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ORIGINAL ARTICLE

Local Structures of Glassy Al under Various Pressures: A Molecular Dynamics Study

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Abstract

Al materials are used in the wide range of application, such as sporting goods, engine components, and aerospace parts. The rapid solidification of Al can save energy and production cost. It has been known that the properties of materials highly depend on their atomic structure. However, there is lack of structural investigation of the Al solidification under various pressures. In this research, we carried out molecular dynamics simulation to investigate the pressure effect on the formation of glassy Al from the rapid solidification process. The embedded-atom-method potential is used to describe the interatomic interaction between Al atoms. Our calculated melting point is in reasonable agreement with the experimental result, confirming the capability of the embedded-atom-method potential for use in the high-temperature simulations. From our molecular dynamics simulation of rapid solidification process, it is obvious that the high pressure shrinks the size of the supercell. We also find that the population of local structures, *i.e*. face-centered cubic, body-centered cubic, and icosahedral cluster, increase at higher pressure except for hexagonal close-packed cluster. The population of hexagonal close-packed local structure in the glassy Al decreases by the increasing of pressure.

Keywords: Al; rapid solidification; pressure; molecular dynamics simulation.

Introduction

In many cases, the fabrication of metals must undergo a solidification from the liquids state. Rapid solidification becomes very popular since it can reduce energy and production cost (Allia et al., 1981; Heeli et al., 1991; Tokarski, 2015). The understanding of the metal structure obtained by rapid solidification is mandatory prior to the production process. Molecular dynamics (MD) simulation allows us to explore the physical processes and the structure of a material on the atomic level.

Many MD simulations have been performed to investigate the solidification of Al (Lu and Szpunar, 1993; Liu et al., 2000; Sarkar et al., 2008; Kolotova et al., 2015; Kolotova et al., 2015; Li et al., 2015; Hou et al., 2016) due to its wide application such as sporting goods, engine components, and aerospace parts (Katgerman and Dom, 2004). Lu and Szpunar

(1993) have studied the structural characteristic of Al during rapid solidification. Later, different pressures have been applied by Sarkar et al. (2008) in their simulation. They have found that crystalline structure of Al is obtained at 2 GPa of pressure. Their report is, however, different from our result, and the reason will be explained in this paper. The MD studies of the structural dependence on the cooling rate have also been reported. The glass structures have been produced from the simulation in the high rate of temperature change within the range of 10^{10} K/s to 10^{13} K/s (Liu et al., 2000; Kolotova et al., 2015; Kolotova et al., 2015; Li et al., 2015). Recently, a large-scale molecular dynamics study has been carried out to obtain the crystal structure of Al at the quenching rate of 0.1 K/s (Hou et al, 2016).

So far we can only find the limited number of molecular dynamics study of the pressure effect on the Al solidification (Sarkar et al., 2008). The structural analysis used in the previous paper is limited to the radial distribution function (RDF). The RDF can only show the general structure of the system whereas the local structures are not known. This paper is aimed to delve the local structures in the glassy Al obtained from rapid solidification under various pressures.

Computational Methods

The embedded-atom-method (EAM) potential is employed in this simulation. The potential parameters for Al have been developed by Zope and Mishin (2003), and the data are available in the database of NIST Interatomic Potentials Repository (Becker et al., 2013). It is confirmed in our preliminary calculation that this potential has been able to reproduce the experimental lattice constant of Al crystal as around 4.05 Å (Witt, 1967). In the EAM potential, the total energy U is expressed by:

$$U = \frac{1}{2}\sum_{i,j(j\neq i)} V(r_{ij}) + \sum_{i} F(\rho_i), \tag{1}$$

where the first term is the sum of pair potential interaction $V(r_{ij})$ between atom *i* and *j*. The second term is the sum of embedding energy F of atom *i* into the atomic electron density ρ_i induced by all other atoms. The atomic electron density of atom *i* is obtained from the sum of electron densities of neighbouring atoms *j*,

$$\rho_i = \sum_{j\neq i} \rho_j(r_{ij}). \tag{2}$$

The MD simulation has been carried out using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) package (Plimpton, 1995). The NPT Nosé-Hoover scheme (Nose, 1984; Hoover, 1985) has been employed to control the pressure and the temperature of the system. The equations of motion are numerically solved using Verlet algorithm, with the timestep of 1 fs. The rate of temperature change during the heating and cooling process is 2.5×10^{11} K/s. The data are averaged from last 100000 MD steps at every 100 K of temperature step.

