Ab initio Molecular-Dynamics Study of Atomic Diffusion in Liquid GeO$_2$ and SrGeO$_3$ under Pressure

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The dyanamic properties of liquids GeO$_2$ and SrGeO$_3$ are studied by *ab initio* molecular-dynamics simulations. We clarify the microscopic diffusion mechanisms in liquids GeO$_2$ and SrGeO$_3$. In both liquids, at ambient pressure, non-bridging oxygen double bonded to only one germanium plays a key role in the atomic diffusion mechanism. It is found that, in liquid SrGeO$_3$, which has non-bridging oxygen in the equilibrium state, atomic diffusion is possible without generating overcoordinated atoms at ambient pressure, in contrast to the fact that the overcoordinated atoms are always needed for the formation of non-bridging oxygens in liquid GeO$_2$. When pressure increases, only liquid GeO$_2$ has a diffusion maximum, because the atomic diffusion occurs with a concerted reaction under higher pressures, while the diffusion coefficients decrease monotonically with pressure in liquid SrGeO$_3$

§1. Introduction

Covalent liquids have been intensively studied because of geological interest, since they are closely related with igneous processes in the Earth. Especially, transport properties of covalent liquids under pressure are very interesting in the sense that an unexpected pressure dependence is observed. For a number of covalent liquids, such as SiO$_2$, GeO$_2$, silicates and germanates, have abnormal behavior of the viscosity, i.e., the viscosity significantly drops with pressure.[1),2)] This anomalous behavior of the viscosity is considered to be related to the atomic diffusion in the liquids under pressure. It is, therefore, of particular interest to investigate the pressure dependence of the microscopic diffusion mechanism in covalent liquids.

Recently, molecular dynamics (MD) studies of liquid GeO$_2$ under pressure have been reported.[3)] It was shown that the diffusivity of atoms increases with pressure, as in other covalent liquids, such as SiO$_2$[4)] and B$_2$O$_3$.[5)] It is, however, unclear how the rearrangement process of the covalent bonds is affected by compression. Because the calculated results obtained by empirical potentials depend on the choice of the potential form, theoretical investigations based on a first-principles theory would be needed to clarify the microscopic mechanism of atomic diffusion in liquid state.

In this paper, we report on a detailed investigation of atomic diffusion in liquids GeO$_2$ and SrGeO$_3$ by *ab initio* MD simulations with interatomic forces calculated quantum mechanically in the framework of the density-functional theory. The structure of crystalline GeO$_2$ and SrGeO$_3$ is well known. The high temperature phase of crystalline GeO$_2$ is α-quartz type structure which is based on corner-sharing GeO$_4$ tetrahedron.[6)] In the structure of crystalline SrGeO$_3$, Ge$_3$O$_9$ molecules form layers and Sr atoms exist between the layers.[7)] The coordination number of Ge to O atoms is four in both crystalline GeO$_2$ and SrGeO$_3$. In SrGeO$_3$ the molecule has two

oxygen sites, the bridging oxygen and non-bridging oxygens sites, which have two and one neighboring Ge atoms, respectively. The local structures of these materials remain the same even in the liquid state, i.e., there exist non-bridging oxygens, in liquid $SrGeO_3$ while there are few non-bridging oxygens in liquid GeO_2. For this reason, it is expected that the mechanisms of atomic diffusion in these liquids are different. The purpose of our study is to clarify the microscopic mechanism of atomic diffusion in liquids GeO_2 and $SrGeO_3$. We discuss how Ge-O bonds are exchanged accompanying the diffusion of atoms and how the diffusion mechanisms change with pressure.

