Molecular-Dynamics Study of Structural and Electronic Properties of Liquid SrGeO₃ under Pressure

Takayuki Sugahara, Fuyuki Shimojo and Masaru Aniya
Department of Physics, Faculty of Science, Kumamoto University, Kumamoto 860-8555, Japan

Abstract. The pressure dependence of the structural and electronic properties of liquid SrGeO₃ is studied by means of ab initio molecular-dynamics simulation. It is found that both the Ge-O bond length and the coordination number for Ge-O increase with increasing pressure, and that the increasing rate changes at about 9 GPa. The population analysis clarifies that the distribution of the bond-overlap population for Ge-O has two peaks corresponding to the bridging and non-bridging oxygens even under pressure, which is considered as the bonding properties unique to this kind of liquid.

1. Introduction
Crystalline solids exhibit the phenomenon, known as the solid-solid phase transition, that shows a sudden structural change into another structure with a different density with changing temperature and pressure. On the other hand, it has been considered that such structural change doesn’t happen in liquid states, and that liquids change their structures continuously. It has, however, been observed that liquid phosphorus shows the first-order liquid-liquid phase transition under high temperature and high pressure [1]. A similar change is suggested for some liquids, such as Si, Ge, C, SiO₂ and GeO₂, which have a tetrahedrally coordinated structure. Since these materials are the principal components of the magma, they are of great geological interest.

The distance between Ge-O in liquid Li₂O-4GeO₂ has been observed to be increased from 1.82 Å to 1.91 Å suddenly in a narrow pressure range around 4 GPa by recent EXAFS experiments [2]. It was found that the oxygen coordination number for Ge changes drastically from 4 to 6 accompanied with the change of the Ge-O distance. A similar change has been observed for liquid B₂O₃-SrGeO₃ [3]. However, details of the structural and electronic properties of these liquids under high temperature and high pressure have not been clarified yet. In this paper, we report on the results of ab initio molecular-dynamics (MD) simulations for liquid SrGeO₃. We discuss the pressure induced structure change in relation to the bonding properties of the liquid.

2. Method of Calculation
The electronic structure calculations were performed using the projector-augmented-wave (PAW) method [4] based on density functional theory within the generalized gradient approximation [5]. The electronic pseudo-wave functions and the electron pseudo-density were expanded in plane waves with cutoff energies of 30 and 200 Ry, respectively. The energy
functional was minimized using an iterative scheme based on the preconditioned conjugate-gradient method. The cubic supercell contains 120 atoms (24Sr+24Ge+72O). For simulations of lower pressures (0-40 GPa) and higher pressures (60-100 GPa), the temperatures were set to 2500 and 4000 K, respectively, and the time step used was 1.2 fs. The quantities of interest were obtained by averaging over about 1.8 ps after an initial equilibration taking about 0.6 ps.

3. Results and Discussion

3.1. Energy-volume relation in crystalline states

The pressure-induced phase transitions in crystalline SrGeO$_3$ were observed by experiments [6] as follows: The pseudowollastonite (PS) structure is transformed into the walstromite (WA) structure at 1 GPa and into the perovskite (PE) structure at 5 GPa. In the PS and WA structures, there are layers consisting of Ge$_3$O$_9$ molecules and Sr atoms exist between layers. The coordination number of O to Ge is four in both structures. The molecule has two oxygen sites, the bridging oxygen (BO) and non-bridging oxygen (NBO) sites, which have two and one neighboring Ge atoms, respectively. In the PE structure, the coordination number of O to Ge is six.

Figure 1 shows the energy-volume curves of the three structures. To obtain the energy, we optimized the atomic structure as well as the shape of the supercell. The slopes of the common tangent lines show that the transition pressures are about 4 and 9 GPa from PS to WA and from WA to PE, respectively, which are in qualitative agreement with the experiment values.