In the beginning of the simulation, the melting point of Al is obtained using two methods, *i.e*. single-phase and two-phase approach. The initial configuration for the single-phase approach is FCC crystalline structure of Al. Our supercell consists of 10×10×10 unit cells containing 4000 Al atoms as shown in Fig. 1(a). The periodic boundary conditions are applied in *x-, y-,* and *z*-directions. The system is incrementally heated from 300 K to 2000 K. At 2000 K, the system exists in the liquid structure as shown in Fig. 1(b). The temperature is decreased gradually until 300 K by the same rate as the heating process. In this approach, the melting point is evaluated using hysteresis method based on classical nucleation theory.

The thermodynamics melting point T_m is estimated using the following formula (Luo et al., 2004):

$$T_m = T_+ + T_- - \sqrt{T_+ T_-}\,, \tag{3}$$

where T_+ and T_- are superheating and supercooling temperatures, respectively.

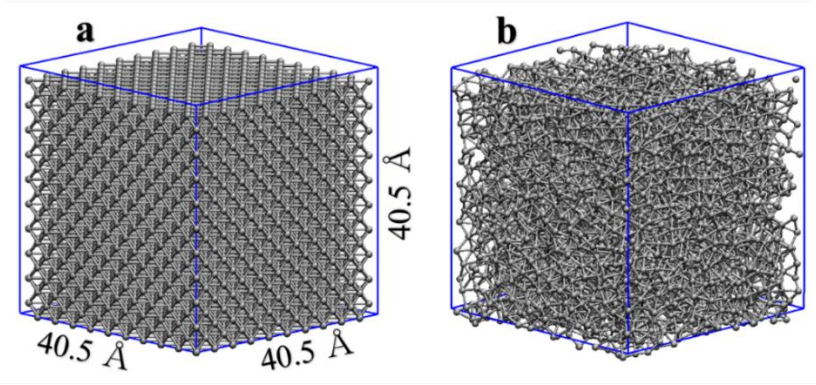

Figure 1. Atomic configuration of the MD simulation systems. The supercell contains 4000 Al atoms. (a) The initial atomic configuration; (b) the liquid structure of the system at temperature *T* = 2000 K.

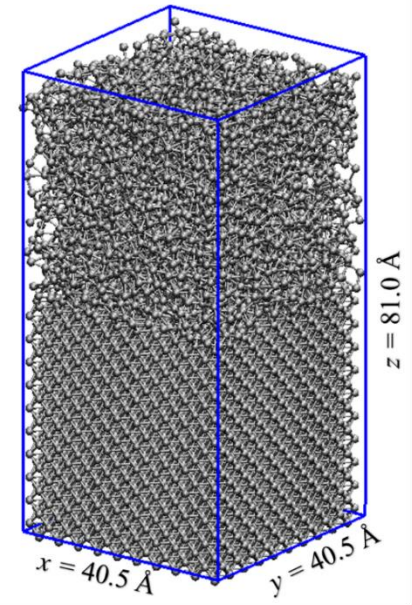

Figure 2. Atomic configuration of the initial configuration of two-phase system showing solid and liquid of Al in coexistence. The supercell contains 8000 atoms.

The initial configuration for the two-phase approach is generated by adding liquid structure on the top of the crystal structure of Al as shown in Fig. 2. Then the equilibration at 300 K for 300 ps is done in the system. This system contains 8000 Al atoms. The melting point is estimated at the temperature when the system has the tendency to change crystal part toward liquids.

The liquid configuration which shown in Fig. 1(b) is used as the initial structure for the simulation of Al solidification. The parallel calculations of Al solidification are performed at various pressures, *i.e*. 0, 2, 5, and 15 GPa. The local structures of the system are analyzed using, so called, a bond-angle method developed by Ackland and Jones (2006).

