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STRUCTURE AND VIBRATIONAL MODES OF Ge-S-Se GLASSES: RAMAN SCATTERING AND AB INITIO CALCULATIONS

HAN XUECAI*, SUN GUANGYING[a], LIU YU[a], YANG HONGBO,
LIU YONGHUA[b]
State key laboratory of silicate materials for architectures, Wuhan University of Technology, Wuhan, 430070, China
[a]*Kunming Institute of Physics, Kunming, 650223, China*
[b]*Institute of Quartz and Special Glasses, China Building Materials Academy, Beijing 100024, PR China*

Amorphous Ge-S-Se glasses samples were prepared by conventional melt-quenching techniques with Ge, S and Se of 99.99% purity. Raman spectra of samples were obtained by a Fourier transform Raman spectrometer (model RM-1000, Renishaw, UK). In addition, we have used a developed computational technique based on Hartree-Fork theory to study the Raman-active modes of five tetrahedral molecular units GeS_xSe_{4-x}(x=0, 1, 2, 3, 4), edge-sharing(ES)-Ge_2S_6, edge-sharing(ES)-Ge_2Se_6 and ethane-like(ETH)-Ge_2S_6,ethane-like(ETH)-Ge_2Se_6. The positions of the calculated stretching modes in the basic cluster models are in excellent agreement with observed Raman spectra. Moreover, the basic cluster results suggest that the changes of calculated stretching modes in GeS_xSe_{4-x}(x=0, 1, 2, 3, 4) are corresponding to vibrational coupling theory.

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Keywords: Ge-S-Se glass, Raman scattering, ab initio calculation

1. Introduction

Chalcogenide glasses have turned out to be a very bright field of experimental and theoretical research over the last 30 years, which is the outcome of an impressive variety of athermal photoinduced phenomena [1]. Among the most promising chalcogenide glasses, great attention has focused on the Ge-S and Ge-Se glasses due to their interesting physical properties. So, it is essential for us to understand details of short-range structural order of chalcogenide glasses in order to advance structure-properties correlations [2]. Raman spectroscopy has been considered to be a significant and powerful tool for investigating the structure of short-range order and network rigidity in chalcogenide glasses [3, 4, 5].Meanwhile, the Raman spectra is a simple and direct probe of the molecular structure of chalcogenide glass alloys, which are particularly easy to interpret [6, 7]. At present, there are several methods of investigation, which have been used to acquire insight into the structural properties of chalcogenide glassy systems such as ab inito method of Hartree-Fork theory [2], density functional theory (DFT) [8] and method of analogy between clusters, which have similar microstructure and reduced mass [9].

In this paper, Amorphous $Ge(S_xSe_{1-x})_2$, x=0、0.2、0.4、0.5、0.6、0.8、1.0 were prepared by conventional melt-quenching techniques. Then, the Hartree-Fork (HF) molecular orbital theory in Gaussian03 program package was used to calculate the basic structural units and the vibrational frequencies of four molecular units GeS_xSe_{4-x}(x=0, 1, 2, 3, 4) 、ES-Ge_2S_6、ES-Ge_2Se_6 and ETH-Ge_2S_6、ETH-Ge_2Se_6.

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*Corresponding author: chinesehanxuecai@yahoo.cn

2. Experimental

Samples of amorphous $Ge(S_xSe_{1-x})_2$ (x=0,0.2,0.4,0.5,0.6,0.8,1.0) were prepared by conventional melt-quenching techniques with Ge, S and Se of 99.99% purity. Afterwards, those powders with composition above were grounded and weighed exactly in appropriate quantity and fused quartz ampoules containing the raw powders were put in evacuated (Vacuum: 10^{-1} Pa) and then inserted into a rocking furnace. The batches were held at 450^0C for about 1 hour in order to promote the reaction completely among Ge, S and Se and subsequently melted in a rocking furnace at 950 ^{0}C for 12-18 hours. With a view to stabilizing the melts for homogeneity without rotation, we keep placing for 1 hour with close of the rock and these samples were quenched in ice water for a few seconds.

