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VIBRATIONAL DYNAMICS OF Si-S-Se GLASSY SYSTEM ON AB INITIO CALCULATION

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Ab initio calculations on the basic clusters approximation have been proven to be a useful method to investigate the structural and spectral properties of chalcogenide glasses. And the vibrational modes of clusters consisting of edge-sharing tetrahedral(ES)、corner-sharing tetrahedral(CS)、ethane-like structure(ETH) and isolated S_nSe_{4-n} tetrahedron (n=0,1,2,3,4) are calculated at Hartree-Fork/6-31G level. The calculated data with vibration modes of several clusters above indicate that the symmetrical stretching modes related to Si-S and Si-Se bond are accordance with the vibrational coupling theory. In addition, the vibrational modes of isolated SiS_4 and $SiSe_4$ tetrahedron cannot be attributed to the main peaks of SiS_2 and $SiSe_2$ glassy system, which is different from those of isolated GeS_4 and $GeSe_4$ tetrahedron in GeS_2 and $GeSe_2$ glassy system. It indicate the effective coupling of SiS_4 and $SiSe_4$ between neighboring tetrahedral is stronger than that of GeS_4 and $GeSe_4$ based on the central-force network model theory.

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1. Introduction

In the recent years chalcogenide glasses have received great attractive for modern optoelectronics and photonics because of their prominent optical properties such as excellent transparency in mid-IR region and high nonlinear refractive indices [1]. In addition, chalcogenide glass optical materials are applied to numerous devices, for example in IR optical fiber lasers、amplifiers and biomedical sensor devices[2]. Among a variety of chalcogenide glasses, tetrahedral sulphides and selenide are considered to be significant with optical amplifiers, inorganic photoresistors and electronic properties [3]. The structure of Si-S-Se glasses has been studied extensively using many measurement technologies to analyze chalcogenide glasses structure such as Transmission electron microscopy (TEM), X-ray diffraction analysis, EXAFS, neutron diffraction, and Raman scattering analysis, etc[4-6]. However, Raman experiments are well suited to probe local structures with structural vibrations [7]. For instance, Raman spectroscopy can interpret the presence of a stochastic random network structure of chalcogenide glasses that is formed by interconnection between SiS_4 tetrahedra or $SiSe_4$ tetrahedra.Considering the closely relation between internal structure of atomic arrangement and external macro performance of material, it is significant to investigate the detail structure information related to chalcogenide glasses for purpose of achieving the better understanding of special physical and chemical properties of chalcogenide glasses. It is well known that typical amorphous materials like chalcogenide glass can be characterized by short range order (SRO), which means the order is limited in the nearest neighbor distances [8]. On the other hand, the structural organization involving larger distances is commonly termed intermediate range order (IRO)[9].In addition, amorphous SiS_2($SiSe_2$) glasses can be considered as a prototype of class of network with

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edge-sharing tetrahedral(ES)、corner-sharing tetrahedral(CS) and other interconnection structure. In order to investigate the structure properties of Si-S-Se system, it is important to analyze the vibrational dynamics of basic units in glassy Si-S-Se system.

In this paper, the vibrational modes of basic units such as edge-sharing tetrahedral(ES)、two edge-sharing tetrahedral(2ES)、corner-sharing tetrahedral(CS)、ethane-like structure and isolated S_nSe_{4-n} tetrahedron （n=0,1,2,3,4）in glassy Si-S-Se system are calculated by ab initio method.

2. Theoretical and calculation details

Ab initio calculation on the basis of clusters approximation in glassy system has proven to be useful to investigate the structural and spectral properties of chalcogenide glasses [10]. Furthermore, in amorphous solids, the vibraitional excaitations cannot spread over a glass network because of the lack of long-range order. In addition,vibrational properties of glasses can be reasonably predicted by ab initio calculation in terms of appropriate cluster models. For example, in 1999, Koblar Jackson et al[11] built the corner-sharing (CS), edge-sharing (ES) and ethane-like (ETH) clusters models of Ge-S and Ge-Se in order to investigate the Raman-active modes of α-GeS_2 and α-$GeSe_2$.In the year of 2011, O.Kostadinova et al[12] use the Hartree-Fork (HF) molecular orbital theory to calculate the vibrational frequencies of two cage-like molecular units As_4Se_n(n=3,4) and of the chalcohalide structural models(pyramidal units) $AsI_m(SeH)_{3-m}$(m=0,1,2,3).