Results and Discussion

Melting Properties

The melting point of the Al metal at absolute pressure is investigated in our MD simulation. The result can confirm the performance of the EAM potential for use in the high-temperature simulations. In the single-phase approach, the volume of the supercell is plotted as the function of temperature during incremental heating and cooling as shown in Fig. 3. The sudden jump of volume upon melting observed at temperature T_+ = 1100 K. However, there is no clear sharp drop upon the cooling process. The highest value of volume difference is found when the temperature changes from 600 K to 500 K, which is estimated as T_-. The melting point obtained in the single-phase approach is around 858 K.

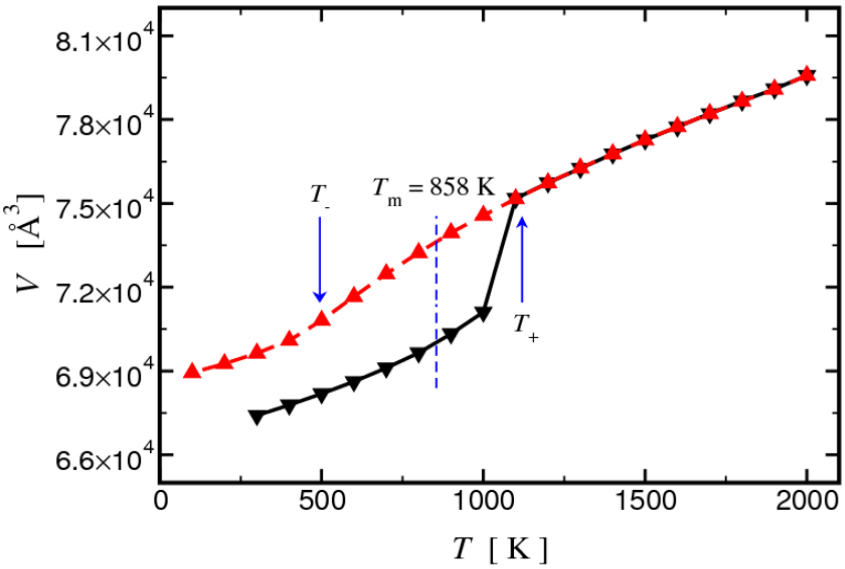

Figure 3. Volume of the supercell *V* at temperature *T* during the incremental heating and cooling. Black triangle down ▼ and red triangle up ▲ represent the heating and the cooling process, respectively.

We also calculate the degree of superheating θ_c^+ and undercooling θ_c^-, since the formation pathway has the direct correlation with microscopic structure of solids. The degree of superheating and undercooling is calculated using the equation: $\theta_c^+ = T_+/T_m - 1$, and $\theta_c^- = 1 - T_-/T_m$, respectively (Zhang et al., 2014). We obtain θ_c^+ and θ_c^- in our system as 0.28 and 0.42, respectively. Those values are in agreement with the previous report of Luo and Ahrens (2003) showing that θ_c^+ for crystalline solids should be between 0.1 – 0.3, and the maximum of θ_c^- is 0.67.