§2. Method of calculation

Electronic states are calculated using the projector-augmented-wave method[8),9)] within the framework of the density-functional theory in which the generalized gradient approximation[10)] is used for the exchange-correlation energy. The plane-wave cutoff energies are 30 and 200 Ry for the electronic pseudo-wave functions and the pseudo-charge density, respectively. The energy functional is minimized using an iterative scheme.[11),12)] The Γ point is used for Brillouin zone sampling. As the valence electrons, we include the $4s$, $4p$ and $5s$ electrons of Sr, $4s$ and $4p$ electrons of Ge, and $2s$ and $2p$ electrons of O. Other electrons in the lower energy electronic states of each atom are treated with the frozen-core approximation. We use two systems of 120 ($24\,Sr + 24\,Ge + 72\,O$) atoms for $SrGeO_3$ and 144 ($48\,Ge + 96\,O$) atoms for GeO_2 in a cubic supercell under periodic boundary conditions. Using the Nosé-Hoover thermostat technique,[13),14)] the equations of motion are solved via an explicit reversible integrator[15)] with a time step of $\Delta t = 1.2$ fs. To obtain a liquid state, we begin by carrying out an *ab initio* MD simulation for about 5 ps at a temperature of 4000 K starting from the crystalline structure.[6),7)] The temperature is selected to be high enough to make the system reach a completely disordered state without the effects of the initial configuration. Then, we decrease the temperature of the system gradually to a target temperature of 2500 K. The number density is determined from the zero-pressure condition. The target temperature we have chosen is rather high in order to observe enough number of atomic-diffusion events to analyze the diffusion mechanism in a statistically meaningful way within a limited amount of simulation time. Note that the temperature dependence of physical quantities is not discussed in this paper, and conclusions derived are independent of the selected temperature. The simulation time 7.2 ps is long enough to achieve good statistics.

§3. Results and discussion

3.1. *Pair distribution function*

Figure 1 shows pressure dependence of the partial pair distribution functions $g_{\alpha\beta}(r)$ of liquids (a) $SrGeO_3$ and (b) GeO_2. The position of the sharp first peak of $g_{GeO}(r)$ is 1.76 Å for both liquids at ambient pressure. The positions shift to large r because the Ge-O bond becomes weak with increasing pressure accompanying the

increase in the average number of O atoms coordinated to Ge atoms. The oxygen coordination number around Ge atoms of liquids SrGeO₃ and GeO₂ approaches nearly 4.5 and 5.1, respectively, around 23 GPa.

The shape of $g_{GeGe}(r)$ of liquid SrGeO₃ is different from that of liquid GeO₂, while the shapes of $g_{OO}(r)$ are almost the same. This difference of $g_{GeGe}(r)$ reflects the fact that there are non-bridging oxygens (NBO) in liquid SrGeO₃, while almost no NBO in liquid GeO₂.
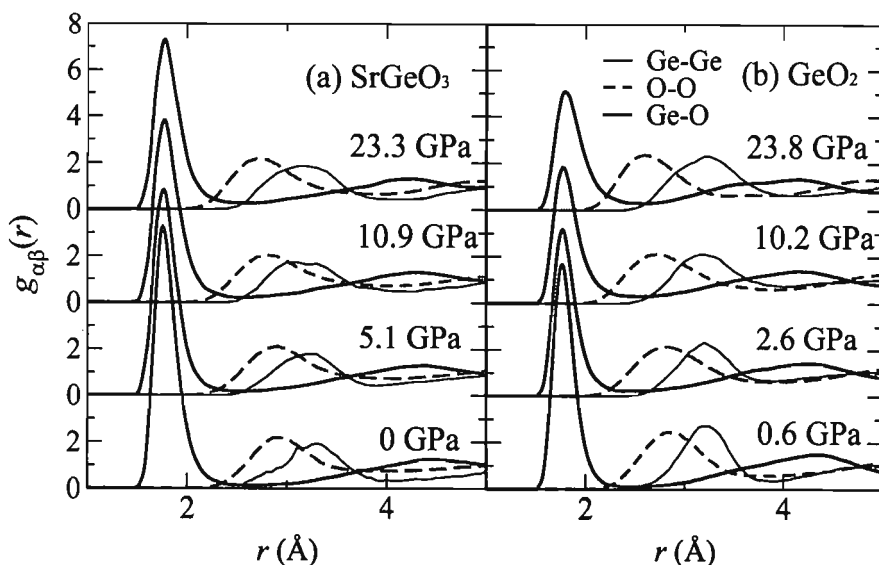

Fig. 1. Pair distribution function $g(r)$ of liquid SrGeO₃ and GeO₂.

