

Structural and vibrational characteristics of Ge-S-Br glass system: ab initio calculation and Raman study

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To improve the understanding of the structure network of chalcogenide glass, we report an investigation of the structure and vibrational property of the Ge-S-Br system chalcogenide glass. The structural origin was interpreted by the result of ab initio calculation performed on the basic units such as ethane-like(ETH) structure(Ge_2S_6 and Ge_2Br_6), edge-sharing(ES) structure $\text{Ge}_2\text{S}_2\text{S}_n\text{Br}_{4-n}$ ($n=0,1,2,3,4$) and isolated $\text{GeS}_n\text{Br}_{4-n}$ tetrahedron ($n=0,1,2,3,4$), which represent the local structure of Ge-S-Br glassy system. In addition, We have compared the experimental spectra of GeS_2 , GeS_3Br , GeSBr_2 glasses and liquid GeBr_4 to the calculated main vibrational modes of basic units by ab initio calculation. The calculated vibrational modes of the $\text{GeS}_n\text{Br}_{4-n}$ cluster are assigned by group theory. Moreover, the symmetrical stretching modes related to the Ge-S and Ge-Br bond are in accordance with the vibrational coupling theory. The variation of calculated main vibrational modes of GeS_mBr_n clusters reveals the structure formations of Ge-S-Br glassy system with different S/Br ratios, which can be in agreement with vibrational spectra of Ge-S-Br glass.

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1. Introduction

Chalcogenide glasses have received great potential interest for materials transmitting in the mid-IR region. In addition, chalcogenide glasses are also good infrared optical materials and are well-known for their low optical loss [1]. However, the relatively poor chemical durability of halide glasses along with low glass transition temperature show a serious problem for practical optical application [2]. Consequently, chalcogenide glasses should have both good IR transmissions extended to the mid-infrared range as well as good chemical stability and glass-forming ability [3]. In general, chalcogenide shows enhanced infrared optical properties and good chemical stability with a profound study of chalcogenide glasses [4]. The earliest structural work using X-ray diffraction on chalcogenide glasses was by Hopkins et al [5]. However, there is no exact agreement among researchers regarding the structure of chalcogenide glasses. So far, we have found at least three different models explaining the GeS_2 glass network structure. The first one proposed the network structure made of two different phases including ethane-like fragment and outrigger raft units [6]. The second model was based on a random network composed of GeS_4

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corner-sharing and edge-sharing tetrahedra with ethane-like clusters [7]. The third one is considered as a network structure similar to α -GeS₂[8]. Among all chalcogenide glass systems, Ge-S-Br glass is a typical example illustrated since 1975. The hypothetical structure of glasses in the Ge-S-Br system was first proposed by Koudelka et al [9] with the research method of Raman spectra analysis. Besides, Uemura et al. studied the structure of chalcogenide glasses in the Ge-S-Br system by Raman and extended X-ray absorption fine structure spectroscopy [10]. However, since limited knowledge of the Ge-S-Br glass system, there is no generally accepted agreement on the presence of structural fragments in Ge-S-Br glasses. Some authors concluded the Ge-S-Br glasses with a polymer network that consists of GeS_{4/2} and S chains linked by bonds and dissolved GeBr₄ molecules [11]. On the other hand, Ge-S-Br glasses were investigated by Raman spectra, which were hypothesized with mixed tetrahedra GeS_{4-n}Br_n formed in Ge-S-Br glasses [12]. It reflects the molecular-like vibrational behavior of their Raman spectra. Despite some experimental research carried out in the past, there has been a lack of theoretical study to prove basic units like GeS_nBr_{4-n} in the Ge-S-Br glassy system.

In this article, the study is devoted to investigating the structure of the Ge-S-Br glass system. The vibrational modes of basic units such as ethane-like(ETH) structure(Ge₂S₆ and Ge₂Br₆),edge-sharing(ES) structure Ge₂S₂S_nBr_{4-n} (n=0,1,2,3,4), and isolated GeS_nBr_{4-n} (n=0,1,2,3,4) tetrahedron in glassy Ge-S-Br system are calculated by ab initio method. According to the calculated frequency of the main vibrational mode, we can investigate the influence of vibrational property in chalcogenide glasses to determine the degree of stability of ternary structural units and the variation of Raman shift in Ge-S-Br glassy system with different S/Se ratio.

2. Experimental and theoretical calculation details

The glasses were synthesized from elemental substances with melt quenching method. The Raman spectra were recorded using a 785 nm excitation wavelength at room temperature with the resolution of 1cm⁻¹. Ab initio calculations have been performed on a range of clusters selected to represent the various basic units in the microstructure of Ge-S-Br glasses. The selection of clusters is based on the central-force network model theory by Frank L. Galeener [13], which reveals the effective coupling between neighboring tetrahedral vibration modes of AX₂ glasses related to the angle of A-X-A. In addition, when the average A-X-A bond angle among AX₄ tetrahedra is smaller than the critical angle $\cos^{-1}(-2m/3M)$, where M and m are the mass of A atom and X atom, respectively, it means that the vibrational modes of corner-sharing(CS) AX₄ tetrahedra are determined more by the isolated AX₄ tetrahedra rather than by the A-X-A bonds. It is also reported that the hydrogen atoms in the cluster are used as pseudo atoms to replace the chalcogenide glass by finite molecular model [14]. 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 from being removed from the analysis of region for related vibrational modes Ge-S-Br main clusters. Furthermore, in amorphous solids, the vibrational excitations can not spread over a whole glass network because of the lack of long-range order. vibrational properties of glasses can be reasonably predicted by ab initio calculation in terms of appropriate cluster models.