To study the Raman-active modes of GeS_xSe_{4-x}, we use finite clusters of atoms containing structural units, which are on the basis of central-force network model reported by Frank L.Galeener [10].The research has demonstrated that effective coupling of neighboring tetrahedral is zero when the angle of A-X-A for AX_2 glasses and 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[11]. We can obtain the critical angle values of Ge-S-Ge and Ge-Se-Ge are 107.11^0 and 136.44^0, respectively. In addition, with the calculation of molecular dynamics simulations in glassy GeS_2 [12] and the analysis of neutron and high-energy X-ray diffraction measurement in glassy $GeSe_2$ [13], it can be easily found that the average angle values of Ge-S-Ge and Ge-Se-Ge are smaller than the critical angle value, so the glassy system can be considered to be isolated tetrahedral for the sake of calculating the vibrational property of short-range structure.

According to the research reported in 1983，J.E.Griffiths[9] have measured the Raman spectra of bulk $Ge(S_xSe_{1-x})_2$ glasses and molecular of $GeCl_xBr_{4-x}$,which predicted the glass of $Ge(S_xSe_{1-x})_2$ may be expected consist of linked tetrahedral of [$GeSe_4$], [$GeSe_3S$], [$GeSe_2S_2$], [$GeSeS_3$] and [GeS_4] in diminishing proportions analogous to molecular [$GeBr_4$], [$GeBr_3Cl$], [$GeBr_2Cl_2$], [$GeBrCl_3$] and [$GeCl_4$].So it is reasonable to calculate the vibrational modes of $GeCl_xBr_{4-x}$ in order to approach the vibrational modes of GeS_xSe_{4-x}.On the other hand, some researches[10] show the hydrogen atoms in the cluster are used as pseudoatoms to replace the solid glass by finite molecular model, because the difference of large mass between H and the heavy atoms can prevent H-atom motion from mixing strongly in the Ge-X (x=S,Se) vibrational modes and any H-atom modes that do fall in this region are removed from the analysis of region for GeS_2 or $GeSe_2$[3].

Calculations reported in this work were performed with the Gaussian 03 and Gaussview 5.0 program package. And the Hartree-Fork molecular orbital theory was utilized in the present study in order to calculate the basic structural details and vibrational frequencies of five molecular units GeS_xSe_{4-x}(x=0, 1, 2, 3, 4) ES-Ge_2S_6、ES-Ge_2Se_6 and ETH-Ge_2S_6、ETH-Ge_2Se_6 with the finite molecular model method. The geometrical optimizations of the basic structures above under the ground state were at the UHF/LanL2DZ level, which was widely used to calculate the equilibrium geometries and spectroscopic properties of clusters, particularly in the investigation on clusters with heavy atoms.

3. Results

3.1 Analogy method

Table 1, Table 2, Table 3 show the Raman vibrational frequencies and Raman activity of [GeS_xSe_{4-x}], which are calculated by the data of [$GeCl_xBr_{4-x}$] plus the similarity factor of 0.921 （x=0、1、2、3、4）. From this three tables, we can see that there are four basic vibrational modes in [GeS_4] and [$GeSe_4$],which have the point group of T_d. When one S atom is replaced by Se atom, the point group of molecule change from T_d to C_{3v} and the basic vibrational modes increase from four to six. Then two S atoms are replaced by Se atoms, the point group of molecule change from C_{3v} to C_{2v}, and the basic vibrational modes increase from six to nine. In addition, ν_1-type mode in Table 1 is attributed to the symmetrical stretching vibration, however, ν_3-type mode is attributed to antisymmetric stretching vibration. Also we can find that the frequencies of ν_3 are higher than those of ν_1, which is accordance with the articles published past [14]. According to the Raman activity value, we can easily find the main Raman vibrational mode in each molecular unit.