3.2. *Diffusion mechanism under ambient pressure*

The local structure of crystal GeO₂ and SrGeO₃ remains even in liquid state. It is obvious that the covalent bond between Ge and O atoms are preserved in both liquids. It is, however, unclear how Ge-O bonds are exchanged with the diffusion of atoms in the liquid state while retaining the covalent bonds. To clarify the mechanism of atomic diffusion, we investigate the time evolution of bonding nature by utilizing the population analysis.[17],[18] The bond-overlap populations, which give a semiquantitive estimate of the strength of the covalent-like bonding between atoms, are calculated as a function of time.

In liquid GeO₂, Ge atoms are mainly coordinated to four O atoms and O atoms bridge two adjacent Ge atoms as in the crystalline phase, even though atoms diffuse in the liquid state. We find that a non-bridging O atom double bonded to a Ge atom is always involved with atomic diffusion accompanied by Ge-O bond switching as in liquid B₂O₃.[5] A typical example of the generation of non-bridging oxygen is shown in Fig. 2, where the time evolution of the bond overlap populations associated with the Ge and O atoms of interest is displayed with snapshots of atomic configuration. In the atomic configuration at 0.18 ps (the bottom panel of Fig. 2) all Ge and O atoms displayed are fourfold- and twofold-coordinated, respectively, to heteroatoms,
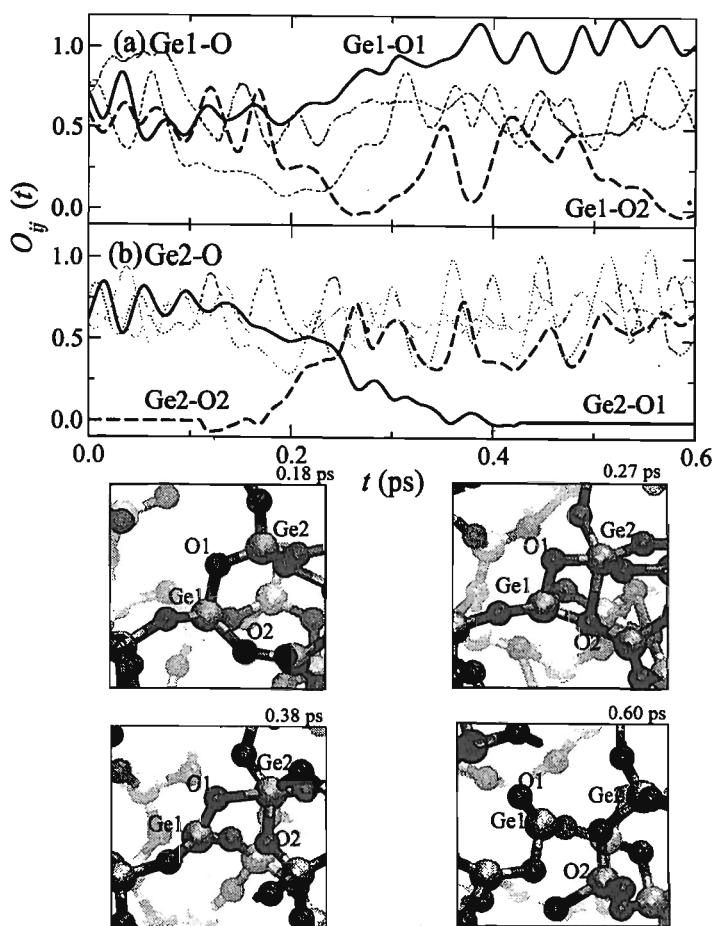
Fig. 2. (Top panel) The time evolution of bond-overlap populations $O_{ij}(t)$ in GEO$_2$ for (a) i = Ge1, $j \in$ O and (b) i = Ge2, $j \in$ O in the process of the formation of a non-bridging oxygen. The thick sold and thick dashed lines show $O_{ij}(t)$ associated with the Ge and O atoms of interest as denoted in the figures. The thin lines show $O_{ij}(t)$ between the Ge atoms of interest (labeled as 'Ge1' and 'Ge2') and their neighboring O atoms except O1 and O2. (Bottom panel) Atomic configurations at t = 0.18, 0.27, 0.38 and 0.60 ps. The large and small spheres indicate Ge and O atoms, respectively.