In this paper, we have carried out ab initio calculations on several basic clusters such as ethane-like(ETH) structure Ge_2S_6 and Ge_2Br_6 , edge-sharing(ES) $\text{Ge}_2\text{S}_2\text{S}_n\text{Br}_{4-n}$ ($n=0,1,2,3,4$), and isolated $\text{GeS}_n\text{Br}_{4-n}$ ($n=0,1,2,3,4$) tetrahedron, which are calculated at the Hartree-Fork level with optimization based on HF/6-31G. The dangling bonds originating from singly bonded sulfur atoms in clusters were neutralized by adding hydrogen-like atoms with masses equal to germanium to provide a better agreement between calculated and experimental vibrational frequencies. After geometry, optimizations of the clusters, and frequency of vibrational modes calculations were achieved to obtain the Raman spectra of the basic units in Ge-S-Br glass structures.

3. Result

The structure diagram of clusters are displayed in Fig.1-3, which can be divided into three groups. The first group are the isolated $\text{GeS}_n\text{Br}_{4-n}$ ($n=0,1,2,3,4$) tetrahedral clusters. Meanwhile, the second group are the ETH- GeX_3 - GeX_3 ($X=\text{S},\text{Se}$) clusters, which can divide into two types named: cis- and trans- ethane-like(ETH) structure. The last group are edge-sharing (ES) $\text{Ge}_2\text{S}_2\text{S}_n\text{Br}_{4-n}$ ($n=0,1,2,3,4$).

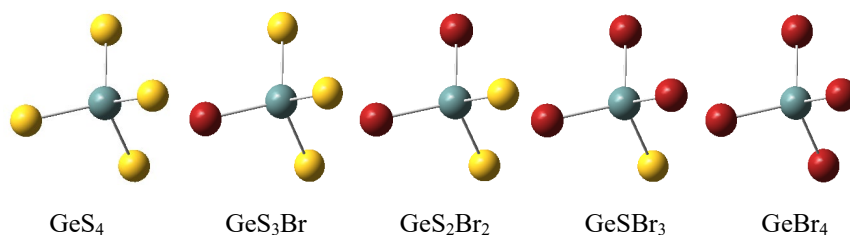


Fig. 1. The structure diagram of isolated $\text{GeS}_n\text{Br}_{4-n}$ ($n=0,1,2,3,4$) tetrahedral clusters.

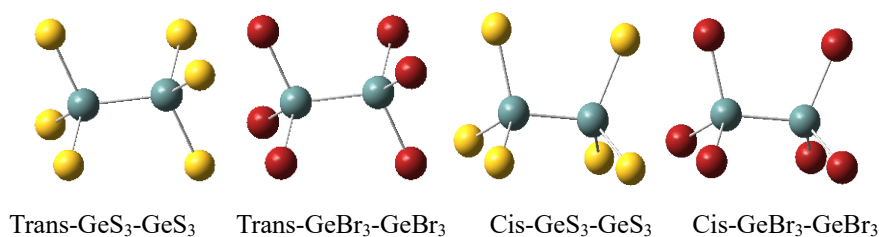


Fig. 2. The structure diagram of ethane-like (ETH) clusters (symmetric and asymmetric).

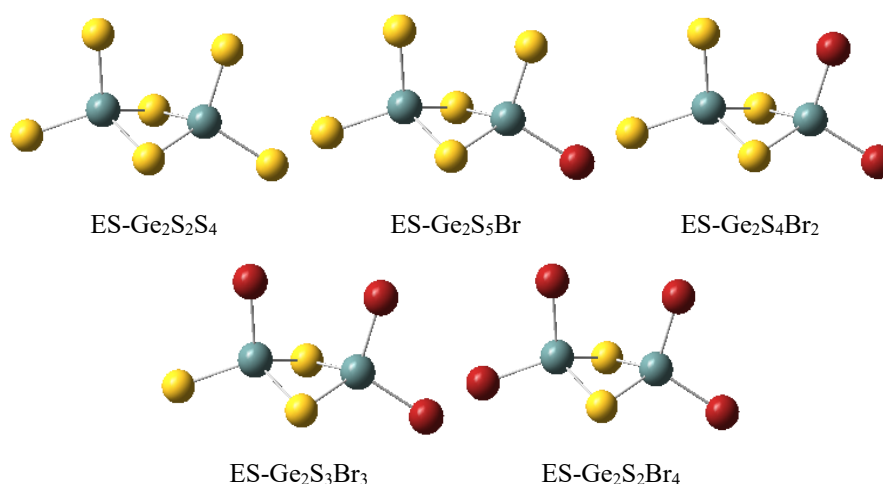


Fig. 3. The structure diagram of $ES-Ge_2S_2S_nBr_{4-n}$ ($n=0,1,2,3,4$).

Table 1-3 show the bond distances and angles of optimized geometries for ethane-like(ETH) structure Ge_2S_6 and Ge_2Br_6 , edge-sharing(ES) $Ge_2S_2S_nBr_{4-n}$ ($n=0,1,2,3,4$), and isolated GeS_nBr_{4-n} ($n=0,1,2,3,4$) tetrahedron. which are considered to the basic units in Ge-S-Br glassy system. It can be seen from Table1 that the bond distances of Ge-S and Ge-Br in isolated GeS_nBr_{4-n} tetrahedral clusters are around 2.25Å and 2.30Å, respectively. In addition, it is interesting that there is an increase of Ge-S bond distance with the increase of S atom in isolated GeS_nBr_{4-n} tetrahedral clusters from 2.238Å to 2.261Å. However, Compared with change of Ge-S bond distance, the the increase of Br atom in isolated GeS_nBr_{4-n} tetrahedral clusters lead to the decrease of Ge-Br bond distance from 2.319Å to 2.296Å. These similar variation phenomenon between Ge-S and Ge-Br bond distance can be explained that mutual coupling effect of Ge-S bond and Ge-Br bond in mixed GeS_nBr_{4-n} tetrahedral clusters, which makes the long bond length shorter (Ge-Br) and the short bond length(Ge-S) longer. Furthermore, the bond angles of isolated GeS_nBr_{4-n} tetrahedral clusters such as S-Ge-S, S-Ge-Br and Br-Ge-Br are near to that of regular tetrahedron. In addition, the Ge-S bonds of $ES-Ge_2S_2S_nBr_{4-n}$ clusters are classified by two types including the Ge-S bond in Ge-S-Ge-S four-membered ring and the Ge-S bond not in Ge-S-Ge-S four-membered ring, which are displayed in Table 3.

