Bergman-type Medium-Range Order in Rapid Quenched $\text{Ag}_{0.74}\text{Ge}_{0.26}$ Eutectic Alloy studied by *ab initio* Molecular Dynamics Simulation

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The structure of liquid and rapid quenched amorphous $\text{Ag}_{0.74}\text{Ge}_{0.26}$ alloy at the eutectic composition was studied by *ab initio* molecular dynamics (MD) simulations. The local structural properties from the liquid at 1123 K to amorphous solid at 300 K were systematically investigated. The pair-correlation function at 1123 K from the MD simulations agrees well with the experimental data. The local structures were also analyzed using Honeycutt-Andersen (HA) indices, Voronoi tessellation, and atomic cluster alignment (ACA) method. The HA indices analysis reveals that pentagonal bipyramid structure has high population which become more predominant upon solidification. Voronoi tessellation analysis indicates strong icosahedral short-range orders (SRO) in the liquid and amorphous samples generated by the MD simulations. Using the ACA, the development of icosahedral SRO upon cooling is further confirmed and a Bergman medium-range order is also observed. The analysis of structural properties and chemical short-range order suggests that Ag atoms trend to have a Bergman-like packing, while the dispersed Ge atoms prevent the alloy from forming a long-range order upon cooling. The Bergman medium-range order is also confirmed by the constrained Reversed Monte Carlo results.

Keywords: *Ab initio molecular dynamics, Local structure, Short-range order, Medium-range order*

1. Introduction

Bulk metallic glasses are new functional materials with outstanding mechanical properties and resistance to corrosion[1-3], which have attracted a lot of experimental and theoretical investigations. Over the last 60 years, various factors that affect the glass formation have been studied, leading to the development of many metallic glasses, among which the maximum thickness is obtained in $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$ with a size of over 100 mm[4]. Despite of extensive studies, the formation mechanism of metallic glasses is still not well understood. Phase transition from liquid to amorphous depends on many factors such as composition, cooling rate etc., and is hard to control without fundamental understanding the microscopic mechanism of the phase selection and phase transformation pathways. One of the widely discussed features in metallic glasses is the icosahedral (ICOS) short-range order, which has been found in many amorphous alloys and was regarded as a crucial signal in glass formation process[5]. Beyond short-range order, medium-range order was also proposed to be an important feature for amorphous phase, which makes the amorphous phase different from other disorder systems and quasicrystals. While the existence of medium-range order has been suggested for many ternary and binary amorphous alloys, the detailed atomic packing that gives rise to the medium-range order is still not well understood[6-10].

As the first metallic glass, binary amorphous AuSi was successfully formed more than 60 years ago[11]. Amorphous AuGe are also obtained afterwards[12]. The capability to form metallic glasses of AuSi and AuGe can be attributed to the deep eutectic point of the semiconductor-noble metal alloy system. In this regard, AgGe alloy also has a eutectic composition at 25.9% of Ge, with the melting point changes from 1235 K for pure Ag and 1211 K for pure Ge to 973 K[13]. Although experimental studies of liquid AgGe alloy near the melting point were done using X-ray or neutron diffraction[14-17], the structural and dynamic properties of this binary alloy have not been well studied. Although silver crystallizes into face-center cubic (FCC) structure and germanium crystallizes into diamond structure, the crystallographic characteristics of their eutectic are still under debate, so it is of interest to make a structural analysis of the Ag-Ge alloy in the molten and amorphous state. It has been reported that AgGe alloy quenched from the liquid or sprayed by plasma-jet at a cooling rate of about 10^7 K/s is in a metastable, single phase hexagonal close packing (HCP) structure[18, 19]. For a faster quenched process, the short-range order structure in AgGe liquid, especially in

supercooled liquid, would influence the formation of amorphous alloy. By using neutron diffraction and isotopic substitution method, it has been show that there is a strong tendency for Ag and Ge to form nearest bonds at the eutectic composition[15].

In this paper, structural order development in rapid quenched $\text{Ag}_{0.74}\text{Ge}_{0.26}$ alloy is studied by *ab initio* molecular dynamics simulations and constrained Reversed Monte Carlo (CRMC). The short-range order in the rapid quenched $\text{Ag}_{0.74}\text{Ge}_{0.26}$ alloy is analyzed using the atomic configuration obtained from *ab initio* molecular dynamics simulations. The results show that under rapid quenched conditions, $\text{Ag}_{0.74}\text{Ge}_{0.26}$ can form glassy structures with strong icosahedral short-range order and Bergman-type medium-range order.