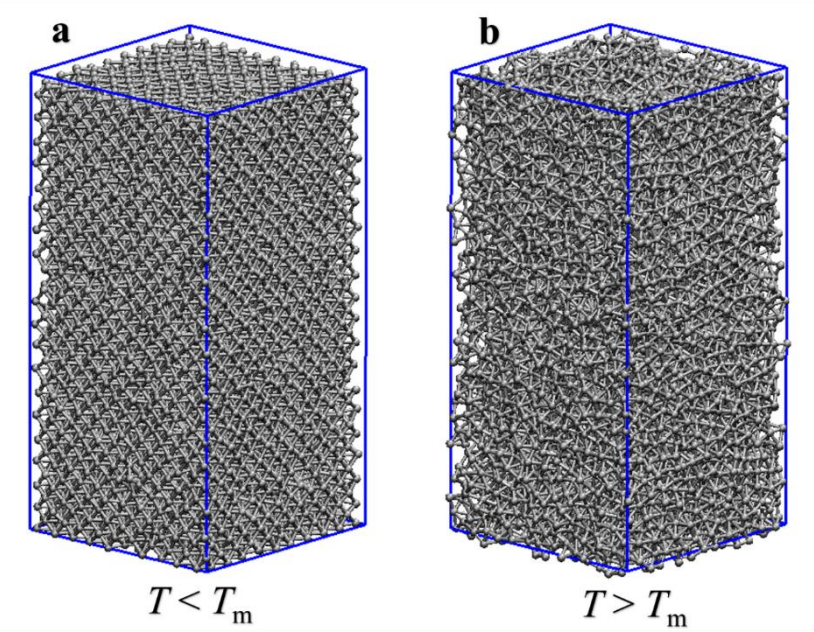

Figure 4. Snapshot of the final atomic configuration of two-phase simulation after 400 ps. (a) Transformation of Al atoms into crystal structure at $T < T_m$; (b) transformation of Al atoms into liquids structure at $T > T_m$.

A two-phase approach is considered more accurate than single-phase approach. It also has significant physical meaning (Zhang et al., 2014). It is shown clearly in Fig 4(a) that the system of solid-liquids coexistence transforms into crystal structure at $T < T_m$ and vice versa (Fig. 4(b)). From two-phase approach, we obtain the melting point of Al as 875 K. Our calculated melting points from one- and two-phase approach are in reasonable agreement with the experimental result (Errandonea, 2010) by the difference only around 8.04 % and 6.22 %, respectively.

Fig. 5 shows the mean square displacement (MSD) of Al atoms at some temperatures. The increasing of the MSD gradient shows the higher atomic diffusion in the system. It has been known that the atomic diffusion in the liquids system is much higher than that of in the solid system. At the temperature of 865 K, the atomic diffusion is quite low. Suddenly, the atoms diffuse largely at 875 K and even higher at 900 K. This indicates that there is a phase change from solid at 865 K to liquids at 875 K.

We also perform another structural investigation using radial distribution function (RDF) analysis. RDF $g(r)$ indicates the average density of neighboring atoms located at a radial distance *r* from a target atom, and is defined as follows:

$$g(r) = \frac{V}{N^2}\left\langle \frac{\sum_i n_i(r)}{4\pi r^2 \Delta r} \right\rangle, \tag{4}$$

where the bracket $\langle \cdots \rangle$ represents the time average, $n_i(r)$ is the number of neighboring atoms at the interval distance from *r* to $r + \Delta r$, *V* is volume, and *N* is the total number of the atom in the system.

It is shown in Fig. 6 that several distinct peaks are found at the temperature 800 K and 865 K, indicating the solid structure. At the temperature of 875 K and 900 K, the lower first peak and the disappearance of the peak (a) and peak (b) correspond to the low degree of

ordering in the liquids structure. These results also confirm that the phase change of Al from solid to liquids occurs at the temperature of 875 K.

From these results, it has been known that the EAM potential of Al by Zope and Mishin (2003) can describe reasonably well the properties of Al material at high temperature. Therefore, we are convinced to employ this potential in our simulation of Al solidification process.