i.e., there is no bond defect. As shown in the top panel of Fig. 2, the bond-overlap population $O_{Ge2-O2}(t)$ begins to increase at about 0.2 ps, which means that a covalent bond is formed between Ge2 and O2. We can see this new Ge2-O2 bond in the snapshot at 0.27 ps. Due to the formation of the bond, both Ge2 and O2 are overcoordinated. Since the overcoordination is unstable, one of covalent bonds around O2 is broken (in the snapshot at 0.38 ps). Note that Ge1 is coordinated to only three oxygens, while Ge2 is still over-coordinated. Finally, the covalent bond between Ge2 and O1 is broken. While fourfold-coordination around Ge2 atom is recovered, O1 is coordinated only one Ge atom (Ge1) as displayed in the snapshot at 0.60 ps. In this way, the non-bridging oxygen is generated.

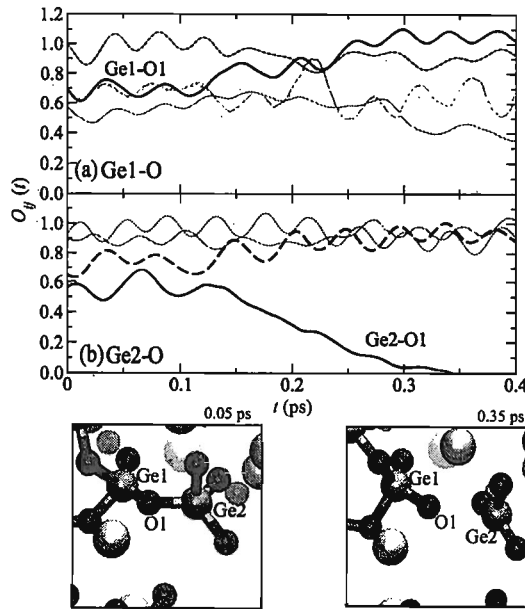In crystalline SrGeO$_3$, all Ge atoms bond to two bridging oxygens and two

Fig. 3.   (Top panel) Same as Fig. 2 but for SrGeO₃ (Bottom panel) Atomic configurations at $t = 0.05$ and 0.35 ps. The large, middle and small spheres indicate Sr, Ge and O atoms, respectively.
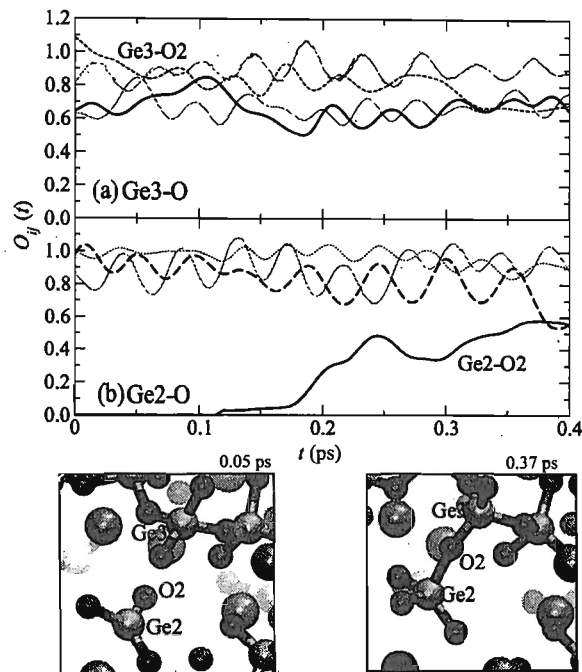

Fig. 4.   (Top panel) Same as Fig. 3 but for Ge3. (Bottom panel) Atomic configurations at $t = 0.05$ and 0.37 ps. The large, middle and small spheres indicate Sr, Ge and O atoms, respectively.

non-bridging oxygen. This form is also the most stable in the liquid state as in the crystalline states. When Ge-O bond is broken, the local structure is deformed, for example, a Ge atom might be bonding to three bridging oxyges and only one non-bridging oxygen. A typical example of the bond breaking is shown in Fig. 3. In the atomic configuration at 0.05 ps, Ge1 bonds to three bridging oxygens and only one non-bridging oxygen. Since this form is not stable, one of bridging oxygens around Ge1 tries to be non-bridging oxygen. As shown in the top panel in Fig. 3, $O_{Ge2-O1}(t)$ begins to decrease at about 0.15 ps. The covalent bond between Ge2 and O1 is broken, as $O_{Ge2-O1}(t)$ is almost zero for t > 0.35 ps. In the snapshot at 0.35 ps, Ge2 is threefold-coordinated to O atoms, and Ge1 has the most stable form, i.e., bonds to two bridging oxygens and two non-bridging oxygens.