2. Computational methods

The *ab initio* MD simulations are performed based on density function theory (DFT) using Vienna *Ab initio* Simulation Package (VASP)[20]. The Perdrew-Burke-Ernzerhof (PBE) form of generalized gradient approximation (GGA) is used for the exchange-correlation energy functional[21]. Projector Augmented-Wave (PAW) method[22] is employed to describe the interaction between electron and ion. A plane wave basis with an energy cutoff of 249.85eV is used to expand the wave function. 148 Ag atoms and 52 Ge atoms in a 200 atom cubic box with periodic conditions were randomly distributed initially and then heated to liquid state to remove the memory effects from the initial configuration. Only the Γ point was used to sample the supercell Brillouin zone. The simulations were carried out in a canonical ensemble with constant atom number of particles, volume and temperature (NVT), accompanied by the Nosé-Hoover thermostat to control the temperature[23]. The MD time step is set as 3 fs throughout the simulation. The system was heated to 1200 K, much higher than the experimental melting point (976 K), and relaxes for over 4000 MD steps to achieve an equilibrium liquid state. Then the system was cooled down to 1123 and 300 K under a uniform cooling rate of 0.1 K/step. The pressure at each temperature is controlled within 0.0 ± 0.5 kBar by adjusting the size of the box. The trajectories at 1123 and 300 K are collected over 4000 steps of MD simulation for the analysis discussed below.

The total pair-correlation functions (PCF), coordination numbers (CN), Honeycutt and Andersen (HA) indices, Voronoi tessellation and atomistic cluster alignment

(ACA) method, are performed to analyze the local structure in the liquid and amorphous states. In order to confirm the Bergman medium-range order in amorphous $\text{Ag}_{74}\text{Ge}_{26}$ alloy, the CRMC simulations[24] was used, the description and details of the CRMC technique can be found from our previous work[25]. For this study, random starting configurations of 25000 atoms at 300 K with the same composition of *ab initio* MD were used, confined to a cubic box with dimensions same as the atomic density at 300 K determined by the *ab initio* MD simulation. The minimum distances between the atoms in the CRMC simulation were set nominally at 2.00Å for all atomic pairs, consistent with the MD partial pair-correlation functions. The *ab initio* MD-derived partial pair-correlation functions provide realistic chemical interactions, at least to the first few shells.

3. Results and discussion

Pair correlation function (PCF) is one of the most commonly used descriptor to describe the structure of liquid and glass, which can compare with experimental results from X-ray diffraction (XRD) or neutron diffraction. The PCF, $g(r)$, gives the probability of finding a particle in the distance r from a center particle relative to the probability expected for a completely homogeneous distribution at the same density and is given in the following form for binary systems when the neutron scattering factors of different elements in the alloy are considered:

$$g(r) = \frac{x^2 b_i^2 g_{ii}(r) + 2x(1-x)b_i b_j g_{ij}(r) + (1-x)^2 b_j^2 g_{jj}(r)}{\langle b \rangle^2} \quad (1)$$

where $\langle b \rangle = x b_i + (1-x)b_j$ and x and $1-x$ are number concentrations for Ag and Ge atoms. The neutron scattering lengths are $b_{\text{Ag}}=5.922 \times 10^{-14}\text{m}$ and $b_{\text{Ge}}=8.185 \times 10^{-14}\text{m}$ [26]. The partial pair correlation functions $g_{ij}(r)$ are defined as

$$g_{ij}(r) = \rho_{ij}^{-2} \left\langle \sum_i \sum_{j \neq i} \delta(\vec{r}_i) \delta(\vec{r}_j - r) \right\rangle \quad (2)$$

where $\rho_{ij} = \rho_0 \sqrt{x(1-x)}$ is the corresponding partial number density, ρ_0 is the average number density of the system, i and j denote the elements of Ag or Ge in the alloy.