Table 1. The Raman vibrational frequencies (cm^{-1}) and Raman activity （A^4、AMU) of molecule with T_d point group

T_d XY_4	$\nu_1(A_1)$ ν_s (XY)	$\nu_2(E)$ δ_d(YXY)	$\nu_3(F_2)$ ν_δ(XY)	$\nu_4(F_2)$ δ_d (YXY)
GeS_4	340	116	417	153
Scattering Activity	41.45	6.47	9.50	6.53
$GeSe_4$	198	71	295	101
Scattering Activity	39.41	6.08	11.20	7.30

Table 2. The Raman vibrational frequencies (cm^{-1}) and Raman activity （A^4、AMU） of molecule with C_{3v} point group

C_{3v} ZXY_3	$\nu_1(A_1)$ ν (XY_3)	$\nu_2(A_1)$ ν (XZ)	$\nu_3(A_1)$ δ (XY_3)	$\nu_4(E)$ ν(XY_3)	$\nu_5(E)$ δ_s(XY_3)	$\nu_6(E)$ ρ_r(XY_3)
GeS_3Se	374	270	107	410	143	102
Scattering Activity	21.85	26.24	8.62	11.06	6.37	6.29
$GeSSe_3$	218	388	110	277	122	79
Scattering Activity	35.40	17.10	7.05	9.50	7.54	6.20

Table 3. The Raman vibrational frequencies (cm^{-1}) and Raman activity （A^4、AMU） of molecule with C_{2v} point group

C_{2v} Z_2XY_2	$\nu_1(A_1)$ ν (XY)	$\nu_2(A_1)$ ν (XZ)	$\nu_3(A_1)$ δ (XY_2)	$\nu_4(A_1)$ δ (XZ_2)	$\nu_5(A_2)$ ρ_r(XY_2)	$\nu_6(B_1)$ ν (XY)	$\nu_7(B_1)$ ρ_m(XY_2)	$\nu_8(B_2)$ ν (XZ)	$\nu_9(B_2)$ ρ_r(XY_2)
GeS_2Se_2	384	241	136	84	95	403	124	308	132
Scattering Activity	19.16	31.04	7.98	6.48	5.97	12.50	6.20	7.82	8.01

3.2 Direct computing by terminate H atom

In order to study the Raman-active modes of GeS_xSe_{4-x}, the finite clusers of atoms should be obtained containing structural units expected to be significant in the glasses. Dangling bonds on the cluster surfaces are terminated by H atoms, which provide a better model the chemical environment of the glasses. Because of the large mass difference between H and the heavy atoms(Ge、S、Se),the vibrational modes related to H-atoms lie well outside the spectral region of Ge-S or Ge-Se vibrational modes. It is easy to remove any H-atom modes that do fall in this region from the analysis. All vibrational modes can be attributed as follows [8]:

Table 4. The Raman vibrational frequencies (cm-1) and Raman activity （A^4、*AMU*）
of molecule with T_d *point group*

T_d XY_4	$\nu_1(A_1)$ ν_s (XY)	$\nu_2(E)$ δ_d(YXY)	$\nu_3(F_2)$ ν_δ(XY)	$\nu_4(F_2)$ δ_d (YXY)
GeS_4	332	123	416	153
Scattering Activity	77.16	2.30	20.19	11.47
$GeSe_4$	194	68	295	98
Scattering Activity	48.70	9.91	13.93	8.40

Table 5. The Raman vibrational frequencies (cm^{-1}*) and Raman activity* （A^4、*AMU*）
of molecule with C_{3v} *point group.*

C_{3v} ZXY_3	$\nu_1(A_1)$ ν (XY_3)	$\nu_2(A_1)$ ν (XZ)	$\nu_3(A_1)$ δ (XY_3)	$\nu_4(E)$ ν(XY_3)	$\nu_5(E)$ δ_s(XY_3)	$\nu_6(E)$ ρ_r(XY_3)
GeS_3Se	367	265	141	395	158	110
Scattering Activity	40.32	42.88	12.95	21.36	17.68	3.66
$GeSSe_3$	208	392	111	303	113	90
Scattering Activity	45.21	31.42	9.04	17.03	9.04	2.51

Table 6. The Raman vibrational frequencies (cm-1) and Raman activity （A^4、*AMU*）
of molecule with C2v point group.

