

POLYAMORPHISM AND TWO STATE MODEL IN LIQUID GeO_2 UNDER COMPRESSION: INSIGHT FROM VISUALIZATION OF MOLECULAR DYNAMICS DATA

NGUYEN VAN HONG, MAI THI LAN, NGUYEN THU NHAN
Hanoi University of Science and Technology

E-mail: hong.nguyenvan@hust.edu.vn

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Abstract. *The polyamorphism and two-state model based on the coordination number distribution in liquid GeO_2 at 3200 K and in a wide pressure range are investigated by molecular dynamics simulation. Results show that the structure of liquid GeO_2 mainly consists of GeO_x coordination units ($x = 4, 5, 6$) and OGe_y linkages ($y = 2, 3$). The distribution of OGe_y linkages in network structure is not uniform but tends to form clusters of OGe_y . The cluster of OGe_2 will form low-density phase region, conversely the cluster of OGe_3 will form high-density phase region. In other word, under compression, in the liquid GeO_2 coexist two states: low-density and high-density. The size of phase regions significantly depends on compression.*

Keywords: MD simulation, GeO .

I. INTRODUCTION

In recent years, a numerous studies focused on so-called polyamorphism and polyamorphic transitions in glass-forming liquids (such as GeO_2 , SiO_2 , TiO_2 , H_2O , P...). The polyamorphism and polyamorphic transitions were first recognized in the H_2O system. When compressed at 77 K, amorphous ice transforms from low-density to a high-density state at 0.60 ± 0.05 GPa [1-5]. Transitions between high density (HD) and low-density (LD) liquids have also been observed in the stable liquid regime for liquid phosphorus [6]. For liquid GeO_2 , SiO_2 and TiO_2 it was found that when applying pressure, it transforms from tetrahedral to octahedral network structure. This corresponds to the transformation from LD phase to HD phase. In the 0-50 GPa pressure range, the structure of liquid GeO_2 coexists both LD and HD phases [7, 8]. It is obvious that the properties of glass-forming liquids depend on the fraction and the distribution of LD and HD phases in material sample but up to now, there is no study about the spatial distribution of LD and HD phases. The structure of amorphous (or liquid) GeO_2 (SiO_2 , TiO_2 , H_2O , P, ...) can be considered comprising two amorphous phases: LD phase and HD phase . The coexistence of these amorphous phases with different fraction will lead to many different amorphous (liquid) states of the same composition [1, 6]. So far, polyamorphism and the liquid-liquid transformation in liquid GeO_2 is still in

debate. Besides, the experimental evidence for polyamorphism is based on macroscopic observables, but in general, a detailed description of the structural differences between polyamorphic states remains elusive. In this paper, we use molecular dynamics and visualization of molecular dynamics data to investigate the polyamorphism and polymorphic transitions in liquid GeO₂ under compression. The structural characteristics of low and high density phases basing on two-state model are discussed to clarify the polyamorphism and the polyamorphic transition in liquid GeO₂.

II. COMPUTATIONAL PROCEDURE

Molecular dynamics simulations are carried out on GeO₂ models consisting of 1998 atoms. The Oeffner-Elliott potential and the periodic boundary conditions are used to construct the models. More detail about the Oeffner-Elliott potential can be found in [9]. To integrate the equation of motion, Verlet algorithm is used with time step of 1.6 fs. The initial configuration is generated by placing all atoms randomly in a simulation box and heating it up to 5000 K to remove possible memory effects. After that the sample is cooled down to 4600, 4200, 3800, 3400 and finally to 3200 K. Next, a long relaxation has been done in ensemble NPT (constant temperature and pressure) to produce a model at 3200 K and upon ambient pressure. Hereafter, the obtained model is called M0. Next we produce 8 different models of liquid GeO₂ by compressing model M0 to different pressures. The structural data of considered models is determined by averaging over 1000 configurations during the last 10⁴ MD steps. To calculate the coordination number, we use the cut-off distance $R_{Ge-O} = 2.5 \text{ \AA}$. Here R_{Ge-O} are chosen as first minimum after the first peak of pair radial distribution function.