Fig. 1 shows the calculated total and partial PCF of $\text{Ag}_{0.74}\text{Ge}_{0.26}$ system at 1123 K, 976K and 300 K respectively. The calculated total PCF at 976K is in good agreement

with the experimental data with the same composition of 26% at Ge [14] from neutron diffraction measurement as one can see from Fig. 1(a), showing that the simulations are reliable for $\text{Ag}_{0.74}\text{Ge}_{0.26}$ system. As 976 K is around the melting point of alloy, 1123 and 300K were chosen to discuss the properties of liquid and amorphous states. The total and partial PCFs from CRMC at 300 K are also plotted in Fig.1. It is shown that the correspondence between the MD simulation total and partial PCFs and the CRMC ones, the CRMC total and partial PCFs agree well with those obtained from the MD simulation. The calculated total PCF becomes sharper as the temperature decreases. The first peak height increases substantially from 2.56 to 3.88 (increase by 51.6%), the second and third peaks also become sharper as the temperature cool down to 300 K. The most noticeable feature in the total $g(r)$ is the splitting of the second peak as the temperature is lowered to 300K. The splitting indicates the tendency of structure order extended beyond the first neighboring shell[27]. For partial PCFs, the same phenomenon is observed. $g_{\text{Ag-Ag}}(r)$ exhibits larger increase in the first peak height, increases 63.6% from 1123 to 300 K, larger than 51.6% in total PCF, which means Ag atoms trend to stay more closer to each other at the amorphous state. The behavior of $g_{\text{Ag-Ge}}(r)$ is close to that of total PCF, while the change in $g_{\text{Ge-Ge}}(r)$ is more similar to that in $g_{\text{Ag-Ag}}(r)$. The first peak height of $g_{\text{Ge-Ge}}(r)$ is much smaller than the other two partials. However, the second and third peak heights increase noticeably when the temperature is lowered, showing that there is significant ordering among Ge atoms in the second and third neighboring shells in the amorphous state. Both the second peaks in $g_{\text{Ag-Ag}}(r)$ and $g_{\text{Ge-Ge}}(r)$ show a clearly splitting, which suggests that Ag-centered and Ge-centered clusters tend to form a medium range orders in the amorphous state. Such medium range orders will be analyzed in more details using the atomic cluster alignment method discussed later in this section.

In order to quantify the short-range order, coordination number (CN) is calculated based on the PCF data. Cutoff radius is determined by the first valley of the PCF. CN increases in total, Ag-Ag, Ag-Ge, and Ge-Ag CNs from 1123 K to 300 K can be seen from the results shown in Table 1. However, the reduction of CN for Ge-Ge suggests effective repulsive interaction between Ge atoms upon cooling.

To obtain a more quantitative estimation for the chemical short-range order (CSRO), the Warren-Cowley parameter was used to measure the CSRO[28]. The Warren-Cowley parameter is defined as

$$a_{ij}=1-N_{ij}/c_jN_{\text{tot}} \quad (3)$$

where, N_{ij} is the CN of j type atoms around i type atoms, c_j the concentration of j type atoms, and N_{tot} the total CN. CSRO parameters of Ge-Ge are positive, and Ag-centered are negative, as shown in Table 2. As temperature drops from 1123 to 300 K, the parameters of $a_{\text{Ag-Ag}}$ and $a_{\text{Ag-Ge}}$ became less negative, while $a_{\text{Ge-Ge}}$ becomes more positive. Since the negative values of a_{ij} indicate affinity between atoms while positive value means repulsion, the CSRO becomes stronger the Warren-Cowley parameter has more negative value. The result of CSRO is consistent with the stronger Ag-Ag and Ag-Ge bonding when the temperature lowers as shown in the partial pair-correlation function discussed above. It is also noted that the value of a_{ij} for Ge-Ge pair increases as the temperature decreases, implying the repulsion between Ge becomes stronger.

PCF only presents the atom density distributions, more information about the local structural changes beyond the PCF and CN is obtained by analyzing the inherent structures and using the common-neighbor analysis proposed by Honeycutt and Andersen (HA)[29, 30]. In this technique pairs of atoms can be classified by the relationship among their neighbors with three indices of integer. This analysis identifies the number of atoms surrounding each nearest-neighbor bond and thus the number of edge sharing tetrahedra whose common edge is the nearest-neighbor bond. The HA method has been widely used to monitor liquid, glass, and crystalline structures, as it extends the structure analysis to more than four-body correlations and offers more detail information about local structure order. Three indices, ijk , are used to describe the local orders. The first index is 1 for the root pairs within a certain cutoff radius. The second index is the number of common neighbors of the root pair, and the third index represents the number of bonds among the common neighbors. An ideal icosahedron consists of the 155-type pairs, while a distorted icosahedron would also have 154-type and 143-type pairs. In crystals, FCC and HCP structures are composed of the 142-type pair, while the body centered cubic (BCC) consists of two pair types, 166 and 144. Table 3 lists the percentages of the top 8 most abundant HA indices in the $\text{Ag}_{0.74}\text{Ge}_{0.26}$ at the two temperatures. The top 2 indices at 1123 K are 143 and 155 pairs, belonging to the distorted ICOS and perfect ICOS structure, respectively. As the temperature decreasing to 300 K, the most favorite index is 155, which is much bigger than 154 or 143. Noticeable amount of 143 and 154 clusters transfer into 155 cluster, and the percentage sum of 155, 154 and 143 pairs increases from 51.6 to 59.6%. At the same time, the sum of 144 and 166 pairs increases from 14.3 to 23.5%, but not as large as the change in the ICOS case. Other kinds of structures, 142 pairs of FCC and HCP, reduce when system is

