

FIRST PRINCIPLES CALCULATIONS OF VIBRATIONAL FREQUENCIES OF CLUSTERS IN SiSe GLASS AND COMPARISON WITH EXPERIMENTAL RAMAN DATA

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ABSTRACT

The vibrational frequencies of several clusters of atoms, Si₄Se, CS-Si₄Se, SiSe₄, CS-SiSe₄, SiSe₃, Si₃Se, Si₂Se₃, Si₃Se₂, L-Si₄Se₅, and ES-Si₂Se₆. In the pyramidal configuration Si₄Se shows nine different phonon modes at 233, 398, 416, 464, 478, 501, 601, 631 and 686 cm⁻¹. When atoms are rearranged as Si₂SeSi₂ stable configuration has only one low lying mode at 56 cm⁻¹. Similarly, planar ion-exchange cluster, corner sharing (CS), CS-SiSe₄ shows only two vibrational modes at 75 and 96 cm⁻¹. The pyramidal SiSe₄ has the expected vibrations of symmetries A₁, A₂ and E. The pyramidal configurations have the normal symmetries which break upon rearranging atoms. By means of ab initio predictions of vibrational frequencies of clusters of atoms, CS-Si₄Se, linear chain mode (CM), CM-Si₄Se₅, Si₂Se₃, Si₃Se₂, Si₄Se and comparison with those found experimentally from the Raman spectra in SiSe₂ glass, we are able to identify that these clusters are present in the glass.

Keywords: SiSe glass, raman, Ab initio, vibrations.

INTRODUCTION

In recent years, there has been considerable interest in the understanding of physical properties of glasses. It has been reported that Ge_xAs_xS_{1-2x} glass exhibits a rigidity transition at a critical value of x which determines the sulphur concentration relative to Ge and As (Qu and Boolchand, 2005). The arrangement of atoms keeps changing with time and the groups of atoms self-organize the orientations which is reflected by the long relaxation times (Boolchand *et al.*, 2005). At a particular concentration in As_xS_{1-x} vibrational modes appear which means that the vibrational spectra of glasses differ considerably from that of the corresponding crystals (Georgiev *et al.*, 2003). Apparently, the glass consists of several different clusters which are smaller than crystallographic cells, often bound by linear chain of atoms. Therefore, vibrations of linear chain type material are predicted in the glass phase. A random network of atoms may form a back-bone type structure. Our recent calculations show that several clusters and linear modes are found in GeSI glass (Devi *et al.*, 2005). Chains of phosphorous and sulphur atoms are also found in Ge_xP_xS_{1-2x} glass along with several clusters of atoms (Kassim *et al.*, 2007a). In the case of GaAs, we find that removing the Ga atoms, one at a time and replacing them by Al atoms leads to a critical concentration at which the electrons are highly correlated (Kassim *et al.*, 2007b).

In the present paper, we report the results of our ab initio calculations of vibrational frequencies of Si₄Se, CS-Si₄Se,

SiSe₄, CS-SiSe₄, SiSe₃, Si₃Se, Si₂Se₃, Si₃Se₂, L-Si₄Se₅, Si₂Se₂, and ES-Si₂Se₆ where CS means corner sharing which is different from pyramidal, L means linear mode and ES means edge sharing configuration of atoms. We compare the calculated values of vibrational frequencies with those measured by the Raman spectra of Si_xSe_{1-x} glass. In this way, we identify the clusters present in the glass.

CALCULATIONS

We use the density functional theory computer programme called the Accelrys run on IBM p.690 with 40 processors of power-5 type at 1.7GHz. Recently, we have also started looking at the Amsterdam Density Functional theory programme. The results given here are those obtained from Accelrys. The programmes optimize the bond lengths and angles for the minimum energy and calculate the vibrational spectra from the first principles.