C_{2v} Z_2XY_2	$\nu_1(A_1)$ ν (XY)	$\nu_2(A_1)$ ν (XZ)	$\nu_3(A_1)$ δ (XY_2)	$\nu_4(A_1)$ δ (XZ_2)	$\nu_5(A_2)$ ρ_r(XY_2)	$\nu_6(B_1)$ ν (XY)	$\nu_7(B_1)$ ρ_m(XY_2)	$\nu_8(B_2)$ ν (XZ)	$\nu_9(B_2)$ ρ_r(XY_2)
GeS_2Se_2	383	236	127	82	102	403	120	309	125
Scattering Activity	33.98	40.07	11.88	13.58	2.35	24.95	5.26	11.97	9.33
Intensity	2.5	3.6	1.5	1.3	0.3	1.9	0.7	1.9	1.4

Apart from the molecule of GeS_xSe_{4-x}, ES-Ge_2S_6、ES-Ge_2Se_6 and ETH-Ge_2S_6、ETH-Ge_2Se_6 are also important basic units in the Ge-S-Se glass system, So we should pay more attention about them. According to the calculation by Gaussian software, there are 12 basic vibrational modes in ETH-Ge_2S_6 and ETH-Ge_2Se_6.In addition, there are 18 basic vibrational modes in ES-Ge_2S_6 and ES-Ge_2Se_6.the data are as follows:

Table 7. The basic calculated vibrational modes of ETH-Ge2S6 and ETH-Ge2Se6.

Vibrational mode	ETH-Ge_2S_6	ETH-Ge_2Se_6
ν_1	373	299
ν_2	257	176
ν_3	110	66
ν_4	14	8
ν_5	346	218
ν_6	149	110
ν_7	394	295
ν_8	164	129
ν_9	116	98
ν_{10}	400	291
ν_{11}	155	100
ν_{12}	65	44

Table 8. The main vibrational modes of ETH-Ge_2S_6 and ETH-Ge_2Se_6

D_{3d}	$\nu_1(A_{1g})$	$\nu_2(A_{1g})$
X_2Y_6	$\nu_s\,(XY_3)$	$\nu(XX)$
Ge_2S_6	373	257
Ge_2Se_6	299	176

Table 9. The basic calculated vibrational modes of ES-Ge_2S_6 and ES-Ge_2Se_6

Vibrational mode	ES-Ge_2S_6	ES-Ge_2Se_6
ν_1	431	315
ν_2	363	219
ν_3	171	144
ν_4	205	190
ν_5	68	44
ν_6	337	244
ν_7	136	99
ν_8	421	308
ν_9	31	15
ν_{10}	187	113
ν_{11}	416	306
ν_{12}	124	79
ν_{13}	398	286
ν_{14}	112	65
ν_{15}	166	78
ν_{16}	406	294
ν_{17}	328	190
ν_{18}	132	86

Table 10. The main vibrational modes of ES-Ge_2S_6 and ES-Ge_2Se_6

D_{2h}	$\nu_1(A_{1g})$	$\nu_2(A_{1g})$
X_2Y_6	ν (XY)	ν(XY)
Ge_2S_6	431	363
Ge_2Se_6	315	219

4. Discussion

Table 11 shows the Raman main vibrational mode of GeS_xSe_{4-x} (x=0, 1, 2, 3, 4) between calculated data and experimental data. We can see that the Raman main vibrational modes calculated by Gaussian are in accordance with those of experimental data. However, from the table, not all main vibrational modes of GeS_xSe_{4-x} are ν_1-type modes, which is quite different from the research of J.E.Griffith in his paper published in the year 1983, where they considered that all main vibrational modes of GeS_xSe_{4-x} are ν_1-type, but we can see the Raman main vibrational modes of [GeS_3Se] and [GeS_2Se_2] are ν_2-type.