Table 1. The calculated bond distance and angles in isolated GeS_nBr_{4-n} tetrahedral clusters.

Model	$GeBr_4$	$GeBr_3S$	$GeBr_2S_2$	$GeBrS_3$	GeS_4
Calculated bond distance(Å)					
Ge-S	---	2.238	2.248	2.253	2.261
Ge-Br	2.296	2.297	2.307	2.319	---
Calculated bond angles (degrees)					
S-Ge-S	---	---	111°13'	104°67'	109°51'
S-Ge-Br	---	106°45'	106°29'	105°86'	---
Br-Ge-Br	109°47'	109°78'	110°65'	---	---

Table 2. The calculated bond distance and angles in ethane-like (ETH) clusters.

Model	Cis-GeBr ₃ -GeBr ₃	Trans-GeBr ₃ -GeBr ₃	Cis-GeS ₃ -GeS ₃	Trans-GeS ₃ -GeS ₃
Calculated bond distance(Å)				
Ge-S	---	---	2.275	2.269
Ge-Br	2.301	2.302	---	---
Ge-Ge	2.392	2.366	2.392	2.382
Calculated bond angles (degrees)				
S-Ge-S	---	---	109°57'	112°35'
S-Ge-Ge	---	---	109°38'	106°41'
Br-Ge-Br	108°91'	109°94'	---	---
Br-Ge-Ge	110°02'	108°99'	---	---

Table 3. The calculated bond distance and angles in ES-Ge₂S₂S_nBr_{4-n} clusters.

Model	Ge ₂ S ₂ S ₄	Ge ₂ S ₂ S ₃ Br	Ge ₂ S ₂ S ₂ Br ₂	Ge ₂ S ₂ SBr ₃	Ge ₂ S ₂ Br ₄
Calculated bond distance(Å)					
Ge-S (in ring)	2.314	2.312	2.306	2.305	2.304
Ge-S	2.259	2.262	2.264	2.257	---
Ge-Br	---	2.335	2.336	2.338	2.334
Calculated bond angles (degrees)					
S-Ge-S (in ring)	92°51'	93°15'	93°43'	94°91'	93°25'
S-Ge-S	106°08'	113°16'	113°20'	116°05'	---
Br-Ge-Br	---	---	109°21'	109°38'	109°53'
S-Ge-Br	---	106°31'	113°35'	113°53'	113°34'

Figure 4-6 show the energy optimization of ethane-like(ETH) structure Ge₂S₆ and Ge₂Br₆,edge-sharing(ES) Ge₂S₂S_nBr_{4-n} (n=0,1,2,3,4), and isolated GeS_nBr_{4-n} (n=0,1,2,3,4) tetrahedron. According to the energy optimization diagram below, all the clusters are optimized smoothly.