III. RESULTS AND DISCUSSION

From Fig. 1, It can be seen that the network structure of liquid GeO₂ is formed from basic structural units (coordination units) cGeO₄, GeO₅ and GeO₆. The GeO_x basic structural units is linked each to other through bridging oxygen atoms forming OGe_y linkages ($y = 2, 3$). At high pressure, it also exists the OGe₄ linkages in model but with a very small fraction (7% at highest pressure). As having been shown in our previous works, the distributions of bond length and bond angle in GeO_x and OGe_y are not dependent on pressure. It means that the topology structure of basic structural units is not dependent of pressure. The models with different densities are only different about fraction of GeO_x units and OGe_y linkages. It can be seen that as pressure increases, the fraction of GeO₄ units decreases while the total fraction of GeO_x (with $x > 4$) increases. Fig.1 also shows that as the total fraction of GeO₅ and GeO₆ increases then fraction of OGe₃ and OGe₄ also increases. This demonstrates that under compression, a transition from GeO₄ to GeO_x ($x > 4$) should be accompanied by a transition from OGe₂ to OGe₃. At low pressure, most of basic structural units

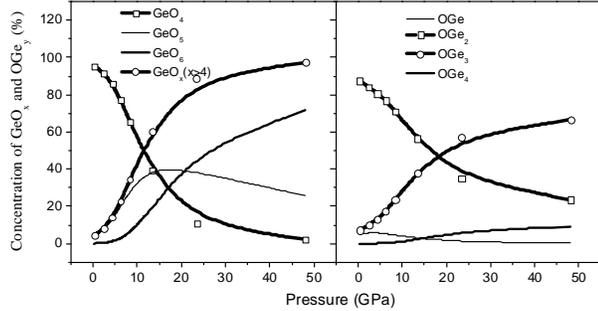


Fig. 1. The distribution of GeO_x units and OGe_y linkages in liquid GeO₂ at 3200 K and in the 0-50 GPa pressure range.

are GeO_4 and these GeO_4 units are linked each to other via OGe_2 linkages. As pressure increases, the increases of total fraction of GeO_5 and GeO_6 is always accompanied the increase of fraction of OGe_3 linkages. It means that the network structure of liquid GeO_2 at high pressure is formed from GeO_5 and GeO_6 that mainly is linked each other via OGe_3 linkages (see Fig. 2). From Fig. 1,

it can be seen that the structure of liquid GeO_2 comprises two states (two phases): LD and HD phases. The low density phase is formed from GeO_4 basic structural units that are linked to each other via OGe_2 linkages, see Figs. 2 (a) and (b). In other word, the LD phase is characteristic by GeO_4 units and OGe_2 linkages. The HD phase is formed from GeO_5 and GeO_6 basic structural units that are linked to each other mainly via OGe_3 linkages, see Figs. 2(c) and 2(d). Under compression, there is a gradual transition from LD phase to HD phase corresponding to the gradual structural transition from OGe_2 to OGe_3 linkages.

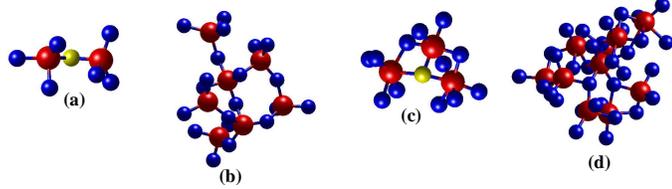


Fig. 2. The linkage between GeO_x units forming clusters with different structure and density: linkage between GeO_4 units (a); linkage between GeO_x units ($x = 5, 6$) (b); cluster of GeO_4 (c); cluster of GeO_x units (d). Large sphere is Ge, small sphere is O.