In this paper, we have carried out ab initio calculations on several basic clusters such as edge-sharing tetrahedral(ES)、two edge-sharing tetrahedral(2ES) 、corner-sharing tetrahedral(CS)、ethane-like structure and isolated S_nSe_{4-n} tetrahedron, which are calculated by Firefly(PC Gamess) software at the Hatree-Fork level with optimization based on HF/6-31G. Moreover, it is reported that the hydrogen atoms in the cluster are used as pseudoatoms to replace the chalcogenide glass by finite molecular model [13]. Due to the difference of large mass between H and the heavy atoms, it can prevent H-atom modes that do fall in this region are removed from the analysis of region for SiS_2 and $SiSe_2$.

3. Results

Table 1 shows the optimized geometries about bond distances and angles for isolated S_nSe_{4-n} tetrahedral clusters in Si-S-Se glassy system. Figure 1 display the schematic representation of isolated S_nSe_{4-n} tetrahedral clusters. In addition, Table 2 demonstrates the Raman vibrational frequencies of isolated SiS_nSe_{4-n} (n=0, 1, 2, 3, 4) tetrahedron. Based on the point group theory and ab initio calculation, there are four basic vibrational modes in SiS_4 and $SiSe_4$ tetrahedron with T_d point group. Among them, V_1 type mode is called symmetry stretching vibration and V_3 type mode is named antisymmetric stretching vibration.

Table 1.Optimized structural parameters (averaged values) of the SiS_nSe_{4-n} tetrahedron calculated at the HF/6-31G level

Average value	Bond distance(Å)		Bond angle（degree）		
	Si-S	Si-Se	S-Si-S	S-Si-Se	Se-Si-Se
SiS_4	2.223	--	114°	--	--
SiS_3Se	2.227	2.361	113°	114°	--
SiS_2Se_2	2.230	2.363	112°	102°	114°
$SiSSe_3$	2.232	2.368	--	113°	114°
$SiSe_4$	--	2.372	--	--	113°

Table 2 The Raman vibrational frequencies of isolated SiS_nSe_{4-n} (n=0, 1, 2, 3, 4) tetrahedron calculated at HF/6-31G

T_d	$\nu_1(A_1)$ ν_s (XY)	$\nu_2(E)$ δ_d(YXY)	$\nu_3(F_2)$ ν□□XY)	$\nu_4(F_2)$ δ_d (YXY)
SiS_4	339	106	500	174
$SiSe_4$	194	80	395	107

C_{3v}	$\nu_1(A_1)$ ν (XY$_3$)	$\nu_5(E)$ δ_s(XY$_3$)	$\nu_2(A_1)$ ν (XZ)	$\nu_4(E)$ ν(XY$_3$)	$\nu_3(A_1)$ δ (XY$_3$)	$\nu_6(E)$ ρ_r(XY$_3$)
SiS_3Se	452	148	295	497	118	96
$SiSSe_3$	227	120	482	400	88	75

C_{2v}	$\nu_1(A_1)$ ν (XY)	$\nu_4(A_1)$ δ (XZ$_2$)	$\nu_5(A_2)$ ρ_r(XY$_2$)	$\nu_2(A_1)$ ν (XZ)	$\nu_6(B_1)$ ν (XY)	$\nu_8(B_2)$ ν (XZ)	$\nu_3(A_1)$ δ (XY$_2$)	$\nu_7(B_1)$ ρ_m(XY$_2$)	$\nu_9(B_2)$ ρ_r(XY$_2$)
SiS_2Se_2	462	83	107	255	501	423	142	135	140