cooling down. The analysis result indicates that the competition mainly emerges between BCC, FCC, HCP and ICOS structures. The total ICOS structure is the domination local order in the system, even at the high temperature liquid. Further analysis from the type of the root pair shows that Ag-Ag bonded pair keeps occupancy around 58% in 155, larger than the case in 144, 143 with the ratio around 54%. In comparison, Ge-Ge root bonded pair in 155 is less than 7%, and Ag-Ge root bonded pair is close to 38%. It can be concluded that Ag-Ag correlation plays an important role in the formation of ICOS structure.

In order to gain more comprehensive picture about the local topological order in the liquid and amorphous, Voronoi tessellation analysis is employed[31]. The Voronoi polyhedral are described by a set of index $\langle n_3, n_4, n_5, \dots, n_i \rangle$, where n_i is the number of i -edged polygon. The standard Voronoi indices of BCC, FCC, and ICOS are $\langle 0, 6, 0, 8, 0 \rangle$, $\langle 0, 12, 0, 0, 0 \rangle$ and $\langle 0, 0, 12, 0, 0 \rangle$, respectively. Table 4 shows the 15 most popular Voronoi indices of in $\text{Ag}_{0.74}\text{Ge}_{0.26}$. The top 3 Voronoi polyhedral (VP) at 1123 K and 300 K are $\langle 0, 3, 6, 4, 0 \rangle$, $\langle 0, 2, 8, 4, 0 \rangle$ and $\langle 0, 3, 6, 5, 0 \rangle$. As the temperature is lowered, the percentages of all the Voronoi indices in table 4 increase, especially the ICOS polyhedral. At 300 K, the icosahedral and icosahedral-like polyhedral with indices $\langle 0, 0, 12, 0, 0 \rangle$, $\langle 0, 1, 10, 2, 0 \rangle$, $\langle 0, 1, 10, 3, 0 \rangle$ and $\langle 0, 2, 8, 2, 0 \rangle$ grow rapidly. The sum of ICOS VP increased from 3.75% at 1123 K to 12.48% at 300 K. Combining this result with that from the HA index analysis discussed above, it can be seen that ICOS become the dominate short-range order in the amorphous state at 300 K. We note although the standard index of FCC doesn't belong to the top 15 list, deformed FCC polyhedral, i.e., $\langle 0, 3, 6, 4, 0 \rangle$, $\langle 0, 3, 6, 5, 0 \rangle$ and $\langle 0, 2, 8, 4, 0 \rangle$ may also play an important competing role in quenched alloy since the population of these three indices are larger at all temperatures.

Finally, the recently developed ACA was also performed to get a direct visualization of the local structure order in the liquid and glass[32]. Different from other methods used above, ACA offers a direct morphological comparison and quantitative measurement of local order. In the present alignment, 2000 clusters each with 16 atoms are randomly selected from the MD simulation trajectories at 1123 and 300 K, respectively. The clusters at the given temperature are translated and rotated to achieve an optimum alignment among the 2000 clusters using the simulated annealing algorithm. The detail description of the ACA method can be found in Ref [32]. As shown in Fig.2,

the spatially resolved distribution functions (SRDF) from this collective alignment scheme directly show the development of ICOS short-range order upon cooling. At 1123 K cluster alignment results show the defective ICOS structures. Competition among BCC, FCC, HCP and ICOS at 1123 K may lead to the defective morphology in the alignment. When the temperature decrease to 300 K, the ICOS order becomes more apparent, which is consistent with the results from HA and Voronoi index analyses.