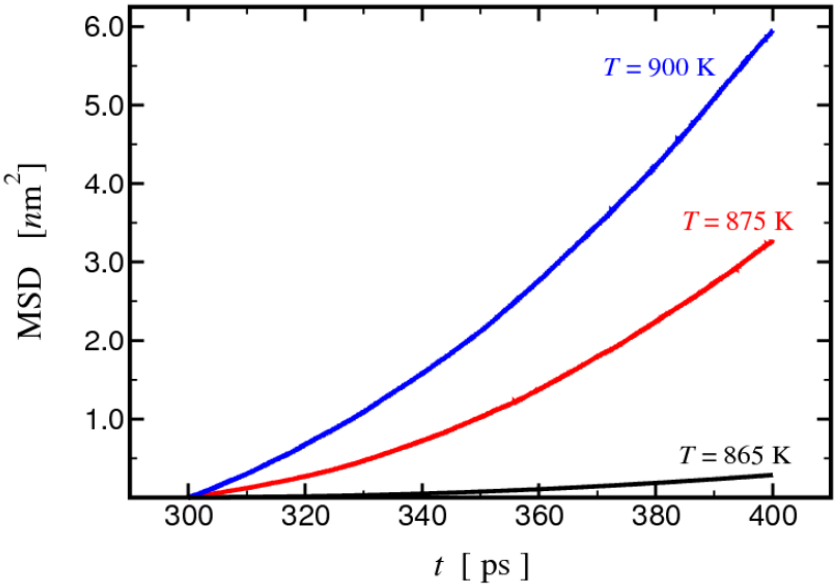

Figure 5. The mean square displacement of two-phase system at temperature T = 865 K, 875 K, and 900 K.

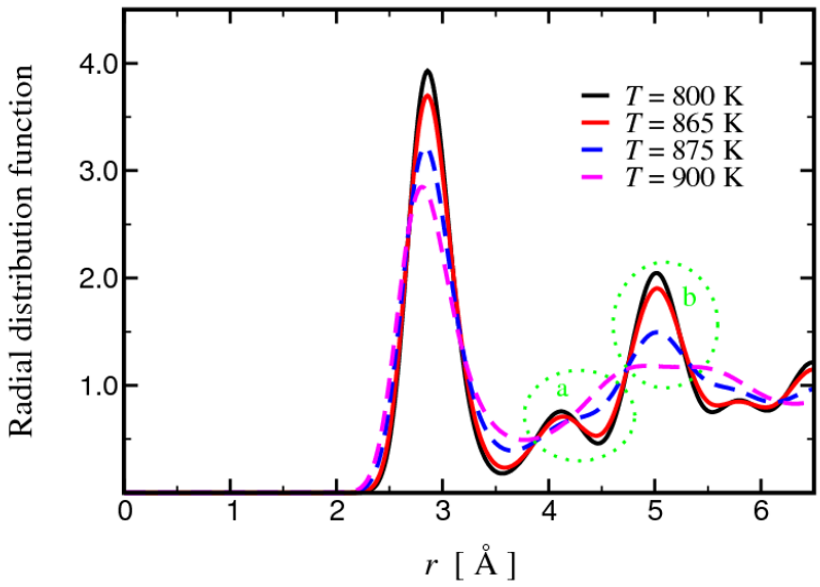

Figure 6. The radial distribution function of two-phase system: solid at temperature T = 800 K and 865 K, liquid at temperature T = 875 K and 900 K.

Effect of Pressure on The Glass Formation of Al

In this subsection, we discuss our result of the Al solidification process at various pressures. The perfect crystalline structure of Al is not found from our rapid solidification which is in agreement with other previous calculations of Cu (Liu et al., 2006) and Au (Zhang et al., 2004). However, as it has been mentioned before that Sarkar et al. (2008) have drawn the different conclusion from their calculation. The few number of Al atoms (500 atoms) used in their system may cause the crystallization occurs easily once the local structure formed at 2 GPa.

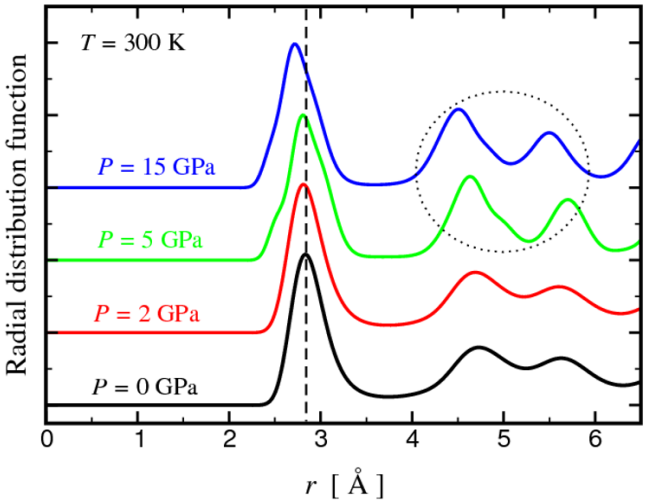

Figure 7. The radial distribution function of Al system at temperature T = 300 K after cooling process at various pressure P = 0 GPa, 2 GPa, 5 GPa, and 15 GPa.