The disappearance process of threefold-coordinated Ge atom (Ge2) is shown in Fig. 4. First, the threefold-coordinated Ge2 approaches non-bridging oxygen O2 to form a new covalent bond between them. We see that $O_{Ge2-O2}(t)$ gradually increases for t > 0.12 ps as shown in the top panel of Fig. 4, which means the formation of a covalent bond between Ge2 and O2 as displayed in the snapshot at 0.37 ps.

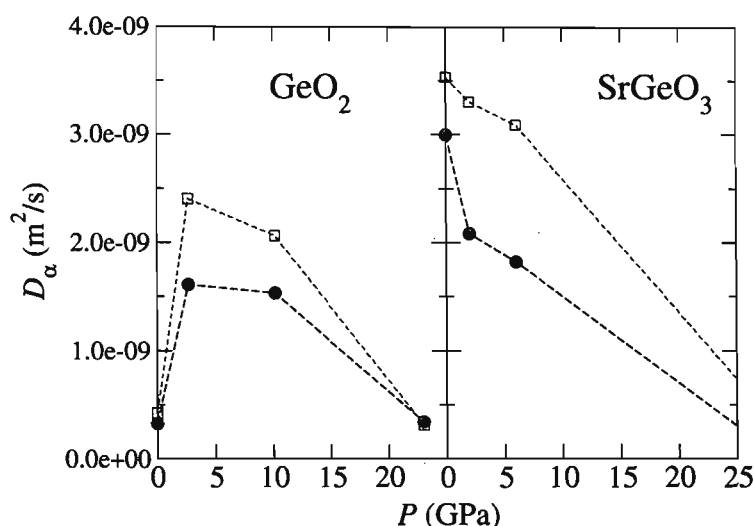### 3.3. *Diffusion mechanism under high pressure*

Fig. 5. Pressure dependence of the diffusion coefficients D_α for α = Ge (solid circles) and O (open squares) atoms.

Figure 5 shows the diffusion coefficients D_α for α = Ge and O atoms as a function of pressure. Clearly, only liquid GeO_2 has a diffusion maximum around 5 GPa, while D_α decreases monotonically in liquid $SrGeO_3$. In liquid GeO_2, the atomic diffusion with concerted reaction appears when pressure increases. Figure 6 shows this process at about 4 GPa. The concerted reactions with two over-coordinated Ge atoms can take place because Ge atoms are more easily coordinated to five O atoms under higher pressure. The important point is that non-bridging oxygen is not required in this mechanism while the formation of non-bridging oxygens is always involved in
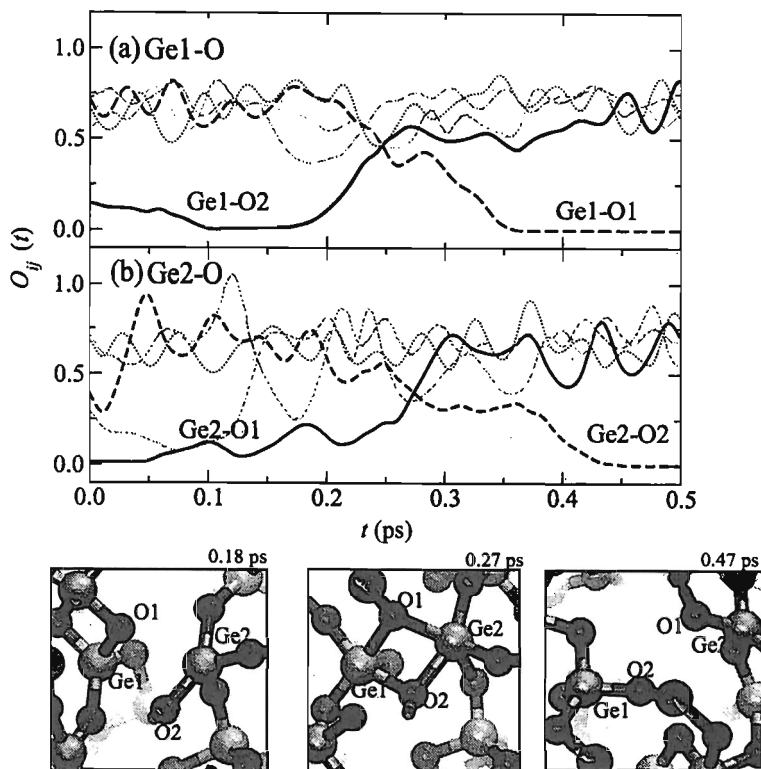
Fig. 6. (Top panel) Same as Fig. 2 but for at about 4GPa. (Bottom panel) Atomic configurations at $t = 0.18$, 0.27 and 0.47 ps. The large and small spheres show Ge and O atoms, respectively.