In order to have a quantitative measurement and comparison of different orders in the system, we have also performed the one-on-one cluster-template alignment. BCC, FCC, HCP fragments and ICOS cluster have been used as templates. As table 5 clearly shows, ICOS becomes the most abundant structure after rapid quenching, consistent with our discussions above. The percentage of both Ag-centered and Ge-centered ICOS clusters rises from 0.87% at 1123K to 20.17% at 300 K, most of ICOS clusters are Ag-centered at 300 K.

Pair-correlation function at 300 K reveals the development of medium-range order upon cooling. In order to identify the type of medium-range order in the system, the cluster alignment was extended to clusters containing 61 atoms each to examine the medium-range order in the system. Fig.3 shows the evolution of aligned clusters from the liquid states (Fig.3(a):1123 K) to amorphous states (Fig.3(b):300 K), showing a trend of Bergman type medium-range order develops beyond the ICOS short-range order. According to the results of partial PCF, the position at the left-shoulder in the second peak of PCF at 300 K correspond to the second shells of Bergman clusters which are dodecahedral, and the position at the right-shoulder of the second peak can be ascribed to the third shells with defective icosahedrons. One feature can be seen from the iso-surfaces of SRDFs is that the second shells of Bergman clusters are defective and the third shells are even worse, probably due to the very rapid quench in the MD simulation. For further quantitatively characterize the medium-range order (MRO) in the liquid and glass, the one-on-one cluster-template alignment is also applied to measure the population of the Bergman clusters. Since the third shells of Bergman clusters are not complete, template with two shells, called Bergman-lite are used to accomplish the template alignment. The clusters similar to Bergman-lite template were collected and the SRDFs generated from these Bergman-lite clusters as shown in Fig.3 (c). The population of Bergman-lite clusters increases for both Ag- and Ge-centered clusters when the system's temperature is lowered. The population of Ag-centered Bergman-lite clusters increases from 0.01% at 1123K to 0.58% at 300K, and that of Ge-centered

Bergman-lite clusters also rises to 0.25% at the amorphous state from 0.005% at liquid state. The increases of the population of the Bergman-lite clusters is responsible for the splitting the second peak of $g(r)$ in this system upon cooling. Therefore, the splitting of the second peak of $g(r)$ in undercooled liquid would be a good indication of glass formation upon cooling. Using the CRMC 3-dimension configurations, 2000 clusters each with 30 atoms were randomly selected to do the alignment, the results were shown in Fig 3(d). Compared with Fig. 3(c), the cluster alignment results from CRMC are more perfect than those from *ab initio* MD. Both Ge-centered and Ag-centered have Bergment-type symmetry, the Ge-centered clusters is more perfect than Ag-centered ones. This is strong evidence that Bergment medium range order dominates in the amorphous state of $\text{Ag}_{74}\text{Ge}_{26}$. This result further confirms the agreement with different structural analyses given above from *ab initio* MD.

In order to gain more insights into the trend of atomic packing in the amorphous alloy, we have also examined the chemical ordering in the Bergman-lite clusters by counting the atom number N_i ($i=\text{Ag}$ or Ge) in the sphere of $r \sim r+dr$ from the center of the Bergman-lite clusters, and calculate the ratio $N_i/(N_{\text{Ag}}+N_{\text{Ge}})$ for each elements. Fig. 4 gives the percentage of Ag atoms as the function of radial distance from the center atom in Ag-centered and Ge-centered Bergman-lite clusters in comparison with the total $g(r)$ at 300 K, respectively. When the atoms distribute randomly, the percentage of Ag atoms should be a constant which equal to the eutectic composition 0.74 as indicated by the purple dashed horizontal line in Fig. 4. In the case of Ag-centered Bergman-lite clusters, the calculation result shows that Ag atom has very high concentration of more than 90% at the first shell (around $2.84\text{\AA}$), while the distributions of Ag atom in second (around $4.93\text{\AA}$) and third shells (around $5.57\text{\AA}$) are close to the random distribution results. These results suggest that the Bergman-lite clusters have an Ag-dominated ICOS cores. In the case of Ge-centered clusters, Ag atoms also prefer to locate in the first shell with a possibility more than 80%, a little lower than that in the Ag-centered cluster but higher than the randomly distributed one. So it can be concluded that most atoms in the first shell of ICOS clusters are Ag. We noted that Ag atom still has a high ratio around 80% in the second shell of Ge-centered Bergman-lite clusters, which is higher than the ratio of Ag in the Ag-centered Bergman-lite clusters.

