

CALCUL AB INITIO ȘI STUDIUL MODURILOR VIBRAȚIONALE ALE CLUSTERILOR $As_xS_ySe_z$ ÎN STICLE CALCOGENIDICE

AB INITIO CALCULATION AND VIBRATIONAL STUDY ON CAGE-LIKE $As_xS_ySe_z$ CLUSTERS IN CHALCOGENIDE GLASSES

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Chalcogenide glasses have many potential applications as a result of their particular optical and electrical properties, which are considered to be strongly determined by the elementary network-forming structural units and their mutual interconnection. The aim of our work is the investigation and modeling of As-rich chalcogenide glasses with possible basic structure units. Ab initio quantum chemical calculation with DFT/B3LYP method is performed to investigate the cage-like $As_xS_ySe_z$ clusters. The calculated total energy reveals that the total energy at the stationary point with the $As_4S_nSe_{3-n}$ ($n=0,1,2,3$) and $As_4S_nSe_{4-n}$ ($n=0,1,2,3,4$) clusters decrease corresponding to the fall of S and Se content in the $As_4S_nSe_{3-n}$ and $As_4S_nSe_{4-n}$ clusters, respectively. The calculated fundamental frequencies were utilized to predict the assignment of unknown peaks in As-S-Se Raman spectra, which is considered to have good accordance between experimental and calculated data, it is concluded that the cage-like $As_xS_ySe_z$ clusters play an important role in the structure of As-S-Se amorphous system.

Keywords: ab initio, DFT, chalcogenide glass, vibration analysis

1. Introduction

It is well known that amorphous related to chalcogen elements such as S and Se have been investigated for a long time because of the practical application in optoelectronics as data processing devices, electronic switches, and optical memories [1-2]. In addition, chalcogenide materials have enormous potential in the IR optical device, holography, optical fiber and solar cells [3-4]. Among all chalcogenide glasses, As-S-Se system is considered to be an ideal candidate for tailoring important optical properties by modification of glass composition [5]. In order to understand their optical behavior, it is necessary for chemical and structural properties of As-S-Se glasses with different composition. In previous research, different measurement techniques have been adopted to investigate the structure of As-S-Se glassy system such as inelastic neutron scattering [6], X-ray absorption fine structure [7], infrared [8] and Raman spectra [9]. Generally speaking, for chalcogenide glasses, the short-range order (SRO) can be used to obtain the nearest neighbor atomic configuration such as the coordination numbers, bond lengths and bond angles [10]. However, for medium-range order (MRO) [11], there is no unique experimental technique that can be used single handedly. Moreover, Raman spectroscopy have been used to study bulk As-S and As-Se system as well as eva-

porated chalcogenide films of As_2S_3 and As_2Se_3 , which is considered to be a significant and useful tool specially for molecular features of structural elements in glassy system and the support of MRO hypotheses. On the other hand, ab initio methods [12-14] have been widely used in calculating the structural parameters and vibrational properties of amorphous system by combining calculated vibrational spectra for different clusters.

Among As-S-Se glasses with different composition of As/S and As/Se ratio, the structure of As-rich chalcogenide glass are more complicated. Contrary to S-rich or Se-rich glassy system, the network of which can be approached with a so-called "chain-crossing" model, Greater variety of structural units occurs in As-rich glasses similar to those found in crystalline counterparts [15-16]. This composition allow the formation of glass structure comprising of network-like clusters such as cage-like molecules of As_4Se_4 , As_4S_4 , As_4Se_3 and As_4S_3 compounds. Understanding details of the short and medium range structural order of As-rich glassy material is essential for advancing structure properties correlations. In addition, ab initio calculation studies of structure and vibrational properties are of paramount importance in understanding the very complex, broad experimental Raman spectra [17-19].

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In the present work, we have concentrated our attention on cage-like $As_xS_ySe_z$ clusters in amorphous system by ab initio method based on DFT/B3LYP method to obtain optimal geometries and vibrational frequencies. For amorphous materials reliable structural models agreeing with the experimental data are very important.