Table 11 also shows the frequency variation of Raman main vibrational modes in different basic units. For example, the frequency of the Raman main vibrational mode of [GeS_4] is about 340cm^{-1}, however, the frequency decreases sharply till 270cm^{-1}, when one S atom is replaced by Se atom. Differential between [GeS_4] and [GeS_3Se] is approximately 70cm^{-1}, but the differential between [GeS_3Se] and [GeS_2Se_2] is about 29cm^{-1}, which is similar to the differential between [GeS_2Se_2] and [$GeSSe_3$] and the differential between [$GeSSe_3$] and [$GeSe_4$]. According to the analysis of vibrational mode and the data in table, only the main vibrational mode of [GeS_4] in this five basic units is related to Ge-S stretching vibration, and others are all related to Ge-Se stretching vibration. This is because the atomic mass of Se is heavier than that of S, and the electron cloud of Se atom change easier than that of S atom. So the Raman activity of Ge-Se bond is larger than that of Ge-S bond, and the interaction force of Ge-Se is smaller than that of Ge-S. Based on the molecular spectroscopy theory as follows:

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

Where f is a constant related to the bond strength, and μ is the discount mass. So when S atoms are replaced by Se atoms, value of f is smaller and μ is bigger, which leads to a decrease of frequency. Fig1 demonstrates the calculated Raman spectroscopy of GeS_xSe_{4-x} by Gaussian03.We can easily find that the highest peak of each tetrahedral unit moves to lower frequency with the increase of Se atoms.

Table 12 illustrates the Ge-S symmetrical stretching vibrations of GeS_xSe_{4-x}, however, Table 13 shows the Ge-Se symmetrical stretching vibrations of GeS_xSe_{4-x}. From the data in these two tables, the law of frequency shifts related to Ge-S bond and Ge-Se bond are similar. For example, there is one Ge-S bond in the molecule of [$GeSSe_3$] and the frequency of Ge-S stretching vibrational mode is 392cm^{-1}. When the Se atom is replaced by S atom in [$GeSSe_3$], the stretching vibration of two Ge-S bonds in [GeS_2Se_2] produce coupling, which are divided into two vibrational modes. One is called symmetrical stretching vibration [$\nu_1(A_1)$], the other is called asymmetrical stretching vibration [$\nu_6(B_1)$]. The frequencies are 383cm-1 and 403cm^{-1} respectively. When there is one Se atom replaced by S atom in [GeS_2Se_2], the stretching vibration of three Ge-S bonds in [GeS_3Se] produce coupling, which are also divided into two vibrational modes. One is called symmetrical stretching vibration [$\nu_1(A_1)$], the other is called asymmetrical stretching vibration [$\nu_4(E)$]. The frequencies are 367cm^{-1} and 395cm^{-1} respectively. When the final Se atom is replaced by S atom in [GeS_3Se], the stretching vibration of four Ge-S bonds in [GeS_4] produce coupling, which are divided into two vibrational modes. One is called symmetrical stretching vibration [$\nu_1(A_1)$], the other is called asymmetrical stretching vibration [$\nu_3(F_2)$]. The frequencies are 340cm^{-1} and 407cm^{-1} respectively. These phenomena can be explained by vibrational coupling theory. For instance, there is only one Ge-S bond in the molecule of [$GeSSe_3$], the Ge-S bond in the [$GeSSe_3$] is not coupled. However, the coupling of stretching vibration produces when there is more than one Ge-S bond in the molecule of GeS_xSe_{4-x}, which divided into symmetrical vibrational mode and asymmetrical vibrational mode. Generally speaking, the frequency of asymmetrical vibrational mode is higher than that of symmetrical vibrational mode in the same molecule. So the frequencies of symmetrical vibrational mode decrease with the increase of number of Ge-S bond. Also, the vibrational frequencies shift related to Ge-Se bond can be interpreted by vibrational coupling theory,which is the same as the explanation of Ge-S bond.