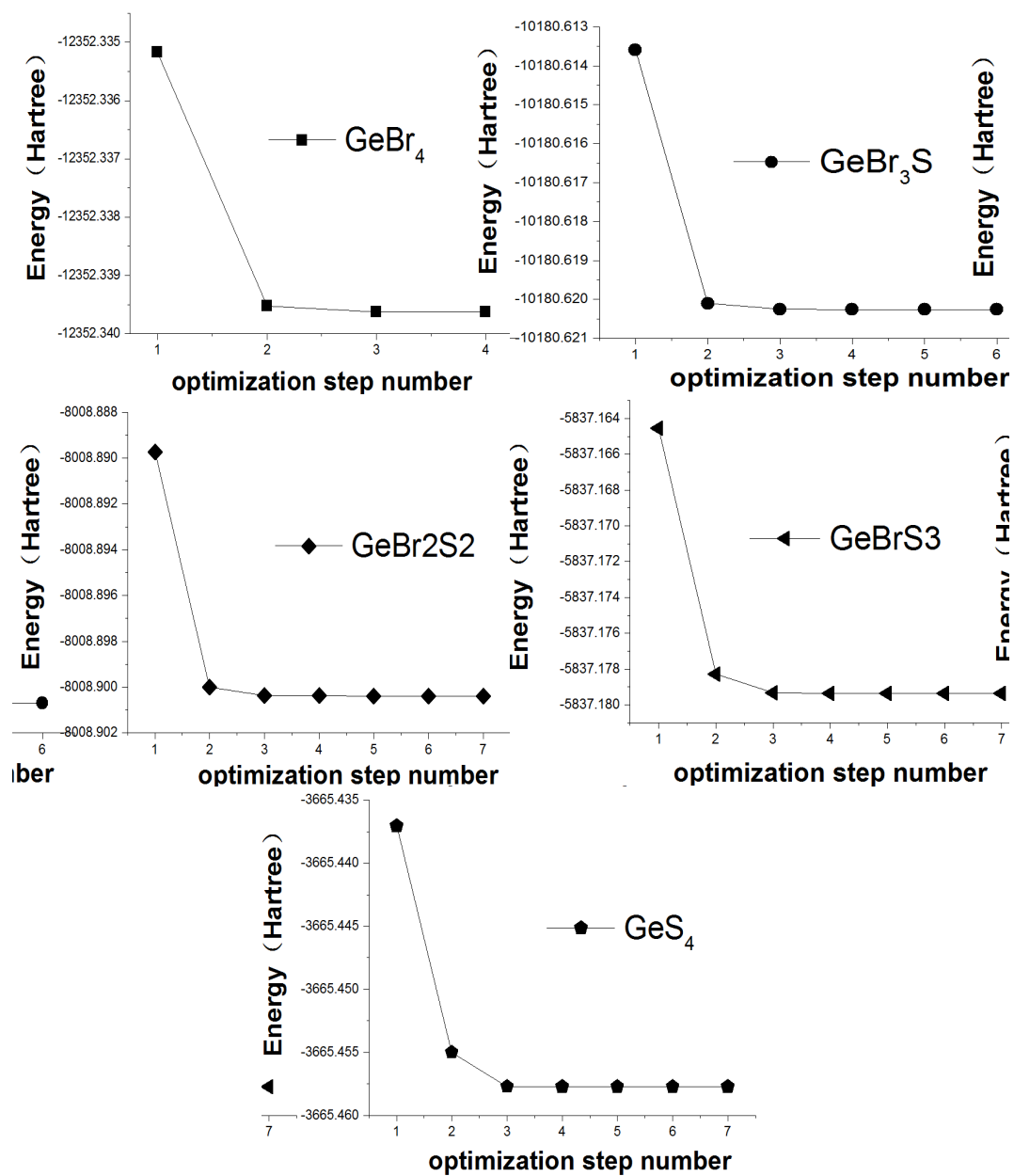


Fig. 4. The energy optimization of isolated GeS_nBr_{4-n} tetrahedral clusters.

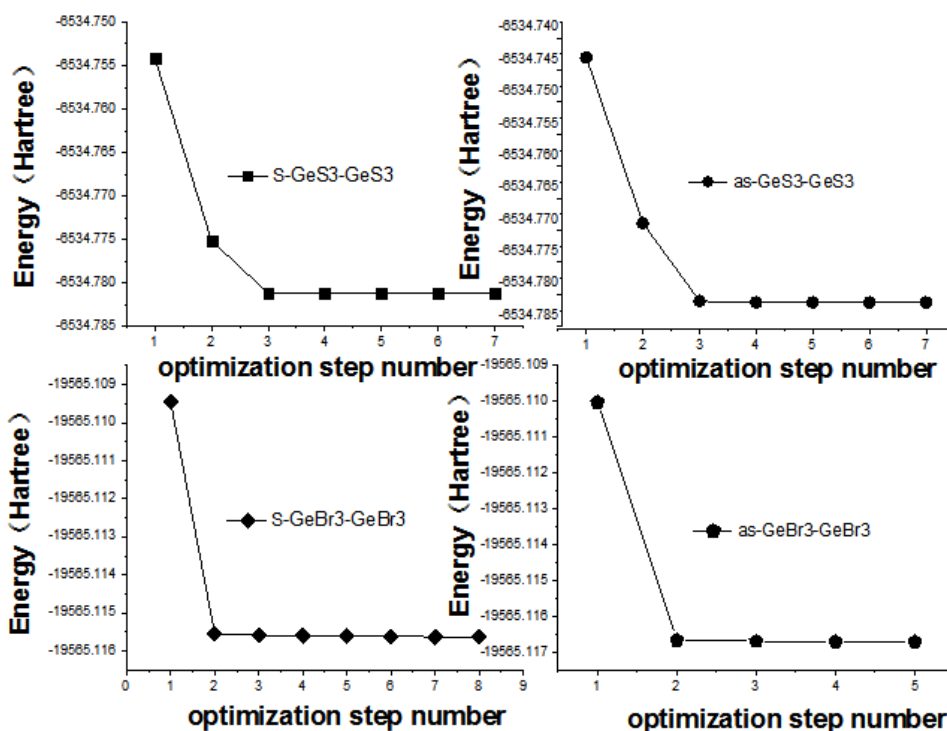


Fig. 5. The energy optimization of ethane-like (ETH) Ge_2S_6 and Ge_2Br_6 clusters.

Based on the group theory, total basic vibrational modes of a nonlinear structure unit are $3n-6$ (n : number of atom) [15]. From Table 4, it can be seen that there are four basic vibrational modes in the isolated GeS_4 and $GeBr_4$. When one S (or Br) atom is replaced by Br (or S) atom, the number of basic vibration mode increase from four to six and the point group varies from T_d to C_{3v} in GeS_3Br and $GeSBr_3$ tetrahedron. Moreover, two S (or Br) atoms are substituted by Br (or S) atoms. And the point group continually shift from C_{3v} to C_{2v} . the basic vibrational mode increase from six to nine. Among them, ν_1 type mode is called symmetry stretching vibration and ν_3 type mode is named antisymmetric stretching vibration. The stretching vibration modes are considered to the main vibrational mode with strong vibrational activity in isolated GeS_nBr_{4-n} ($n=0, 1, 2, 3, 4$) tetrahedron.