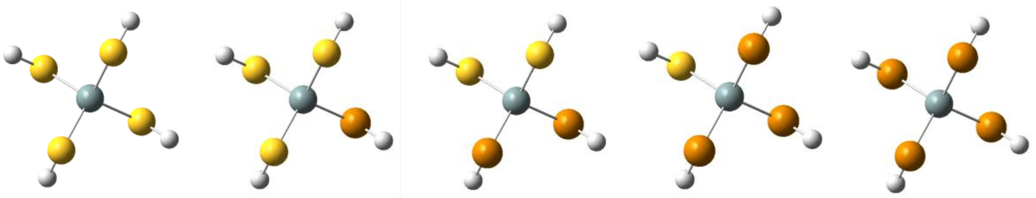
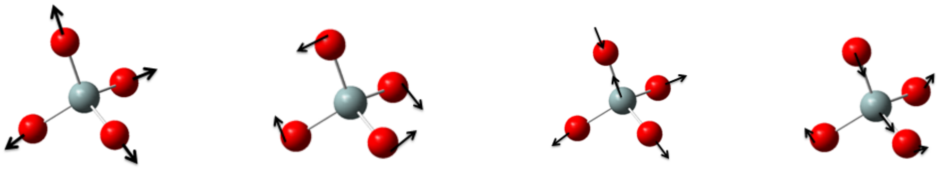


Fig.1. Schematic representation of the SiS_nSe_{4-n} tetrahedron with different ratio of S/Se



V_1 (A_1) *V_2 (E)* *V_3 (F_2)* *V_4 (F_2)*

Fig.2.Schematic illustration of four basic vibrationg modes in the isolated SiS_4 and $SiSe_4$ tetrahedron

The four basic vibrational modes in the isolated SiS_4 and $SiSe_4$ are shown in Figure 2.When one S(or Se) atom is replaced by Se(or S) atom, the basic vibration mode increase from four to six and the point group change from T_d to C_{3v} in SiS_3Se and $SiSSe_3$ tetrahedron. Moreover, two S (or Se) atoms are substituded by Se (or S) atoms. And the point group change from C_{3v} to C_{2v}.the basic vibration mode increase from six to nine.

Table 3.Optimized structural parameters (averaged values) of CS-Si_2S_7, ES-Si_2S_6, 2ES-Si_3S_8 and ETH-Si_2S_6 clusters calculated at the HF/6-31G level

Average value	Bond distance（Å）			Bond angle（degree）	
	Si-S	S-S	Si-Si	Si-S-Si	S-Si-S
CS-Si_2S_7	2.227	3.708	3.776	115^{o}	112^{o}
ES-Si_2S_6	2.247	3.693	3.077	86^{o}	113^{o}
ETH-Si_2S_6	2.229	3.691	2.386	--	112^{o}
2ES-Si_3S_8	2.234	--	--	85^{o}	114^{o},94^{o}

Table 4. Optimized structural parameters (averaged values) of CS-Si_2Se_7, ES-Si_2Se_6, 2ES-Si_3Se_8 and ETH-Si_2Se_6 clusters calculated at the HF/6-31G level

Average value	Bond distance（Å）			Bond angle（degree）	
	Si-Se	Se-Se	Si-Si	Si-Se-Si	Se-Si-Se
CS-Si_2Se_7	2.298	3.861	3.634	103^{o}	114^{o}
ES-Si_2Se_6	2.319	3.844	3.023	80^{o}	112^{o}
ETH-Si_2Se_6	2.297	3.807	2.327	--	110^{o}
2ES-Si_3Se_8	2.317	--	--	84^{o}	116^{o},96^{o}

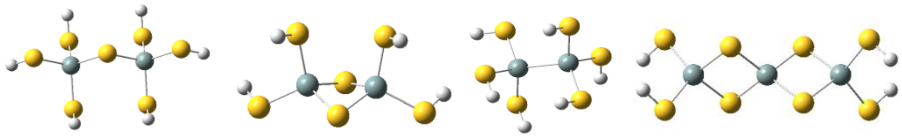
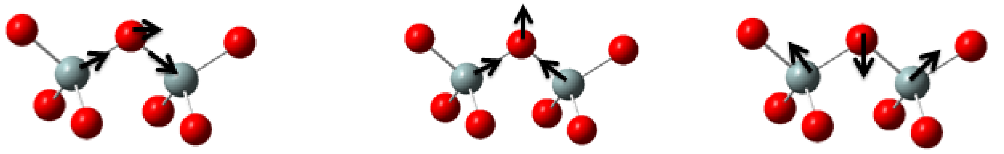