Table11. The Raman main vibrational mode between calculated data and experimental data

Type	Main vibrational mode		Calculated (cm^{-1})	Experimental (cm^{-1}))
GeS_4	$\nu_1(A_1)$	ν_s (GeS)	340	340
GeS_3Se	$\nu_2(A_1)$	ν (GeSe)	270	248
GeS_2Se_2	$\nu_2(A_1)$	ν (GeSe)	241	232
$GeSSe_3$	$\nu_1(A_1)$	ν ($GeSe_3$)	218	218
$GeSe_4$	$\nu_1(A_1)$	ν_s (GeSe)	198	203

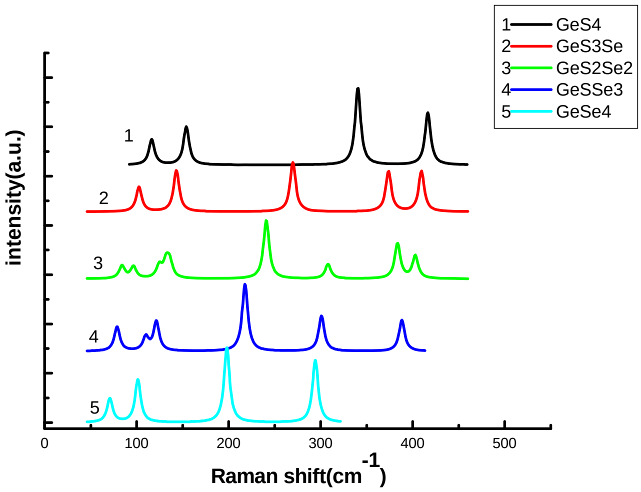

Fig 1.the calculated Raman spectroscopy of GeS_xSe_{4-x} by Gaussian03

Table 12. The Ge-S symmetrical stretching vibrations of GeS_nSe_{4-n} calculated by Gaussian software

Type	Ge-S symmetrical stretching vibration		Calculated (cm^{-1})
GeS_4	$\nu_1(A_1)$	ν_s (GeS)	340
GeS_3Se	$\nu_1(A_1)$	ν (GeS3)	374
GeS_2Se_2	$\nu_1(A_1)$	ν (GeS)	384
$GeSSe_3$	$\nu_2(A_1)$	ν (GeS)	388

Table 13. The Ge-Se symmetrical stretching vibrations of GeS_xSe_{4-x} calculated by Gaussian software

Type	Ge-Se Symmetric stretching vibration mode		Calculated (cm^{-1})
$GeSe_4$	$\nu_1(A_1)$	ν_s (GeSe)	198
$GeSSe_3$	$\nu_1(A_1)$	ν ($GeSe_3$)	218
GeS_2Se_2	$\nu_2(A_1)$	ν (GeSe)	241
GeS_3Se	$\nu_2(A_1)$	ν (GeSe)	270

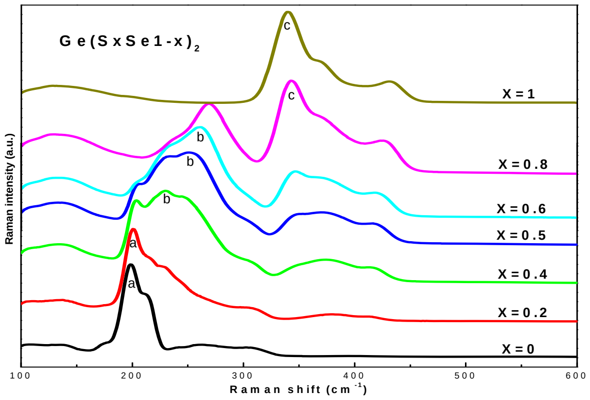

Fig 2 Raman spectroscopy of $Ge(S_xSe_{1-x})_2$ glass system.

Fig 2 shows the Raman spectroscopy of $Ge(S_xSe_{1-x})_2$ glass system, and x=0、0.2、0.4、0.5、0.6、0.8、1.0. It can be seen that there are two obviously range of peak in the whole area of Raman spectroscopy, which are located in 180-300cm^{-1} and 300-450cm^{-1} respectively. According to a paper published in the past [15] and data calculated by Gaussian, the two main peak areas can be attributed to the stretching vibrational mode related to Ge-Se bond and related to Ge-S bond respectively. With the decrease of percentage of S in $Ge(S_xSe_{1-x})_2$ system, the intensity of main peak in the Raman spectroscopy reduces and the peak in stretching vibrational area disappear when the percentage of S is close to 0. At the same time, the peaks in the stretching vibrational area related to Ge-Se move to lower frequency with the higher intensity.