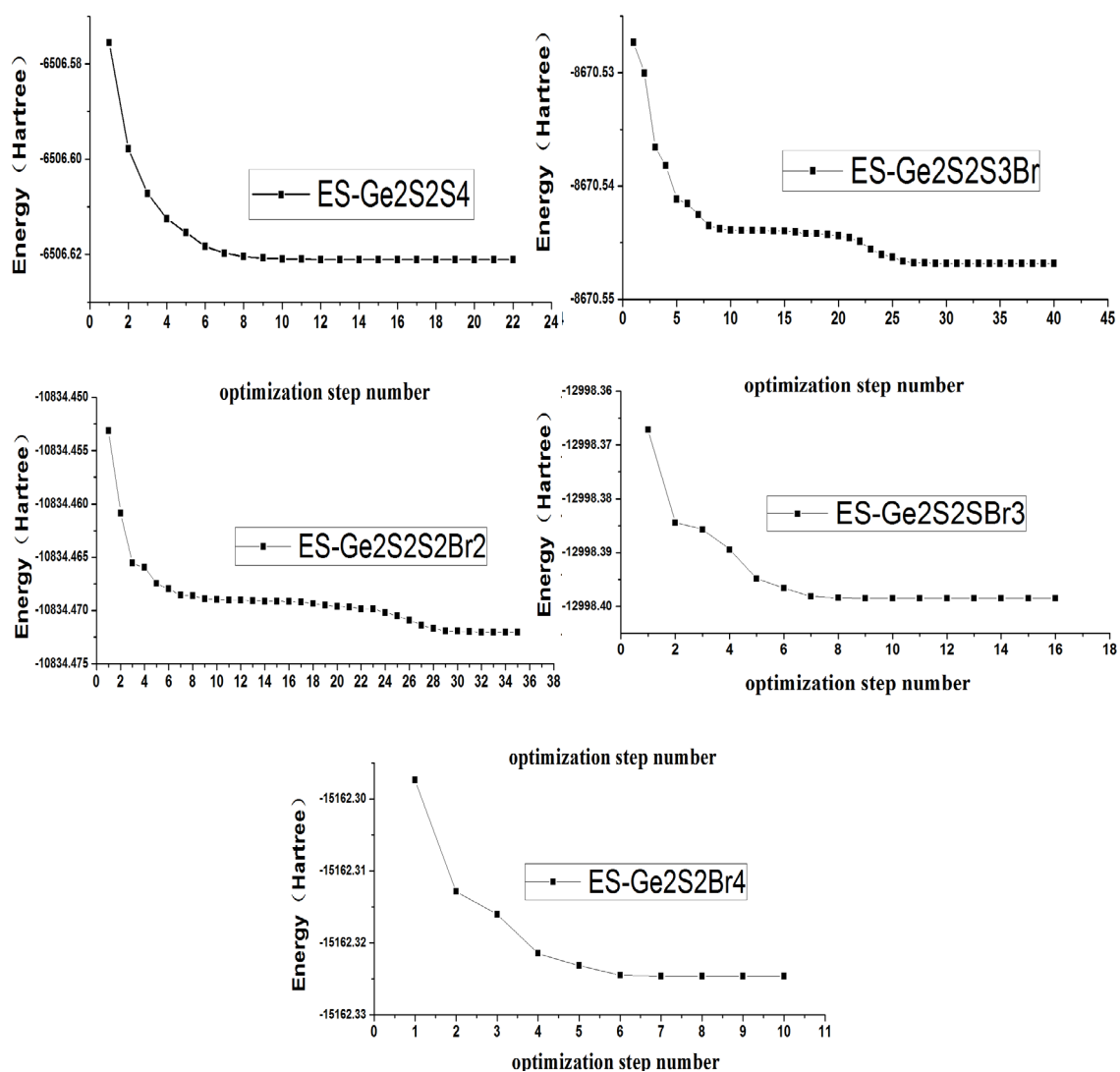


Fig. 6. The energy optimization of ES-Ge₂S₂SnBr_{4-n} clusters.

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

T _d	v ₁ (A ₁)	v ₂ (E)		v ₃ (F ₂)			v ₄ (F ₂)		
	v _s (XY)	δ _d (YXY)		v ₈ (XY)			δ _d (YXY)		
GeBr ₄	239	100		342			114		
GeS ₄	348	134		410			136		
C _{3v}	v ₁ (A ₁)	v ₅ (E)		v ₂ (A ₁)	v ₄ (E)		v ₃ (A ₁)	v ₆ (E)	
	v(XY ₃)	δ _s (XY ₃)		v(XZ)	v(XY ₃)		δ(XY ₃)	ρ _t (XY ₃)	
GeBr ₃ S ₁	255	128		421	338		121	102	
GeBr ₁ S ₃	383	126		288	421		123	121	
C _{2v}	v ₁ (A ₁)	v ₄ (A ₁)	v ₅ (A ₂)	v ₂ (A ₁)	v ₆ (B ₁)	v ₈ (B ₂)	v ₃ (A ₁)	v ₇ (B ₁)	v ₉ (B ₂)
	v(XY)	δ(XZ ₂)	ρ _t (XY ₂)	v(XZ)	v(XY)	v(XZ)	δ(XY ₂)	ρ _m (XY ₂)	ρ _t (XY ₂)
GeBr ₂ S ₂	403	129	120	273	423	333	139	104	121

Table 5 show the calculated vibrational modes of ETH-Ge₂S₆ and ETH-Ge₂Se₆ with Trans- and Cis- cluster structure. Based on the group theory, there are 12 basic vibrational modes in ETH-Ge₂S₆ and ETH-Ge₂Se₆.

Table 5. The vibrational modes of ETH-Ge₂S₆ and ETH-Ge₂Se₆ calculated at HF/6-31G.

Vibrational mode	Trans-Ge ₂ S ₆	Cis-Ge ₂ S ₆	Trans-Ge ₂ Br ₆	Cis-Ge ₂ Br ₆
v ₁	383	392	210	206
v ₂	276	271	324	356
v ₃	399	395	364	329
v ₄	144	139	346	343
v ₅	114	109	81	98
v ₆	108	128	71	81
v ₇	409	408	102	93
v ₈	359	358	267	270
v ₉	138	143	123	132
v ₁₀	128	147	98	118
v ₁₁	65	55	37	48
v ₁₂	24	19	20	15

Table 6 shows the calculated vibrational modes of edge-sharing(ES) Ge₂S₂S_nBr_{4-n} (n=0,1,2,3,4), there are 18 basic vibrational modes as follows.

Table 6. The Raman vibrational frequencies of ES-Ge₂S₂S_nBr_{4-n} (n=0,1,2,3,4) calculated at HF/6-31G.