Fig.3. Schematic representation of CS-, ES- and ETH-SiX_4 clusters(X=S or Se)

Table 3 and Table 4 show the optimized bond distances and bond angles of CS-Si_2S_7, ES-Si_2S_6, ETH-Si_2S_6, 2ES-Si_3S_8, CS-Si_2Se_7, ES-Si_2Se_6 and ETH-Si_2Se_6, 2ES-Si_3Se_8 clusters. Besides the single SiS_4 and $SiSe_4$ tetrahedron, the vibration modes of corner-sharing tetrahedral should be considered due to the effective coupling between neighbour tetrahedral. In terms of group theory analysis, there are twenty-one vibrational modes in the corner-sharing tetrahedron. Among them, three vibrational modes named “out of phase”, “In-phase” and “cage motion” [14]. The schematic diagrams and calculated data of them are as follows:



Out of phase **In-phase** **silicon cage motion**

Fig.4.Schematic illustration of coupled vibration modes in corner-sharing cluster

Table 5 Calculated data of main coupled mode related to "Si-O-Si" in Si_2O_7 cluster (cm^{-1})

Cluster	"Out of phase"	"in-phase"	"Silicon cage motion"
Si_2S_7	527	488	327
Si_2Se_7	423	400	192

In addition, edge-sharing tetrahedral such as ES-Si_2S_6 and ES-Si_2Se_6 are also important basic clusters in SiS_2 and $SiSe_2$ glass system. According to point group analysis, there are 18 basic vibrational modes in ES-Si_2S_6 and ES-Si_2Se_6.and two vibrational modes of them are considered to the main vibrational modes. More details are as follows:

Table 6 the main vibrational modes of ES-Si_2S_6 and ES-Si_2Se_6 calculated at HF/6-31G

D_{2h}	$V_1(A_{1g})$	$V_2(A_{1g})$
X_2Y_6	V(XY)	V(XY)
Si_2S_6	377	563
Si_2Se_6	212	470

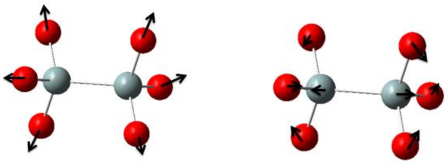
$V_1(A_{1g})$ **$V_2(A_{1g})$**

Fig.5.Schematic illustration of the main vibrational modes of ES-Si_2S_6 and ES-Si_2Se_6

Apart from clusters above, the ethane-like structure also play an important role in SiS_2 and $SiSe_2$ glass system. Based on the point group, there are 12 basic vibrational modes in ETH-Si_2S_6 and ETH-Si_2Se_6. Two vibrational modes of them are considered to the main vibrational modes. More details are as follows:

Table 7 the main vibrational modes of ETH-Si_2S_6 and ETH-Si_2Se_6 calculated at HF/6-31G

D_{2h}	$V_1(A_{1g})$	$V_2(A_{1g})$
X_2Y_6	$V(XY_3)$	V(XX)
Si_2S_6	387	530
Si_2Se_6	179	496



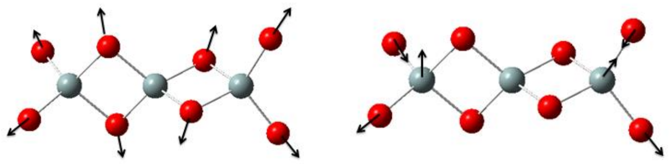
$V_1(A_{1g})$ $V_2(A_{1g})$

Fig.6.Schematic illustration of the main vibrational modes of ES-Si_2S_6 and ES-Si_2Se_6

Besides the clusters above, the 2ES-Si_3S_8 and 2ES-Si_3Se_8 clusters are considered to be significant clusters in Si-S-Se glassy system.