2. Theoretical and calculation details

The use of density functional theory (DFT) in the ab initio calculation of molecular properties to the prediction of vibrational spectra has recently increased [20,21]. In this paper, the density functional theory (DFT) as implemented in the Firefly (PC Gamess) software was utilized, which are nowadays considered to be very powerful tools in structure research. The computations consist of ab initio calculation on small cage-like structure such as

As_4S_4 , As_4S_3 , As_4Se_4 , As_4Se_3 , $As_4S_nSe_{4-n}$, $As_4S_mSe_{3-m}$, which clusters are present in the local structure of As-S-Se crystals. This method was selected for the calculation of the structural details and the vibrational properties with fully optimization based on DFT/B3LYP method with the 6-31G basis set. B3LYP means the Becke's three-parameter functional, which defines the corrected exchange functional proposed by Beck and the widely used gradient-corrected correlation functional of Lee, Yang, and Parr (BLYP)[22]. The accuracy and good performance of the computational method and basis sets in the cage-like clusters of As_4S_4 and As_4S_3 have been tested by comparing the calculated vibrational frequencies with experimental Raman spectra of glassy and polycrystalline As_2S_3 that are available in the literature [14]. Considering the similarity of chemical structure between S and Se, this computational method and basis sets can also be applied to the As_4Se_4 , As_4Se_3 cage-like clusters for As-Se

system and $As_4S_nSe_{4-n}$, $As_4S_mSe_{3-m}$ cage-like clusters for As-S-Se system.

3. Result and discussion

3.1. Pure cage-like clusters

Figure 1 shows the schematic illustration with a fully optimization of the structure of the cage-like clusters As_4S_3 , As_4S_4 , As_4Se_3 and As_4Se_4 . Based on group theory analysis [23], the cage-like structures of As_4S_4 and As_4Se_4 are D_{2d} symmetry of realgar-type molecule. In addition, there are two homonuclear As-As bonds and all As atoms are equivalent. On the other hand, the cage-like structure of As_4S_3 and As_4Se_3 is C_{3v} symmetry and there are three equivalent As atoms forming the basal triangle of the unit and an apex As atom which is bonded to three chalcogen atoms. In addition, the optimized structural parameters of cage-like clusters As_4S_3 , As_4S_4 , As_4Se_3 and As_4Se_4 with average bond distance and bond angle are showed in Table 1.

3.2. Mixed cage-like clusters

Figure 2 demonstrate the schematic illustration of the six mixed cage-like structure due to different ratio of S/Se in clusters. It can be seen that there are two clusters for the type of $As_4S_nSe_{3-n}$ and four clusters for the type of $As_4S_mSe_{4-m}$. Moreover, the cluster of $As_4S_2Se_2$ derive two types called adjacent- $As_4S_2Se_2$, which means the same atoms(S or Se) are adjacent to each other and opposite- $As_4S_2Se_2$, which means the same atoms(S or Se) are located at opposite side.

Energy optimization of the cage-like clusters is the process of finding an arrangement in space of a collection of atoms. Based on the model of chemical bonding, the inter-atomic force of each atom is close to zero and the position on

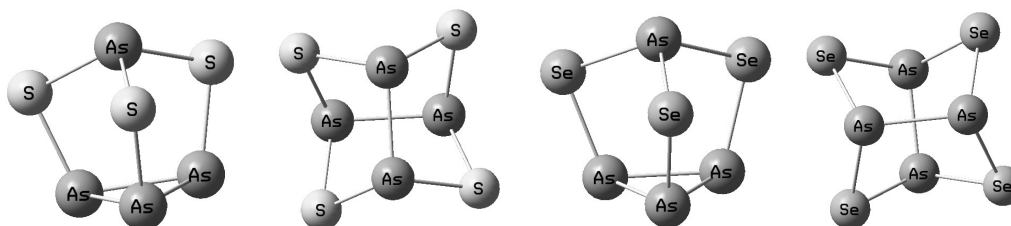


Fig.1 - Schematic illustration of the pure cage-like clusters with As_4S_3 , As_4S_4 , As_4Se_3 and As_4Se_4 .

Optimized structural parameters (averaged values) of the model calculated at the DFT/6-31G (d) level

Table 1

Cluster	Average bond distance			Average bond angle		
	As-As	As-S	As-Se	As-As-As	As-S-As	As-Se-As
As_4S_3	2.627	2.336	--	60°	106°	--
As_4S_4	3.688	2.362	--	---	102°	--
As_4Se_3	2.617	--	2.465	60°	--	103°
As_4Se_4	3.780	--	2.493	---	--	98°

