different pressures.

4. Conclusion

The amorphous GeO_2 exhibited a change in structure as the pressure increased to 70 GPa. The results show that the structure of GeO_2 was transformed from GeO_4 network at ambient pressure to GeO_5 and GeO_6 network at 70 GPa. There was an amorphous-amorphous phase transition from GeO_4 network to GeO_5 and GeO_6 network under compression at 30 GPa. The MD results show that the calculated structure factors were in good agreement with the Neutron diffraction experiment. The change in the peaks in Q space of the structure factor $S_N(Q)$ was mostly observed for the Ge-Ge and Ge-O correlation due to GeO_4 tetrahedral network at ambient pressure and GeO_5 and GeO_6 network at high pressure.

Acknowledgments

This research was funded by Vietnam National Foundation for Science and Technology Development (NAFOSTED) under Grant103.05-2021.05

References

[1] M. Vaccari, G. Aquilanti, S. Pascarelli, O. Mathon, A New EXAFS Investigation of Local Structural Changes in Amorphous and Crystalline GeO_2 at High Pressure, Journal of Physics: Condensed Matter, Vol. 21, No. 14, 2009, pp. 145403(1)-145403(8), https://doi.org/10.1088/0953-8984/21/14/145403.

[2] M. Baldini, G. Aquilanti, H. K. Mao, W. Yang, G. Shen, S. Pascarelli, W. L. Mao, High Pressure EXAFS Study of Vitreous GeO_2 up to 44 GPa, Physical Review B, Vol. 81, No. 2, 2010, pp. 024201(1)-024201(6), https://doi.org/10.1103/PhysRevB.81.024201.

[3] M. Micoulaut, Structure of Densified Amorphous Germanium Dioxide, Journal of Physics: Condensed Matter, Vol. 16, 2004, pp. L131-L138, https://www.lptmc.jussieu.fr/user/mmi/reprint/JPCM2004_geo2.pdf/ (accesed on: August 15th, 2020).

[4] T. Li, S. Huang, J. Zhu, The Structure and Void Analysis of Pressure-Induced Amorphous GeO_2: Molecular Dynamics Simulation, Chemical Physics Letters, Vol. 471, No. 4-6, 2009, pp. 253-257, https://doi.org/10.1016/j.cplett.2009.02.059.

[5] M. Guthrie, C. A. Tulk, C. J. Benmore, J. Xu, J. L. Yarger, D. D. Klug, J. S. Tse, H. K. Mao, R. J. Hemley, Formation and Structure of A Dense Octahedral Glass, Phys. Rev. Lett, Vol. 93, No. 11, 2004, pp. 115502(1)-115502(2), https://doi.org/10.1103/PhysRevLett.93.115502.

[6] X. Hong, M. Newville, V. B. Prakapenka, M. L. Rivers, S. R. Sutton, High Quality X-Ray Absorption Spectroscopy Measurements with Long Energy Range at High Pressure Using Diamond Anvil Cell, Review of Scientific Instruments, Vol. 80, No. 7, 2009, pp. 073908(1)- 073908(10), https://doi.org/10.1063/1.3186736.

[7] J. W. E. Drewitt, P. S. Salmon, A. C. Barnes, S. Klotz, H. E. Fischer, W. A. Crichton, Structure of GeO2 Glass at Pressures up to 8.6 GPa, Physical Review B, Vol. 81, No. 1, 2010, pp. 014202(1)-014202(13), https://journals.aps.org/prb/abstract/10.1103/PhysRevB.81.014202.

[8] P. S. Salmon, A. C. Barnes, R. A. Martin, G. J. Cuello, Structure of Glassy GeO2, Journal of Physics: Condensed Matter, Vol. 19, No. 41, 2007, pp. 415110(1)- 415110(10), https://doi.org/10.1088/0953-8984/19/41/415110.

[9] J. Peralta, G. Guti´errez, J. Rogan, Structural and Vibrational Properties of Amorphous GeO2: A Molecular Dynamics Study, Journal of Physics Condensed Matter, Vol. 20, No. 14, 2008, pp. 145215(1)-145215(7), https://iopscience.iop.org/article/10.1088/0953-8984/20/14/145215.

[10] G. Guti´errez, J. Rogan, Structure of Liquid Geo2 from A Computer Simulation Model, Physical Review E, Vol. 69, No. 3, 2004, pp. 031201(1)-031201(8), https://journals.aps.org/pre/abstract/10.1103/PhysRevE.69.031201.

[11] K. V. Shanavas, N. Garg, S. M. Sharma, Classical Molecular Dynamics Simulations of Behavior of GeO2 under High Pressures and at High Temperatures, Physical Review B, Vol. 73, No. 9, 2006, pp. 094120(1)-094120(12), https://doi.org/10.1103/PhysRevB.73.094120.

[12] I. S. Voivod, F. Sciortino, P. H. Poole, Simulated Silica, Philosophical Transactions of the Royal Society A Mathematical Physical and Engineering Sciences, Vol. 363, 2005, pp. 525-535, https://royalsocietypublishing.org/doi/10.1098/rsta.2004.1506.