3.2. Structure factors

In Fig. 2, we show the total structure factors $S(k)$ for liquid SrGeO$_3$, which are obtained from the partial structure factors calculated by our $ab$ initio MD simulations using the neutron scattering lengths. We are unaware of the experimental $S(k)$ for liquid SrGeO$_3$. When compared with the experimental $S(k)$ for glass MgSiO$_3$ reported recently [7], we see that the profile of the calculated $S(k)$ at lower pressures is reasonable. A remarkable feature exhibited in the $S(k)$ is
the small peak at about $k = 1$ Å$^{-1}$. It means that there exists the spatial correlation on an intermediate distance $\sim 6$ Å at each pressure. Also, it is seen that the height of the peak at about $k = 3$ Å$^{-1}$ grows to a clear peak with increasing pressure, which means that the liquid contracts nonuniformly.

3.3. Pair distribution functions
The partial pair distribution functions $g_{\alpha\beta}(r)$ for the liquid SrGeO$_3$ are shown in Fig. 3. In $g_{\text{GeO}}(r)$, there is a sharp first peak at about 1.8 Å followed by a low second peak at about 4.2 Å and deep and shallow minima at about 2.4 Å and 5.2 Å respectively. The sharp first peak reflects the strong covalent bonding between Ge-O. Figure 4 shows the pressure dependence of the first peak position $r_{\text{GeO}}$ of $g_{\text{GeO}}(r)$ and the oxygen coordination number $N_{\text{GeO}}$. $N_{\text{GeO}}$ was estimated by the integration of $4\pi r^2 g_{\text{GeO}}(r)$ up to a cutoff distance $R_{\text{GeO}}$. We used two $R_{\text{GeO}}$, the first-peak and first-minimum positions of $4\pi r^2 g_{\text{GeO}}(r)$, which correspond to circles and squares, respectively, in Fig. 4. $r_{\text{GeO}}$ increases slightly with increasing pressure. Note that we doubled the integration values for integration up to the first-peak position. It is found that the increasing rate of $N_{\text{GeO}}$ changes around 9 GPa.

In other correlations, most of peaks shift to shorter distances with increasing pressure (see Fig. 3). In particular, it is seen that the first peak in $g_{\text{SrSr}}(r)$ shifts greatly from 4.3 Å to 3.0 Å, when the pressure is increased from 0 to 40 GPa.

3.4. Bond-overlap populations
To investigate bonding properties between atoms, we used the population analysis by expanding the electronic wave functions in atomic-orbital basis sets [8]. Figure 5 shows the time-averaged distributions $P_{\alpha\beta}(\overline{O})$ of bond-overlap populations for the six pairs of $\alpha$-atomic and $\beta$-atomic types. It is found that there is an antibonding interaction between Ge-Ge atoms as $P_{\text{GeGe}}(\overline{O})$ has a peak at a negative value of $\overline{O} \approx -0.5$. A remarkable feature is that there exist two peaks at about $\overline{O} = 0.5$ and 1.0 in $P_{\text{GeO}}(\overline{O})$. There are two inequivalent oxygen sites, NBO and BO in the crystals (PS and WA). The existence of two peaks in $P_{\text{GeO}}(\overline{O})$ means that two oxygen sites remain in the liquid states. Figure 6 shows the pressure dependence of $P_{\text{GeO}}(\overline{O})$. The solid and
open circles correspond to O atoms which have one and two neighboring Ge atoms, respectively. It is found that, with increasing pressure, the two peaks become broad and the positions of the two peaks shift to larger \( \overline{O} \) values. At higher pressures, the profile of \( P_{\text{GeO}}(\overline{O}) \) deviates from the sum of the contributions of one- and two-fold Ge-coordinated O atoms, which indicates that there appear O atoms with higher coordinations to Ge atoms.

4. Conclusion
The pressure dependencies of the atomic structure and bonding properties in liquid SrGeO\(_3\) have been studied by means of \textit{ab initio} molecular dynamics simulations. The conclusions of our study are as follows: (1) Both the bond length and coordination number for Ge-O increase with increasing pressure. (2) The increasing rate of the Ge-O coordination number changes at about 9 GPa. (3) The distribution of the bond-overlap population for Ge-O has two peaks corresponding to BO and NBO even under pressure.

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