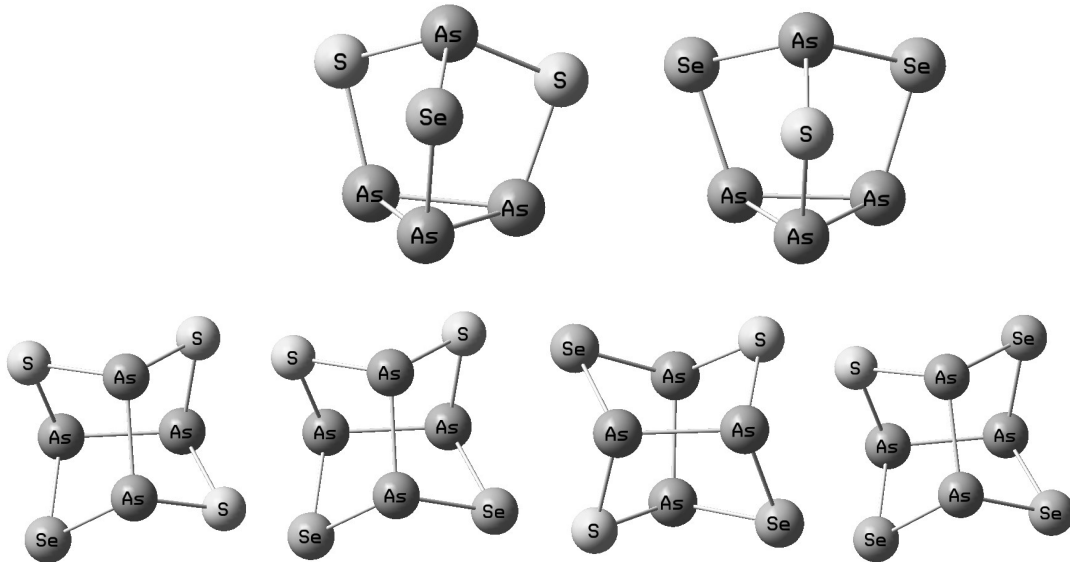


Fig.2 - Schematic illustration of the mixed cage-like clusters with As_4S_2Se , As_4SSe_2 , As_4S_3Se , adjacent- $As_4S_2Se_2$, opposite- $As_4S_2Se_2$ and As_4SSe_3 .

Table 2

Optimized structural parameters (averaged values) of the mixed cage-like clusters calculated at the DFT/6-31G (d) level

Cluster	Average bond distance			Average bond angle		
	As-As	As-S	As-Se	As-As-As	As-S-As	As-Se-As
As_4S_2Se	2.622	2.337	2.464	60°	107°	102°
As_4SSe_2	2.622	2.338	2.464	60°	108°	102°
As_4S_3Se	3.686	2.360	2.492	42°	103°	97°
ad- $As_4S_2Se_2$	3.698	2.363	2.492	43°	103°	98°
op- $As_4S_2Se_2$	3.711	2.362	2.493	43°	103°	98°
As_4SSe_3	3.766	2.362	2.493	42°	103°	99°

the potential energy surface is a stationary point. In addition, Figure 3 shows the variation of total energy of $As_4S_nSe_{3-n}$ clusters with optimization step number, which indicate the total energy at the stationary point with the $As_4S_nSe_{3-n}$ clusters decrease corresponding to the fall of S content in

the $As_4S_nSe_{3-n}$ clusters from As_4S_3 to As_4Se_3 . On the other hand, Figure 4 display the variation of total energy of $As_4S_nSe_{4-n}$ clusters with optimization step number. The tendency of total energy with $As_4S_nSe_{4-n}$ clusters is similar to that of $As_4S_nSe_{3-n}$ clusters.

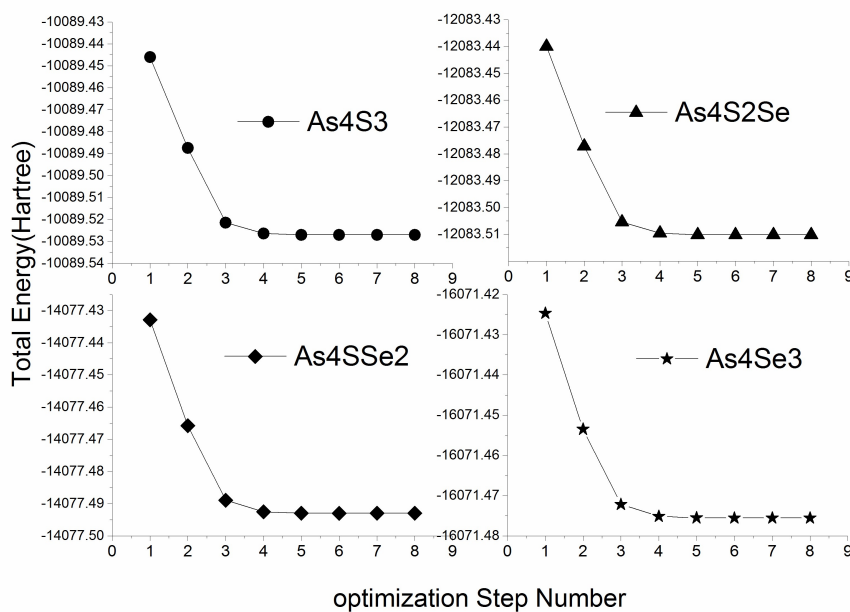


Fig.3 - The variation of total energy of $As_4S_nSe_{3-n}$ clusters with optimization Step Number.