Fig. 7 shows the RDF of the Al system at different pressures. At the pressure of 0 GPa and 2 GPa, the second peaks are split showing the characteristic of glass structure. At higher pressure (5 GPa and 15 GPa), it can be seen that the second peaks are sharper, and also the splits are more obvious indicating the increasing in order degree of glassy structure. We can also find in Fig. 7 that the first peaks show an inward shift at higher pressures corresponding to the smaller distance of the nearest-neighbour atoms. Some values of nearest-neighbour distance (R_0) and their degree of inward shift (ΔR_0) at various pressures are presented in Table 1. The values of R_0 decrease from 2.83 Å at 0 GPa to 2.72 Å at 15 GPa. The shift distances of the first peak of 2 GPa, 5 GPa, and 15 GPa from that of 0 GPa are 0.02 Å, 0.03 Å, and 0.11 Å, respectively. In general, these results indicate that the higher pressure applied during the solidification process increase the level of order degree of the glassy Al.

The effect of the pressure on the volume of the system is analyzed. Fig. 8 shows the change of the supercell volume of Al during cooling process under various pressures. It is obvious that the higher pressures shrink the volume of the system. During the cooling process, we find the points exhibiting nonlinear change (T_-) in volume at certain temperatures. We estimate the same value of T_- = 500 K at 0 GPa, 2 GPa, and 5 GPa. At 15 GPa, the value of T_- is approximately 700 GPa.

Further, the detailed structural information is obtained using bond-angle method [16] as shown in Fig. 9. It can be seen in Fig. 9 (a) that the tendency of the formation of FCC local structure increases as the temperature decreases. The highest percentage of this structure is obtained at the pressure of 5 GPa. The similar tendency is shown in BCC local structure. The pressure of 5 GPa and 15 GPa give the ratio of BCC local structure around 60 % of Al atoms in the system (Fig. 9(b)). The different tendency is found for the HCP local structure. Fig. 9 (c) shows that the percentage of HCP local structure increase until specific temperature, and

later decrease at the lower temperature. It is also clearly seen that this structure is not favoured for high pressure. From Fig. 9 (d), we can see that the higher number of the icosahedral local structure is obtained when the temperature decreases. More icosahedral local structures are found in the higher pressure system. By comparing the percentage of the local structures in Fig. 9, it is known that the BCC cluster are dominant at higher pressure. It is believed that BCC cluster easily transform into FCC local structure compared to the icosahedral and HCP due to their symmetrical similarity (Li et al., 2011).

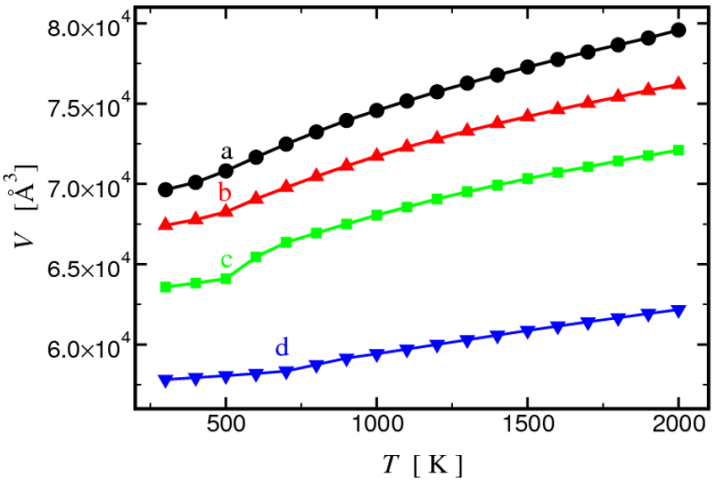

Figure 8. The change of volume of Al system during cooling process at various pressures *P* = 0 GPa, 2 GPa, 5 GPa, and 15 GPa represented by a, b, c, and d, respectively.