Table 8 the main vibrational modes of 2ES-Si_3S_8 and 2ES-Si_3Se_8 calculated at HF/6-31G

	V_S	V_{as}
Si_3S_8	421	557
Si_3Se_8	259	508



V_s V_{as}

Fig.7.Schematic illustration of the main vibrational modes of 2ES-Si_3S_8 and 2ES-Si_3Se_8

4. Discussion

Table 9 and Table 10 display the calculated Si-S and Si-Se symmetrical stretching vibrational modes in SiS_nSe_{4-n} tetrahedron, which indicate the similar variation of vibration mode frequencies with different number of symmetrical stretching bond. For example, there is one Si-S bond in the Si-S symmetrical stretching vibration mode of $SiSSe_3$ with frequency of 482cm^{-1}. Then, there are two Si-S bonds in the Si-S symmetrical stretching vibration mode of SiS_2Se_2, which frequency decrease from 482cm^{-1} to 462cm^{-1}.when continuing to increase the number of Si-S bonds, the frequency drop continually until 339cm^{-1} with four Si-S bonds in the Si-S symmetrical stretching vibration mode of SiS_4 tetrahedron.

Table 9 The calculated Si-S symmetrical stretching vibrational modes in SiS_nSe_{4-n} tetrahedron

Type	Si-S symmetrical stretching vibration		Calculated(cm^{-1})
$SiSSe_3$	1(Si-S)	$\nu_2(A_1)$	482
SiS_2Se_2	2(Si-S)	$\nu_1(A_1)$	462
SiS_3Se	3(Si-S)	$\nu_1(A_1)$	452
SiS_4	4(Si-S)	$\nu_1(A_1)$	339

Table 10 The calculated Si-Se symmetrical stretching vibrational modes in SiS_nSe_{4-n} tetrahedron

Type	Si-Se symmetrical stretching vibration		Calculated(cm^{-1})
SiS_3Se	1(Si-Se)	$\nu_2(A_1)$	295
SiS_2Se_2	2(Si-Se)	$\nu_2(A_1)$	255
$SiSSe_3$	3(Si-Se)	$\nu_1(A_1)$	227
$SiSe_4$	4(Si-Se)	$\nu_1(A_1)$	194

On the other hand, there is one Si-Se bond in the Si-Se symmetrical stretching vibration mode of SiS_3Se with frequency of 295cm^{-1}.With the increase of Si-Se bonds, the frequency decrease from 295cm^{-1},255cm^{-1},227cm^{-1} to 194cm^{-1}.Those similar variation can be explained by vibration coupling theory. For instance, when there is one Si-S bond, which induces the one type of Si-S stretching vibration (482cm^{-1}).

Then, when there are two Si-S bond, which induce two type of vibration modes called symmetry stretching vibration(462cm^{-1}), which is lower than one Si-S bond stretching vibration and antisymmetry stretching vibration(501cm^{-1}),which is higher than one Si-S bond stretching vibration. Continually, when there are three Si-S bonds, the Si-S symmetry stretching vibration drop gradually to 452cm^{-1}, which is lower than 462cm^{-1} and the Si-S antisymmetry stretching vibration (497cm^{-1}),which is higher than 462cm^{-1}. Finally, when there are four Si-S bonds, the Si-S symmetry stretching vibration (339cm^{-1}) is lower than 452cm^{-1}.however, the Si-S antisymmetry stretching vibration (500cm^{-1}) is higher than 452cm^{-1}.Meanwhile, the variation of Si-Se stretching vibration mode is the same.