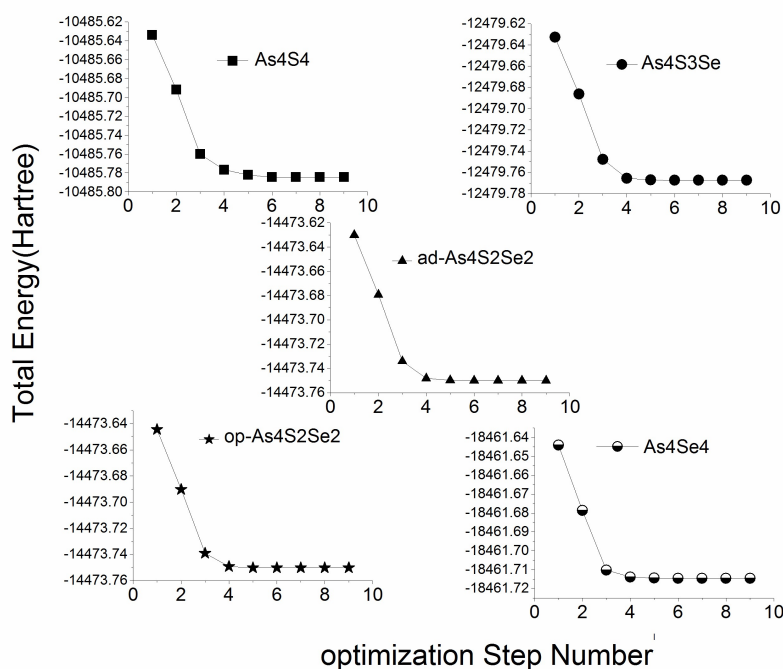


Fig.4 - The variation of total energy of $As_4S_nSe_{4-n}$ clusters with optimization Step Number.

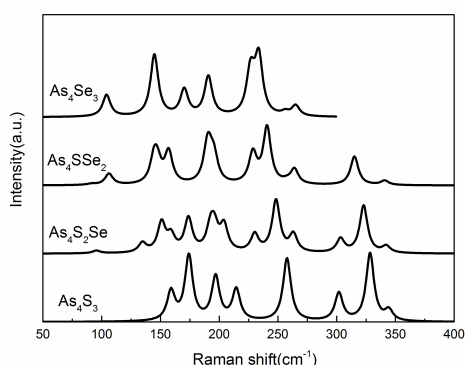


Fig.5 - The calculated Raman spectra of cage-like clusters such as As_4S_3 , As_4S_2Se , As_4SSe_2 and As_4Se_3 .

Figure 5 demonstrate the calculated Raman spectra of cage-like clusters such as As_4S_3 , As_4S_2Se , As_4SSe_2 and As_4Se_3 . As is shown above the cage-like structure of As_4S_3 and As_4Se_3 is C_{3v} symmetry. When S atom (Se atom) is replaced by Se atom (S atom), the vibrational modes of mixed clusters such as As_4S_2Se and As_4SSe_2 increase because of decrease of symmetry. According to the calculated Raman spectra of cage-like $As_4S_nSe_{3-n}$, All the vibrational modes with frequencies are in the range of $50cm^{-1} \sim 400cm^{-1}$. Based on the vibrational mode analysis, the frequencies of As_4S_3 cluster between $300 \sim 350cm^{-1}$ are attributed to stretching vibrational modes related to As-S bond. However, the frequency around $257cm^{-1}$ is assign to the symmetry stretching vibrational mode related to As-As bond. The rest of other vibrational modes can belong to the non-stretching vibrational modes.

However, on the other hand, for the cluster of As_4Se_3 , there is a weak vibration mode at $265cm^{-1}$, which is related to the As-As symmetry stretching vibrational mode. In addition, there is a strong vibrational mode at $256cm^{-1}$ and $233cm^{-1}$, which is attributed to the antisymmetry and symmetry stretching vibrational modes, respectively. The rest of other vibrational modes with frequency lower than $200cm^{-1}$ can belong to the non-stretching vibrational modes.