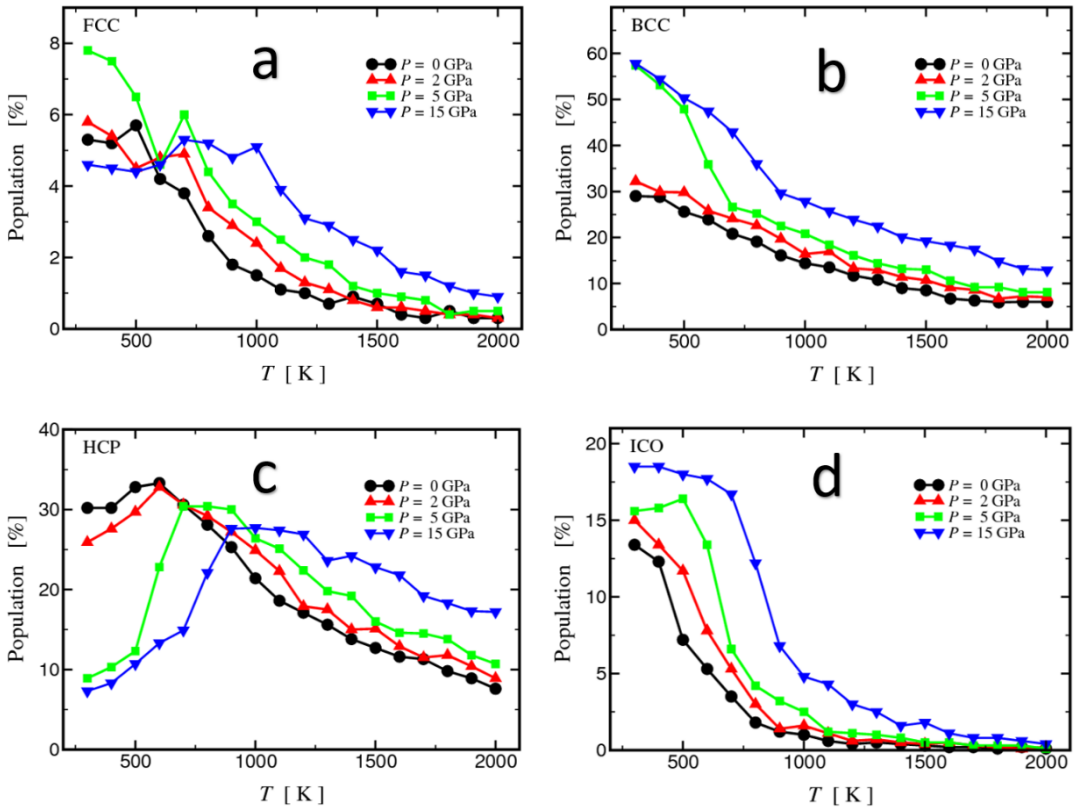

Figure 9. The population of local structure of Al system during cooling process at various pressure *P* = 0 GPa, 2 GPa, 5 GPa, and 15 GPa.

Table 1. The values of nearest neighbor distance (R_0) under 0 GPa, 2 GPa, 5 GPa, and 15 GPa. The value of peak shift ΔR_0 is obtained from the relation $\Delta R_0 = \left|R_{0(\text{higher } P)} - R_{0(\text{lower } P)}\right|$.

***P* (GPa)**	**R_0 (Å)**	**ΔR_0 (Å)**
0	2.83	-
2	2.81	0.02
5	2.80	0.01
15	2.72	0.08

Conclusion

The effect of pressure on the formation of glassy Al has been studied using molecular dynamics simulation. First, we have confirmed the capability of EAM potential for use in the high-temperature simulation shown by the reasonable agreement of calculated melting point of Al with the experimental result. Further, it has been clarified from our simulation that the high pressure increases the order degree of glassy Al and shrink the volume of the system. The percentage of the local structures, *i.e*. FCC, BCC, and icosahedral cluster, increase at higher pressure and lower temperature, except HCP structure. The population of HCP local structure in the glassy Al decreases by the increasing of pressure.

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