diffusion process at ambient pressure. Since liquid SrGeO$_3$ has non-bridging oxygens in normal condition, the formation of non-bridging oxygens is not needed for atomic diffusion at ambient pressure. This is why the diffusivities of liquid SrGeO$_3$ are much higher than those of liquid GeO$_2$ which does not have non-bridging oxygens at ambient conditions. The diffusion mechanism of liquid SrGeO$_3$ does not change so much even when the pressure increases. Therefore, the diffusivities of liquid SrGeO$_3$ decrease monotonically with increasing pressure.

§4. Summary

The microscopic mechanism of atomic diffusion in liquids GeO$_2$ and SrGeO$_3$ has been investigated by *ab initio* molecular-dynamics simulations. In liquid GeO$_2$, it has been found that the formation of non-bridging oxygen is always necessary for atomic diffusion at ambient pressure. When the pressure increases, the usual concerted reactions become possible. We have found that the atomic diffusion with concerted reaction gives the diffusion maximum under pressure. In liquid SrGeO$_3$, on the other hand, the atomic diffusion without generating non-bridging oxygens is possible at ambient pressure. Even when the pressure increases, the diffusion mechanism of liquid SrGeO$_3$ does not change. Therefore, liquid SrGeO$_3$ have no

diffusion maximum under pressure.

Acknowledgments

References

1) S. K. Sharma, D. Virgo and I. Kushiro, J. Non-Cryst. Solids **33** (1979), 235.
2) K. Funakoshi, A. Suzuki and H. Terasaki, J. Phys.: Condens. Matter **14** (2002), 11343.
3) D. Marrocchelli, M. Salanne and P. A. Madden, J. Phys.: Condens. Matter **22** (2010), 152102.
4) B. B. Karki, D. Bhattaria and L. Stixrude, Phys. Rev. B **78** (2007), 104205.
5) S. Ohmura and F. Shimojo, Phys. Rev. B **81** (2010), 014208.
6) G. Gordon, S. Smith and P. B. Isaacs, Acta. Cryst. **17** (1964), 842.
7) Y. Shimizu, Y. Syono and S. Akimoto, High Temp. High Press. **2** (1970), 113.
8) P. E. Blöchl, Phys. Rev. B **50** (1994), 17953.
9) G. Kresse and D. Joubert, Phys. Rev. B **59** (1999), 1758.
10) J. P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett. **77** (1996), 3865.
11) G. Kresse and J. Hafner, Phys. Rev. B **49** (1994), 14251.
12) F. Shimojo, R. K. Kalia, A. Nakano and P. Vashishta, Comp. Phys. Comm. **140** (2001), 303.
13) S. Nosé, Mol. Phys. **52** (1984), 255.
14) W. G. Hoover, Phys. Rev. A **31** (1985), 1695.
15) M. Tuckerman, B. J. Berne and G. J. Martyna, J. Chem. Phys. **97** (1992), 1990.
16) P. B. Macedo, W. Capps and T. A. Litovitz, J. Chem. Phys. **44** (1966), 3357.
17) R. S. Mulliken, J. Chem. Phys. **23** (1955), 1833; *ibid.* **23** (1955), 1841.
18) F. Shimojo, A. Nakano, R. K. Kalia and P. Vashishta, Phys. Rev. E **77** (2008), 066103.