Moreover, the vibrational modes of As_4S_2Se and As_4SSe_2 are more complicated than those of As_4S_3 and As_4Se_3 . Similarly, for the cluster of As_4S_2Se , the frequencies between $300 \sim 350cm^{-1}$ are also attributed to the vibrational mode related to As-S bond. And the peak at $263cm^{-1}$ is assigned to As-As symmetry stretching vibrational mode. Meanwhile, the peaks at $248cm^{-1}$ and $230cm^{-1}$ are related to As-Se stretching vibrational modes.

Figure 6 shows the calculated Raman spectra of cage-like $As_4S_nSe_{4-n}$ clusters, which are similar to those of cage-like $As_4S_nSe_{3-n}$ clusters. For the cluster of As_4S_4 , the frequencies between $300cm^{-1} \sim 380cm^{-1}$ are also attributed to vibrational modes related to As-S bond. However, the peaks around $200cm^{-1}$ are assigned to breath-vibrational mode related to As atoms. On the other hand, for the cluster of As_4S_3Se the peaks around $250cm^{-1}$ are attributed to the stretching vibration mode related to As-Se bond. Similar to the cluster of As_4S_4 , the peaks of As_4Se_4 around $200cm^{-1}$ are also assigned to breath-vibrational mode related to As atoms. In addition, for the mixed clusters such as As_4S_3Se , $ad-As_4S_2Se_2$, $op-As_4S_2Se_2$, As_4SSe_3 , the frequencies around $300 \sim 350cm^{-1}$, $250cm^{-1}$ and

200cm^{-1} can also be attributed to As-S stretching vibrational mode, As-Se vibrational mode and breath-vibrational mode related to As atoms.

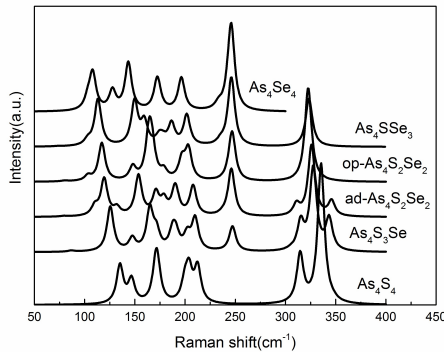


Fig.6 -The calculated Raman spectra of cage-like clusters such as As_4S_4 , As_4S_3Se , ad- $As_4S_2Se_2$, op - $As_4S_2Se_2$, As_4SSe_3 , and As_4Se_4 .

It is well known that the pyramidal AsS_3 and $AsSe_3$ are considered to be the basic units in As_2S_3 and As_2Se_3 glassy system, respectively. For the ternary system, there are four possible As_nS_{3-n} pyramids with $n=0, 1, 2, 3$ in As-S-Se system [24]. And all of these pyramids clusters have been widely discussed in the past [25, 26]. Compared with chalcogen atom-rich system, the Raman spectra of As-rich chalcogenide glasses is more complicated, there are still some unknown peaks related to the vibrational mode of cage-like clusters, which cannot be attributed to the pyramid clusters. Based on the calculation above, more structure information can be given to interpret the Raman spectra of As-rich chalcogenide glassy system.

For example, compared to the stoichiometry As_2S_3 and As_2Se_3 glassy system, there are more peaks occur in the stretching vibration area of As-rich system such as 256cm^{-1} , 238cm^{-1} , which cannot be seen in the Raman spectra of stoichiometry As_2Se_3 glassy system and also cannot be only explained by any vibrational modes related to pyramid clusters. According to the vibration mode calculation of cage-like clusters above, the peak of Raman spectra of As-rich chalcogenide glassy system around 256cm^{-1} is attributed to As-Se stretching vibrational mode in cage-like cluster of As_4Se_4 . In addition, the peak of 238cm^{-1} can be assigned to As-Se stretching vibrational mode of As_4Se_3 cluster.

4. Conclusion

In this paper, we studied the structure and vibrational properties of cage-like clusters in As-S-Se amorphous system by ab initio method. In addition, we built the basic cage-like structure model containing types of pure cages and mixed

cages and calculated all vibrational modes of cage-like clusters such as $As_4S_nSe_{3-n}$ ($n=0, 1, 2, 3$) and $As_4S_mSe_{4-m}$. In addition, those predictions are in accordance with the experimentally observed As-rich Raman spectra. Specifically, the unknown Raman peaks of As-rich As-Se glassy system at 258cm^{-1} and 238cm^{-1} can be attributed to As-Se stretching vibrational mode in cage-like cluster of As_4Se_4 and As_4Se_3 clusters, respectively.

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