Vibrational mode	Ge ₂ S ₂ S ₄	Ge ₂ S ₂ S ₃ Br	Ge ₂ S ₂ S ₂ Br ₂	Ge ₂ S ₂ SBr ₃	Ge ₂ S ₂ Br ₄
v ₁	374	391	358	317	315
v ₂	429	357	441	415	433
v ₃	448	447	405	443	168
v ₄	94	199	187	176	337
v ₅	203	422	432	346	346
v ₆	339	431	345	382	118
v ₇	106	119	341	342	89
v ₈	139	344	88	82	77
v ₉	113	107	290	120	130
v ₁₀	47	305	125	184	411
v ₁₁	121	94	96	133	391
v ₁₂	343	135	134	92	347
v ₁₃	418	113	120	109	266
v ₁₄	402	184	407	410	178
v ₁₅	129	126	184	278	106
v ₁₆	435	408	108	105	99
v ₁₇	186	60	58	51	45
v ₁₈	28	24	23	21	21

3. Discussion

According to the main vibrational modes of $\text{GeS}_n\text{Br}_{4-n}$ showed in Table 7, it is interesting that the type of main vibrational mode shift from stretching vibrational mode related Ge-S (GeS_4) to Ge-Br ($\text{GeS}_n\text{Br}_{4-n}, n=1,2,3$), which means the main vibrational mode of $\text{GeS}_n\text{Br}_{4-n}$ is largely attributed to Ge-Br stretching vibrational mode rather than Ge-S stretching vibrational mode.

Table 7. The Raman main vibrational mode of $\text{GeS}_n\text{Br}_{4-n}$ between calculated data and experimental data.

Type	Main vibrational mode		Calculated value
GeS_4	$\nu_1(\text{A}_1)$	$\nu_s(\text{GeS})$	348
GeS_3Br	$\nu_2(\text{A}_1)$	$\nu(\text{GeBr})$	288
GeS_2Br_2	$\nu_2(\text{A}_1)$	$\nu(\text{GeBr})$	273
GeSBr_3	$\nu_1(\text{A}_1)$	$\nu(\text{GeBr}_3)$	255
GeBr_4	$\nu_1(\text{A}_1)$	$\nu_s(\text{GeBr})$	234

This is because the Br atomic mass is heavier than S atomic mass, and the changes of electron cloud in Br atom are easier than that in S atom. So the vibrational activity of Ge-Br bond is stronger than that of Ge-S bond, and the interaction force of Ge-Br is smaller than that of Ge-S. which can be explained by molecular spectroscopy theory as follows [16]:

$$\nu \propto \sqrt{\frac{f}{\mu}}$$

where f is a constant related to the bond strength, and μ is the discount mass. So when S atoms are replaced by Br atoms, the value of f is smaller and μ is bigger, which leads to a decrease of frequency.

Table 8. The Ge-S symmetrical stretching vibrations of $\text{GeS}_n\text{Br}_{4-n}$ clusters.

Type	Ge-S symmetrical stretching vibration		Calculated value
GeS_4	$\nu_1(\text{A}_1)$	$\nu(\text{GeS}_4)$	348
GeS_3Br	$\nu_1(\text{A}_1)$	$\nu(\text{GeS}_3)$	383
GeS_2Br_2	$\nu_1(\text{A}_1)$	$\nu(\text{GeS}_2)$	403
GeSBr_3	$\nu_2(\text{A}_1)$	$\nu(\text{GeS})$	421

Table 9. The Ge-Br symmetrical stretching vibrations of $\text{GeS}_n\text{Br}_{4-n}$ clusters.

Type	Ge-Br symmetrical stretching vibration		Calculated value
GeBr_4	$\nu_1(\text{A}_1)$	$\nu(\text{GeBr}_4)$	239
GeSBr_3	$\nu_1(\text{A}_1)$	$\nu(\text{GeBr}_3)$	255
GeS_2Br_2	$\nu_2(\text{A}_1)$	$\nu(\text{GeBr}_2)$	273
GeS_3Br	$\nu_2(\text{A}_1)$	$\nu(\text{GeBr})$	288

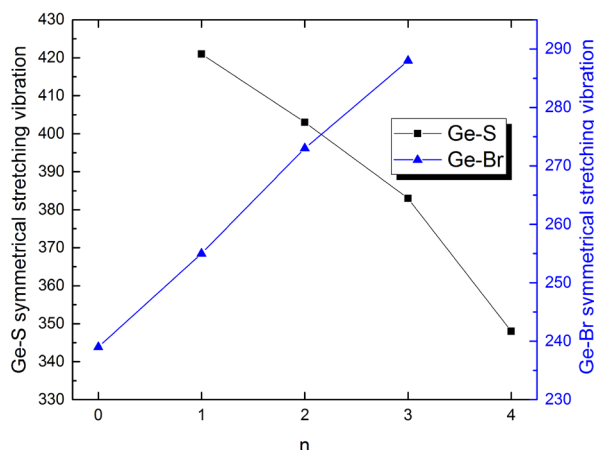


Fig. 7. The Ge-S and Ge-Br symmetrical stretching vibrational modes of $\text{GeS}_n\text{Br}_{4-n}$ clusters.

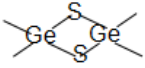
Table 8 and 9 display the calculated Ge-S and Ge-Br symmetrical stretching vibrational modes in $\text{GeS}_n\text{Br}_{4-n}$ tetrahedron, which indicate the similar variation of vibration mode frequencies with different number of symmetrical stretching bond. The Ge-S symmetrical stretching vibrational modes of $\text{GeS}_n\text{Br}_{4-n}$ clusters are shown in Table 8. the vibrational mode $\nu(\text{GeS}_4)$ means the stretching vibration mode with four Ge-S bond. A similar situation of $\nu(\text{GeS}_3)$, $\nu(\text{GeS}_2)$ and $\nu(\text{GeS})$ mode indicate the stretching vibration mode with three Ge-S bond, two Ge-S bond and one Ge-S bond. Considering the relation between the vibrational mode and calculated value, we can discover a interesting rule. For example, there is one Ge-S bond in the Ge-S symmetrical stretching vibration mode of GeSBr_3 with frequency of 421cm^{-1} . Then, the frequency of Ge-S symmetrical stretching vibration mode of GeS_2Br_2 with two Ge-S bond is 403cm^{-1} , which is lower than the one Ge-S bond symmetrical stretching vibration mode (421cm^{-1}). when continuing to increase the number of Ge-S bonds, the frequency drop continually to 383cm^{-1} and 348cm^{-1} with three and four Ge-S bonds in the Ge-S symmetrical stretching vibration mode of GeS_4 tetrahedron, respectively. On the other hand, the Ge-Br symmetrical stretching vibration mode of $\text{GeS}_n\text{Br}_{4-n}$ clusters has the similar rule. the frequency decrease from 288cm^{-1} , 273cm^{-1} , 255cm^{-1} to 239cm^{-1} with the increase of Ge-Br bonds from one to four.