The Raman spectroscopy of GeS_2 and $GeSe_2$ system are very simple compared with that of $Ge(S_xSe_{1-x})_2$ system. So we can analyze these two systems first. According to T.G.Edwards [16], the shoulder around 180cm^{-1} in $GeSe_2$ Raman spectroscopy is due to the stretching vibration related to Ge-Ge bond, which is accordance with the calculated data that attributed to the $\nu_3(A_{1g})$ mode in ES- Ge_2Se_6.And the main Raman peak of $GeSe_2$ in 197cm^{-1} are assigned to the symmetrical stretching vibration of [$GeSe_4$] unit, which is attributed to the $\nu_1(A_1)$ mode. In addition, the shoulder in 214cm^{-1} is due to the vibrational mode of the two inner Se in the dimer in ES-Ge_2Se_6, which can be attributed to the $\nu_2(A_{1g})$ mode. The peak around 310cm^{-1} is mainly attributed to the $\nu_1(A_{1g})$ mode of ES- Ge_2Se_6 and it is also partially assigned to the $\nu_3(F_2)$ mode of [$GeSe_4$] unit. On the other hand, the main Raman peak of GeS_2 system in 340cm^{-1} is related to the symmetrical stretching vibration of [GeS_4] unit with $\nu_1(A_{1g})$ mode [17]. The shoulder of the main Raman peak in 370cm^{-1} is assigned to the $\nu_2(A_{1g})$ mode in ES- Ge_2S_6[18], moreover,the peak around 430cm^{-1} is mainly attributed to the $\nu_1(A_{1g})$ mode of ES- Ge_2S_6 and partially assigned to the $\nu_3(F_2)$ mode of [GeS_4] unit.

Apart from GeS_2 and $GeSe_2$ system, the Raman spectroscopies of Ge $(S_xSe_{1-x})_2$ glass system are a bit complicated. It can be seen from Fig 2 that the relative intensity change of the main peak is consistent with the change of the relative ratio of S/Se in these glasses. According to the calculated data, there are five possible GeS_xSe_{4-x} units with n=0, 1, 2, 3, 4. Among them, four units can contribute to stretching vibrational mode related to Ge-Se bond, namely [GeS_3Se], [GeS_2Se_2], [$GeSSe_3$] and [$GeSe_4$]. With increasing Se in the units, the frequency would be expected to be lower. At the same time, the relative intensity in Ge-Se vibration area are higher. However, the relative intensity in Ge-S vibration area is lower. The peak around 265cm^{-1} is due to $\nu_2(A_1)$ mode in [GeS_3Se] unit. In addition, the shoulder about 230cm^{-1} is attributed to $\nu_2(A_1)$ mode in [GeS_2Se_2]. Finally, the peak around 218cm^{-1} is assigned to $\nu_1(A_1)$ mode in [$GeSSe_3$].

5. Conclusion

In conclusion, ab initio Raman vibrational modes calculations were carried out on basic units of Ge-S-Se glasses. It can be shown that change of point group and symmetry corresponds to the ratio of S/Se in GeS_xSe_{4-x} and not all main Raman vibrational modes are attributed to ν_1,when compared the results of vibrational frequencies and modes in GeS_xSe_{4-x}. Furthermore, Raman vibrational modes of GeS_xSe_{4-x} are 340cm^{-1}、248cm^{-1}、232cm^{-1}、218cm^{-1}、203cm^{-1} and the shifts of vibrational frequencies are consistent with the change from stretching vibration of Ge-S to stretching vibration of Ge-Se. Finally, the stretching vibrational modes of GeS_xSe_{4-x} can be divided in Ge-S relation vibration and Ge-Se relation vibration, which are consistent with vibrational coupling theory.

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