(i) The pyramidal Si₄Se has 4 atoms of Si on the base and one Se atom on top. The Si-Si distance is 0.246 nm and Se-Si bond distance is 0.2338 nm. The frequencies (intensities) calculated from the first principles are found to be 233(0.197), 398(0.240), 416(0.226), 478(0.013), 501(0.004), 601(0.192), 631(0.069), 686(0.009) cm⁻¹ (arb. units). We show the calculated spectrum in Fig. 1. Because of the pyramidal structure all of the Si atoms are on one side of Se and it is also possible to optimize with two Si on the right and two on the left. We call this as corner sharing CS-Si₄Se and the first principles optimization for this system gave Si-Si distance 0.223 nm

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and large Si-Se bond distance of 0.402 nm. The vibrational spectrum now has only one peak at 56 cm^{-1} as shown in Fig. 2. Thus in going from pyramidal to corner sharing arrangement of atoms there is clearly “disappearance” of modes. This phenomenon is similar to that of “soft phonons” where the frequency of a phonon mode goes to zero. In the present case, the intensity goes to zero so that we can call them “soft amplitude” phonons. Usually, for a harmonic oscillator $\langle a_k \rangle = 0$. However, when a distortion is introduced $\langle a_k \rangle = (\Delta/\hbar\omega)\delta_{k,Q}$ where a_k is a phonon operator with k as the wave vector, Δ is the energy gap due to distortion and it is divided by a single particle energy to make it dimensionless. There are other ways of making it dimensionless such as by using interaction energy instead of single-particle energy. Similarly, the intensity is made to go to zero by setting the operators of the matrix element to zero.

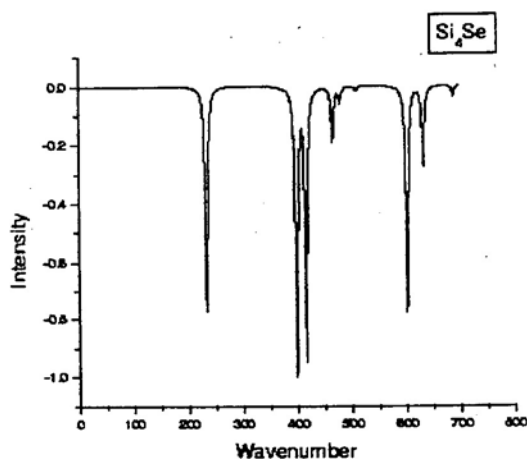


Fig. 1. The ab initio calculated vibrational spectrum of Si_4Se .

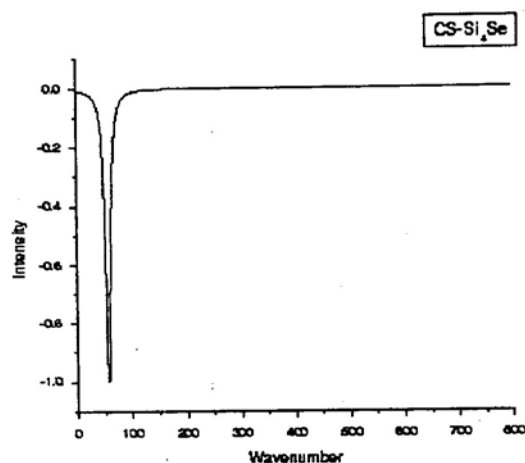


Fig. 2. The ab initio calculated vibrational spectrum of $\text{CS-Si}_4\text{Se}$.

(ii) The cluster SiSe_4 is well behaved pyramidal system with its vibrations corresponding to C_{4v} symmetry. The C_{3v} gives A_1 , A_2 and E and in going to SiSe_4 , the mode of

symmetry E is also split so that the calculated modes occur at frequencies (intensities) of $356(0.051)$, $358(0.087)$, $528(0.386)$ and $604(0.474) \text{ cm}^{-1}$ (arb. units) as shown in Fig.3. When corner sharing configuration is made, CS-SiSe_4 shows only two modes one at $75(0.0750)$ and the other at $96(0.249) \text{ cm}^{-1}$ (arb. units) shown in Fig. 4.

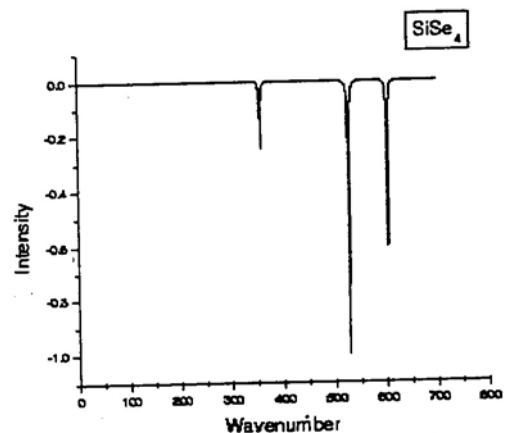


Fig. 3. The ab initio calculated vibrational spectrum of SiSe_4 .