As discussed above, chemical arrangement in AgGe glass is Ag-Ag-R-R (R represents Ag or Ge at random) or Ge-Ag-Ag-R, showing that Ag-Ag and Ag-Ge combinations are constructive to the formation of Bergman clusters, which is in agreement with the analysis of CSRO. Furthermore, metal-metal bonding is indispensable in quasicrystal with an ICOS phase[33], which also give an explanation to the wide spread of Ag-Ag bonding. It infers that there are some stability differences between Ag and Ge-centered ICOS motifs. *Ab initio* calculation was applied to examine energetics of ICOS clusters with different compositions. For Ag-centered clusters, a standard 13-atom icosahedral cluster with pure Ag was constructed and then the 12 neighbor atoms were replaced by Ge one-by-one to increase the Ge composition. Corresponding calculations was also done for Ge-centered clusters. After geometric optimization, the formation energies of 26 different clusters were calculated and shown in Fig. 5. As the composition of Ag increases, energy of the cluster decreases linearly in both Ag- and Ge-centered clusters. These result suggests that Ge atoms are not preferred in the ICOS clusters and ICOS clusters with all Ag atoms in its shell are energetically most stable. This result is consistent with the above analysis on CSRO and the radial distribution of Ag in Bergman clusters.

4. Conclusions

Ab initio molecular dynamic simulation and RMC simulation are employed to study the structures of rapidly quenched $\text{Ag}_{0.74}\text{Ge}_{0.26}$ eutectic alloy. The atomic trajectories of system from the MD simulations are analyzed. The pair-correlation functions show that the short-range and medium-range order is strengthened upon cooling. The splitting of second peak in total and partial $g(r)$ indicates that there exists some structure order extended beyond the second coordinate shell. HA and Voronoi indices as well as the clusters alignment indicate that the growth of ICOS structures are faster than BCC, FCC, HCP structures, and the ICOS structure prevails in a short-range scale. The ACA approach reveals the almost perfect ICOS structures and defective Bergman clusters at 300 K. The Bergman MRO is also confirmed by CRMC. Our simulation results suggest that the affinity between Ag and Ag or Ge atoms and the repulsion between Ge and Ge atoms are the predominant factors for the formation of ICOS SRO and MRO, which are the signals of metallic glass formation.

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Figure and Table Captions:

Fig. 1. Total and partial PFCs of $\text{Ag}_{0.74}\text{Ge}_{0.26}$ at 1123 , 976 and 300 K with the CRMC fit at 300 K and experimental total PFC at 976 K.

Fig.2. The total and partial collective alignment results of $\text{Ag}_{0.74}\text{Ge}_{0.26}$ at 1123 and 300 K from *ab initio* MD.

Fig.3. The collective alignment SRDFs expanded to 61 atoms in $\text{Ag}_{0.74}\text{Ge}_{0.26}$ at 1123 K (a), and 300 K (b), the SRDFs of Bergman-lite clusters at 300 K(c) and in the CRMC simulation at 300K (d). Different colors are used here to indicate different coordination shells: blue (first shell, icosahedron), dark orange(second shell, dodecahedraon), yellow (third shell, icosahedron).

Fig.4. Radial composition ratios of Ag in Bergman clusters in $\text{Ag}_{0.74}\text{Ge}_{0.26}$ at 300 K, the straight lines represent the first peak and the left and right-shoulder in the second peak position in total PCF.

Fig.5. The Energy of Ag- and Ge-centered ICOS clusters with different compositions.

Table 1 The calculated CN of $\text{Ag}_{0.74}\text{Ge}_{0.26}$ at 1123 and 300 K

Table 2 The calculated Warren-Cowley parameters of $\text{Ag}_{0.74}\text{Ge}_{0.26}$ at 1123 and 300 K

Table 3 The calculated population of HA index of $\text{Ag}_{0.74}\text{Ge}_{0.26}$

Table 4 The population of top 15 Voronoi indices in $\text{Ag}_{0.74}\text{Ge}_{0.26}$

Table 5. The percentage of different clusters in $\text{Ag}_{0.74}\text{Ge}_{0.26}$ at 1123 K and 300 K

Fig. 1. Total and partial PFCs of $\text{Ag}_{0.74}\text{Ge}_{0.26}$ at 1123 , 976 and 300 K with the CRMC fit at 300 K and experimental total PFC at 976 K.