Those similar variation of symmetrical stretching vibration related Ge-S and Ge-Br can be explained by vibration coupling theory, which reveal the frequency shift of Ge-X ($X=\text{S}, \text{Se}$) symmetrical stretching vibration have a deep relation with the number of Ge-X bond. Specifically speaking, the frequency of symmetrical stretching vibration decrease with the increasing number of Ge-X bond. The Ge-S and Ge-Br symmetrical stretching vibrational modes of $\text{GeS}_n\text{Br}_{4-n}$ clusters are shown in Fig.7.

Table 10 shows the breathing vibrational modes of $\text{ES-Ge}_2\text{S}_2\text{S}_n\text{Br}_{4-n}$, which can be classified by two types: symmetrical and asymmetrical breathing stretching vibration. From the data, it can be seen the frequency of symmetrical breathing stretching vibration in Ge-S-Ge-S ring clusters generally shift lower with n decreasing in $\text{ES-Ge}_2\text{S}_2\text{S}_n\text{Br}_{4-n}$ clusters. However, the frequency of asymmetrical breathing stretching vibration in Ge-S-Ge-S ring clusters generally

shift higher with n decreasing in $ES-Ge_2S_2S_nBr_{4-n}$ clusters. The variation of breathing vibrational modes of $ES-Ge_2S_2S_nBr_{4-n}$ is shown in Fig.8.

Table 10. The breathing vibrational modes of $ES-Ge_2S_2S_nBr_{4-n}(n=0,1,2,3,4)$.

Type		
	symmetrical breathing stretching	asymmetrical breathing stretching
$ES-Ge_2S_2S_4$	448	339
$ES-Ge_2S_2S_3Br$	447	344
$ES-Ge_2S_2S_2Br_2$	441	345
$ES-Ge_2S_2SBr_3$	443	346
$ES-Ge_2S_2Br_4$	433	346

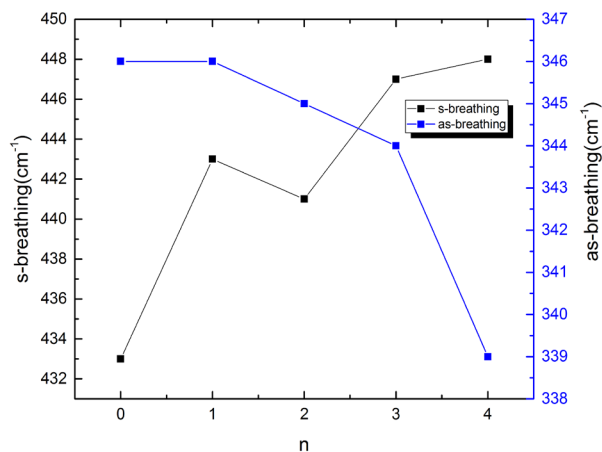


Fig. 8. The breathing vibrational modes of $ES-Ge_2S_2S_nBr_{4-n}(n=0,1,2,3,4)$.

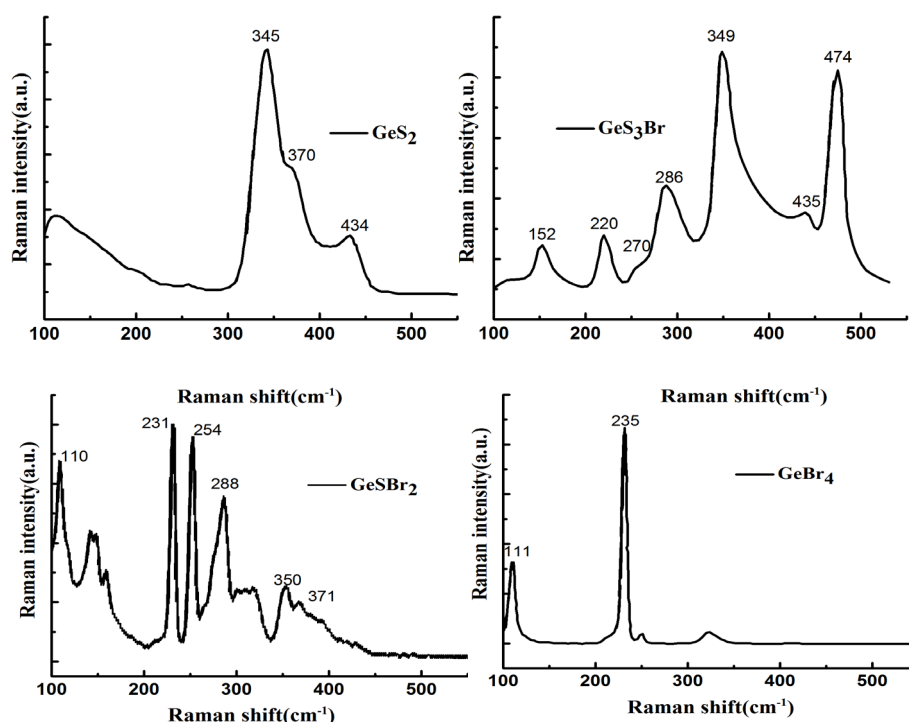


Fig. 9. The Raman spectra of GeS_2 , GeS_3Br , GeSBr_2 glasses and liquid GeBr_4 .

Table 11. Summary of the Assignment of the main experimental peaks.