In the 0-50 GPa pressure range, the structure of liquid GeO_2 comprises both two phases: LD and HD. At a certain density, most of linkages between GeO_x units are OGe_2 and OGe_3 . The OGe_2 linkages relate to LD phase, the OGe_3 linkages relate to HD phase. So, the density of model at certain pressure can be determined through the fraction of OGe_x linkages as follows:

$$\rho = C_L \rho_L + C_H \rho_H \quad (1)$$

where C_L and C_H are the fraction of OGe_L (with $L \leq 2$) and OGe_H (with $H \geq 3$) linkages, respectively. ρ_L and ρ_H are the densities of low density and high densities with corresponding values are 3.61 and 6.55 g/cm^3 .

Fig. 3 shows the pressure dependence of density of liquid GeO_2 in the 0-50 GPa pressure range. It can be seen that the values of density calculated by equation (1) are in good agreement with simulation results. In the crystal state, the two predominant polymorphs of GeO_2 are hexagonal and tetragonal. Hexagonal GeO_2 has the same structure as β -quartz with density of 4.29 g/cm^3 (in this motif, Ge atoms having coordination number 4). Tetragonal GeO_2 has the rutile-like structure with density of 6.27 g/cm^3 (in this motif, Ge atoms have the coordination number 6). It can be seen that the value of ρ_L close to the density of hexagonal GeO_2 meanwhile, the value of ρ_H close to the density of tetragonal GeO_2 .

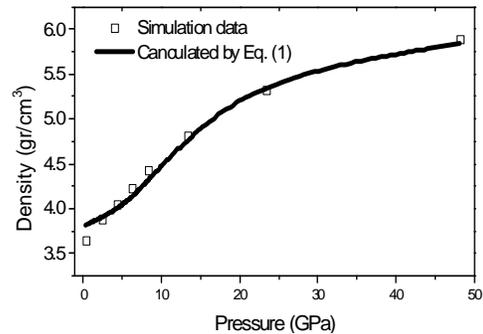


Fig. 3. The dependence of density of liquid GeO_2 on pressure.

To clarify the polyamorphism and the polyamorphic transformation in the liquid GeO₂, the network structure has been visualized at atomic level. Fig. 4 shows the distribution of OGe_y in model. It can be seen that the distribution of OGe₂ linkages in model is not uniform but it tends to cluster forming regions of LD. Conversely, the OGe₃ tends to cluster forming regions of HD. The size of LD and HD regions depends strongly on pressure. At low pressure (8 GPa), the structure of model is mainly formed from LD phases, characteristic by GeO₄ units and OGe₂ linkages that are highlighted by yellow color), Fig. 4(a). As the pressure increases, the size of LD regions decreases while the size of HD regions is increases. At high pressure (48 GPa), the structure of model is mainly formed from HD phases, characteristic by GeO₅, GeO₆ units and OSi₃ linkages that are highlighted by black color, see Fig. 4(b). At certain pressure, the structure of liquid silica comprises both two phases and its density can be determined via Eq. (1).

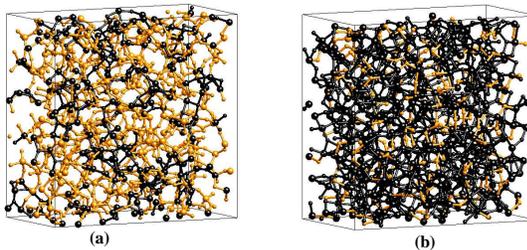


Fig. 4. The distribution of OGe₂ and OGe₃ linkages in liquid GeO₂: The OGe₂ linkage with yellow color; The OGe₃ linkage with black color. (a) the structure at 8 GPa; (b) the structure at 48 GPa.

IV. CONCLUSIONS

In summary, our present MD simulation reveals that the structure of network-forming liquid GeO₂ is formed from GeO_x unit and OGe_y linkages. The structure of liquid GeO₂ comprises two phases (two-state model): LD and HD. The structure of LD phase is formed from the GeO₄ basic structural units and OGe₂ linkages. Conversely, The structure of HD phase is formed from the GeO₅ and GeO₆ basic structural units, and OGe₃ linkages. The network structure of model is heterogeneous and tends separating in to low and high density regions. The size of low and high density regions depend strongly on pressure. The density of model at certain pressure can be determined via fraction of OGe_y linkages in model (see Eq. (1)).

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