Fig.2. The total and partial collective alignment results of $\text{Ag}_{0.74}\text{Ge}_{0.26}$ at 1123 and 300 K from *ab initio* MD.

Fig.3. The collective alignment SRDFs expanded to 61 atoms in $\text{Ag}_{0.74}\text{Ge}_{0.26}$ at 1123 K (a), and 300 K (b), the SRDFs of Bergman-lite clusters at 300 K(c) and in the CRMC simulation at 300K (d). Different colors are used here to indicate different coordination shells: blue (first shell, icosahedron), dark orange(second shell, dodecahedraon), yellow (third shell, icosahedron).

Fig.4. Radial composition ratios of Ag in Bergman clusters in $\text{Ag}_{0.74}\text{Ge}_{0.26}$ at 300 K, the straight lines represent the first peak and the left and right-shoulder in the second peak position in total PCF.

Fig.5. The Energy of Ag- and Ge-centered ICOS clusters with different compositions.

Table 1 The calculated CN of $\text{Ag}_{0.74}\text{Ge}_{0.26}$ at 1123 and 300 K

T/K	Total	Ag-Ag	Ag-Ge	Ge-Ag	Ge-Ge
1123	12.46	9.27	3.33	9.47	2.63
300	12.71	9.74	3.42	9.74	2.38

Table 2 The calculated Warren-Cowley parameters of $\text{Ag}_{0.74}\text{Ge}_{0.26}$ at 1123 and 300 K

T/K	Ag-Ag	Ag-Ge	Ge-Ge
1123	-0.00538	-0.0277	0.188
300	-0.03558	-0.0351	0.280

Table 3 The calculated population of HA index of $\text{Ag}_{0.74}\text{Ge}_{0.26}$

	155	154	143	144	166	142	132	131
1123 K	17.02	16.06	18.50	7.04	7.31	8.05	5.27	4.09
300 K	35.03	13.95	10.59	9.22	14.29	2.33	1.02	0.40

Table 4 The population of top 15 Voronoi indices in $\text{Ag}_{0.74}\text{Ge}_{0.26}$

T/K	1123			300		
Type	Total	Ag-centered	Ge-centered	Total	Ag-centered	Ge-centered
$\langle 0,3,6,4,0 \rangle$	3.05	2.18	0.87	6.67	4.98	1.69
$\langle 0,2,8,4,0 \rangle$	2.22	1.83	0.39	5.92	4.96	0.96
$\langle 0,3,6,5,0 \rangle$	2.16	1.75	0.41	4.92	3.76	1.16
$\langle 0,1,10,2,0 \rangle$	1.27	1.03	0.24	5.04	4.2	0.84
$\langle 0,2,8,5,0 \rangle$	1.00	0.89	0.11	3.33	2.99	0.34
$\langle 0,1,10,3,0 \rangle$	0.65	0.56	0.09	2.95	2.6	0.35
$\langle 0,3,6,6,0 \rangle$	1.14	1.02	0.12	2.94	2.7	0.24
$\langle 0,2,8,2,0 \rangle$	1.43	0.98	0.45	2.77	1.42	1.35
$\langle 0,4,4,6,0 \rangle$	1.56	1.21	0.35	2.56	2.11	0.45
$\langle 0,2,8,3,0 \rangle$	1.25	0.87	0.38	1.91	1.28	0.63
$\langle 0,1,10,4,0 \rangle$	0.43	0.38	0.05	1.85	1.78	0.07
$\langle 0,0,12,0,0 \rangle$	0.40	0.30	0.10	1.71	1.49	0.22
$\langle 0,4,5,4,1 \rangle$	1.25	0.96	0.29	0.97	0.69	0.28
$\langle 0,3,7,4,1 \rangle$	1.10	0.92	0.18	1.08	0.79	0.29
$\langle 0,3,6,3,0 \rangle$	1.02	0.58	0.44	0.92	0.47	0.45

Table 5. The percentage of different clusters in $\text{Ag}_{0.74}\text{Ge}_{0.26}$ at 1123 K and 300 K

Cluster type	BCC		FCC		HCP		ICOS	
Center atom	Ag	Ge	Ag	Ge	Ag	Ge	Ag	Ge
1123 K	0.0348	0.0001	0.3924	0.0430	0.2681	0.1088	0.5998	0.2738
300 K	0.7745	0.1601	5.4188	1.7832	9.1400	1.8082	12.4010	7.7668