POLYAMORPHISM AND TWO STATE MODEL IN LIQUID GEO\textsubscript{2} UNDER COMPRESSION: INSIGHT FROM VISUALIZATION OF MOLECULAR DYNAMICS DATA

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Abstract. The polyamorphism and two-state model based on the coordination number distribution in liquid GeO\textsubscript{2} at 3200 K and in a wide pressure range are investigated by molecular dynamics simulation. Results show that the structure of liquid GeO\textsubscript{2} mainly consists of GeO\textsubscript{x} coordination units (x = 4, 5, 6) and OGe\textsubscript{y} linkages (y = 2, 3). The distribution of OGe\textsubscript{y} linkages in network structure is not uniform but tends to form clusters of OGe\textsubscript{y}. The cluster of OGe\textsubscript{2} will form low-density phase region, conversely the cluster of OGe\textsubscript{3} will form high-density phase region. In other word, under compression, in the liquid GeO\textsubscript{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\textsubscript{2}, SiO\textsubscript{2}, TiO\textsubscript{2}, H\textsubscript{2}O, P, . . .). The polyamorphism and polyamorphic transitions were first recognized in the H\textsubscript{2}O 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\textsubscript{2}, SiO\textsubscript{2} and TiO\textsubscript{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\textsubscript{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\textsubscript{2} (SiO\textsubscript{2}, TiO\textsubscript{2}, H\textsubscript{2}O, 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\textsubscript{2} is still in

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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 polymorphic 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 10^4 MD steps. To calculate the coordination number, we use the cut-off distance R_{Ge-O} = 2.5 Å. 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, GeO₃ and GeO₆. The GeO₃ basic structural units is linked each to other through bridging oxygen atoms forming OGe₄ 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 GeO₃ and OGe₄ 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 GeO₄ units and OGe₄ linkages. It can be seen that as pressure increases, the fraction of GeO₄ units decreases while the total fraction of GeO₃ (with x > 4) increases. Fig.1 also shows that as the total fraction of GeO₃ and GeO₆ increases then fraction of OGe₃ and OGe₅ also increases. This demonstrates that under compression, a transition from GeO₄ to GeO₃ (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 GeO₃ units and OGe₄ 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$_3$ and GeO$_4$ 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$_3$ and GeO$_4$ 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$_2$ 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. 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:

$$\rho = C_L \rho_L + C_H \rho_H$$  \hspace{1cm} (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. $\rho_L$ and $\rho_H$ 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 $\rho_L$ close to the density of hexagonal GeO$_2$ meanwhile, the value of $\rho_H$ close to the density of tetragonal GeO$_2$.
To clarify the polyamorphism and the polyamorphic transformation in the liquid GeO$_2$, 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 OGe$_2$ linkages in model is not uniform but it tends to cluster forming regions of LD. Conversely, the OGe$_3$ 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 GeO$_4$ units and OGe$_2$ 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 GeO$_5$, GeO$_6$ units and OSi$_3$ 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).

IV. CONCLUSIONS

In summary, our present MD simulation reveals that the structure of network-forming liquid GeO$_2$ is formed from GeO$_4$ unit and OGe$_y$ linkages. The structure of liquid GeO$_2$ comprises two phases (two-state model): LD and HD. The structure of LD phase is formed from the GeO$_4$ basic structural units and OGe$_2$ linkages. Conversely, The structure of HD phase is formed from the GeO$_5$ and GeO$_6$ basic structural units, and OGe$_3$ 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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REFERENCES


![Fig. 4. The distribution of OGe$_2$ and OGe$_3$ linkages in liquid GeO$_2$: The OGe$_2$ linkage with yellow color; The OGe$_3$ linkage with black color. (a) the structure at 8 GPa; (b) the structure at 48 GPa.](attachment:fig4.png)