Experimental peaks	Calculated data	Assignment(cluster)
110,111	112	$\nu_4(\text{F}_2)$ mode in GeBr_4
231,235	239	$\nu_1(\text{A}_1)$ mode in GeBr_4
254	255	$\nu_1(\text{A}_1)$ mode in GeSBr_3
270	273	$\nu_2(\text{A}_1)$ mode in GeS_2Br_2
286,288	288	$\nu_2(\text{A}_1)$ mode in GeS_3Br
345,349,350	348	$\nu_1(\text{A}_1)$ mode in GeS_4
370,371	374	$\nu_1(\text{A}_1)$ mode in ES-GeS_4

The Raman spectra of GeS_2 , GeS_3Br , GeSBr_2 glasses and liquid GeBr_4 are shown in Fig. 9, which reveal continuous variation from the characteristic of Raman bands of Ge-S-Br glasses with different S/Br ratio. The main variation of Raman bands are considered to result from the vibrational modes of basic structural units in Ge-S-Br glass [17]. The ab initio calculated data give evidence to enable us to apply the vibrational modes analysis of Ge-S-Br glass Raman spectra. The local coordination of Ge-S glass in short range order has been considered to obey the 8-N rule of the classical valence-bond theory [18], which means each Ge atom has fourfold coordination bonded to S atom. Therefore, it can be assumed that the basic structural units in Ge-S glass is made of GeS_4 tetrahedra. The strongest Raman spectra band around 345cm^{-1} in GeS_2 glass and 349cm^{-1} in GeS_3Br glass are assigned to symmetrical stretching vibration of GeS_4 tetrahedra,

which bring into correspondence with the $\nu_1(\mathbf{A}_1)$ mode (348cm^{-1}) of GeS_4 in calculated data in Table 4. In addition, the large shoulder at 370cm^{-1} have been assigned to the vibration mode in ES- Ge_2S_6 cluster. It corresponds to the calculated ν_1 vibrational mode (374cm^{-1}) of edge-shared (ES)- Ge_2S_6 cluster. On the other hand, there are similar character in Ge-Br system. The most intense band of Raman scattering spectrum in liquid GeBr_4 is at 235cm^{-1} , which can be attributed to $\nu_1(\mathbf{A}_1)$ symmetric vibrations of the GeBr_4 tetrahedron. It is consistent with the $\nu_1(\mathbf{A}_1)$ vibrational mode (239cm^{-1}) of GeBr_4 in calculated data in Table 4. The second strongest peak at 111cm^{-1} in Raman spectrum of liquid GeBr_4 is attributed to $\nu_4(\mathbf{F}_2)$ mode (112cm^{-1}) of the GeBr_4 tetrahedron. It indicates that the main Raman band of liquid GeBr_4 and GeS_2 binary glass system are influenced largely by the main vibrations mode of single GeBr_4 and GeS_4 tetrahedron rather than the main vibration mode related to topological connectivity among molecules. In addition, when Br atom introduced into glasses in the Ge-S system, Continuous alternation in the evolution of the Raman spectra in Ge-S-Br system is considered to be largely attributed to the vibrational modes related to $\text{GeS}_n\text{Br}_{4-n}$ ($n=1, 2, 3, 4$) structural units. For example, The peak of Raman spectra at 286cm^{-1} in GeS_3Br glass is attributed to $\nu_2(\mathbf{A}_1)$ mode (288cm^{-1}) in GeS_3Br mixed tetrahedron, which can also be considered to result in the peak at 288cm^{-1} in GeSBr_2 glass Raman spectra. The peak around 474cm^{-1} are corresponding to the \mathbf{A}_1 vibration mode of S_8 ring, because the high S content of GeS_3Br glass lead to generation of S_8 clusters vibration, which are calculated in my previous work[19]. Meanwhile, the occurrence of two strong bands at 152, 220 is also characteristic for the presence of S_8 molecules with an over stoichiometric content of sulphur in Ge-S-Br glasses. In addition, the small band shoulder around 270cm^{-1} bring into correspondence with the $\nu_2(\mathbf{A}_1)$ vibrational mode of GeS_2Br_2 cluster. The peak at 254cm^{-1} are related to $\nu_1(\mathbf{A}_1)$ mode in GeSBr_3 mixed tetrahedron. The summary of the assignment of the main experimental peaks are shown in Table 11.

4. Conclusion

The purpose of this work was to determine the degree of the stability of the basic clusters such as ethane-like(ETH) structure Ge_2S_6 and Ge_2Br_6 , edge-sharing(ES) $\text{Ge}_2\text{S}_2\text{S}_n\text{Br}_{4-n}$ ($n=0,1,2,3,4$) and isolated $\text{GeS}_n\text{Br}_{4-n}$ tetrahedron ($n=0,1,2,3,4$) in Ge-S-Br system. the Raman vibrational modes of those basic clusters have been calculated by ab initio calculation and the main vibrational modes of isolated $\text{GeS}_n\text{Br}_{4-n}$ tetrahedron were attributed by the point group theory. Compared with those experimentally measured from the Raman spectra of Ge-S-Br glass with different S/Br ratio. it was found that the calculated main vibrational modes are of basic clusters in well agreement with the main peaks of Raman spectra of Ge-S-Br system, which is reflecting molecular-like vibrational behavior of Raman spectra in Ge-S-Br glass in agreement with central-force network model theory. In addition, the main vibrational modes with different atomic ratio of S/Br in $\text{GeS}_n\text{Br}_{4-n}$ tetrahedron ($n=0,1,2,3,4$) by ab initio calculation indicate the shift of the main Raman scattering frequency of structural units of $\text{GeS}_n\text{Br}_{4-n}$ tetrahedron in Ge-S-Br system, which can be considered to the alteration of the nearest neighbor local surroundings rather than the topological connectivity of global glassy network. Moreover, the main symmetrical stretching vibrations related to Ge-S and Ge-Br with different atomic ratio of S/Br in $\text{GeS}_n\text{Br}_{4-n}$ tetrahedron are consistent with vibrational coupling theory.

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