On the other hand, Si-S-Se glassy system is similar to Ge-S-Se glassy system because of the similarity between Si and Ge atom. According to the central-force network model theory by Frank L.Galeener[15], the effective coupling between neighboring tetrahedral vibration modes of AX_2 glasses are related to the angle of A-X-A. In addition, the vibrational modes are determined more by the isolated AX_4 tetrahedra rather than by the A-X-A bonds, when the average A-X-A bond angle is smaller than the critical angle $\cos^{-1}(-2m/3M)$,where M is the mass of the A atom and m is that of the X atom. On the contrary, if the A-X-A angle is larger than the critical angle, the stretching modes of adjacent tetrahedra became strongly coupled. Based on the theory above, for the Ge-S-Se glassy system, the critical angle values of Ge-S-Ge and Ge-Se-Ge are 107.11^{o} and 136.44^{o}, respectively. In addition, the vibrational modes of basic clusters of isolated GeS_4 and $GeSe_4$ tetrahedron are corresponding to strongest peaks of Ge-S-Se Raman spectra [16].However, according to the calculated data above, we found the dominant strong peaks at 427cm^{-1} and 242cm^{-1} in the Raman spectra of SiS_2 and $SiSe_2$ glassy system, respectively [17].which cannot be attributed to vibrational modes of SiS_4 and $SiSe_4$ clusters. That indicates the effective coupling of SiS_4 and $SiSe_4$ between neighboring tetrahedral is stronger than that of GeS_4 and $GeSe_4$ based on the central-force network model theory. The calculation data indicate that there are dominant strong peaks at 427cm^{-1} and 242cm^{-1}， which should be attributed to the symmetrical stretching vibrational mode of 2ES-Si_3S_8 and 2ES-Si_3Se_8 clusters, respectively, which means the Vibrational properties of Si-S-Se system are more related to the intermediate range order, not short range order, compared to the Ge-S-Se system.

5. Conclusions

We have carried out ab initio calculations at the HF/6-31G level on the different basic clusters in Si-S-Se glassy systems such as edge-sharing tetrahedral(ES)、two edge-sharing tetrahedral(2ES)、corner-sharing tetrahedral(CS) 、ethane-like structure and isolated S_nSe_{4-n} tetrahedron （n=0,1,2,3,4）terminated by hydrogen atoms as pseudoatom. According to the point group theory, we found the vibrational modes of clusters increase with the decrease of point group symmetry. Furthermore, the Si-S and Si-Se symmetrical stretching vibration modes of

S_nSe_{4-n} tetrahedron clusters are accordance with vibration coupling theory. Finally，the effective coupling of SiS_4 and $SiSe_4$ between neighboring tetrahedral is stronger than that of GeS_4 and $GeSe_4$.

References

[1] T.M. Monro,Y.D. West,D.W. Hewak, N. G. R. Broderick,D. J. Richardson,Electronics Letters, **36**, 24 (2000).
[2] J. Hu,V. Tarasov, A. Agarwal, L. Kimerling, N. Carlie, L. Petit,K. Richardson,Optics Express, **15**, 5 (2007).
[3] S. Blaineau,P. Jund,Physical Review B,**70**, 18 (2004).
[4] A. Shavel,J. Arbiol,A. Cabot,Journal of the American Chemical Society, **132**, 13 (2010).
[5] C.J. Benmore,P.S. Salmon, Physical review letters, **73**, 2 (1994).
[6] R. Ahmad, M. Rochette, Optics letters, **37**, 21, (2012).
[7] C. Lin,Z. Li,L. Ying,Y. Xu,P. Zhang,S. Dai,The Journal of Physical Chemistry C, **116**, 9 (2012).
[8] A.H. Moharram,M.A. El-Oyoun,A.M. Abdel-Baset,Applied Physics A, **115**, 3 (2014).
[9] D.L. Sidebottom,T.D. Tran,S.E. Schnell, Journal of Non-Crystalline Solids, **402** (2014).
[10] T. Yomei,U. Takashi,Y. Toshinobu,Journal of Non-Crystalline Solids **282** (2001).
[11] J. Koblar,B. Arlin,G. Shau,Physical Review B **60**, 22 (1999).
[12] O. Kostadinova,A. Chrissanthopoulos,T. Petkova,P. Petkov,S.N. Yannopoulos,Journal of Solid State Chemistry,**184** (2011).
[13] Z. Cernosek,E. Cernoskova,L. Benes,Journal of Molecular Structure **435**, 2 (1997).
[14] P. McMillan, Am Mineral, **69**, 622 (1984).
[15] F.L. Galeener,Physical Review B, **19**, 8 (1979).
[16] H. Xuecai,S. Guangying,L. Yu,Y. , Hongbo, L. Yonghua,Chalcogenide Lett, **9**, 11 (2012).
[17] M. Tenhover,M.A. Hazle,R.K. Grasselli,Physical review letters, **51**, 5 (1983).