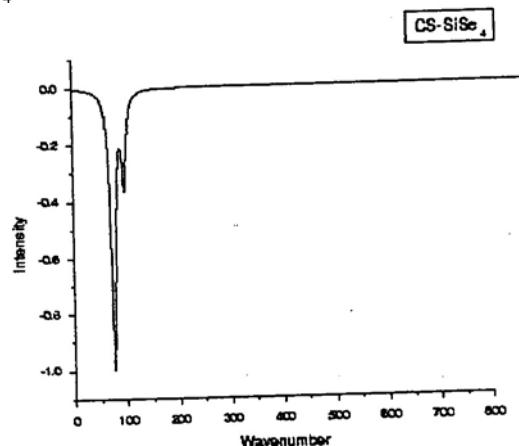


Fig. 4. The ab initio calculated vibrational spectrum of CS-SiSe_4 .

(iii) The cluster SiSe_3 is pyramidal with Si-Se bond distance 0.227 nm and Se-Se bond distance 0.240 nm. That means that all of the three Se atoms form a triangle with one Si on top. It is also possible not to put all of the three Se atoms on one side of Si. It may be possible to stabilize in such a way that two Se are on one side and one Se on the other side of Si. In the case of pyramidal configuration, the calculated vibrational frequencies (intensities) are found to be $299(0.134)$, $408(0.046)$, $424(0.261)$ and $602(0.134) \text{ cm}^{-1}$ (arb. units). The spectrum calculated from the first principles is shown in Fig. 5. When we exchange the atoms, the resulting cluster Si_3Se gives Si-Si bond distance 0.207 nm and Si-Se bond distance is 0.2304 nm. The calculated vibrational frequencies in this case are $375(0.185)$, $453(0.685)$, $553(0.052)$ and $700(0.075) \text{ cm}^{-1}$ (arb. units). The spectrum

obtained from the first principles calculations is shown in Fig. 6. The atomic number of Se is 34 and its electronic configuration is $4s^2p^4$, whereas the atomic number of Si is 14 and the electronic configuration is $3s^2p^2$. Adding more Si reduces the mass so that we expect higher frequencies for Si_3Se than for SiSe_3 . Indeed 700 cm^{-1} is higher than 602 cm^{-1} which we can assign to “mass effect”. The effect of ion exchange thus appears like a mass effect. However, Si also has 4 vacancies in the 3p shell whereas Se has only two in the 4p shell. Therefore, there is also a strong effect of vacancies in Si. The Si atoms work like acceptors of electrons whereas Se can donate 4 electrons.

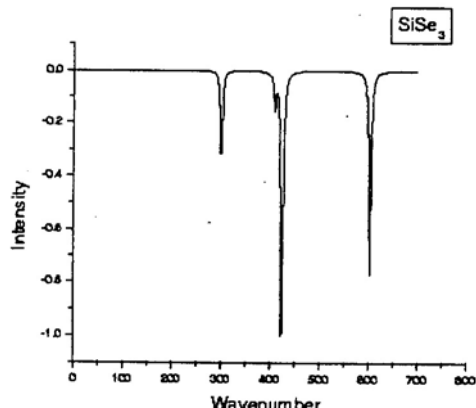


Fig. 5. The ab initio calculated vibrational spectrum of SiSe_3 .

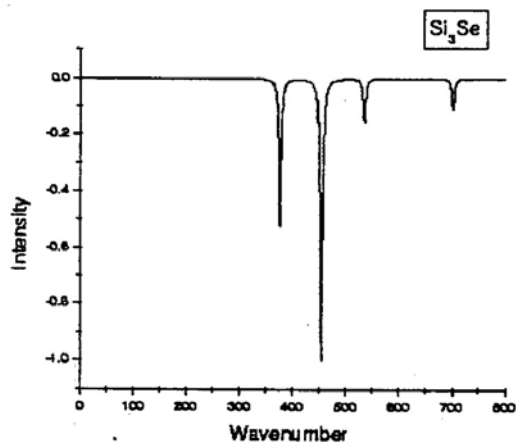


Fig. 6. The ab initio calculated vibrational spectrum of Si_3Se .

(iv) The cluster Si_2Se_3 . In this cluster three Se atoms are in a triangle with one Si on top and another Si symmetrically on bottom as in a bipyramid. In the optimized configuration Se-Se distance is 0.2408 nm and Se-Si bond distance is 0.2275 nm. The calculated frequencies (intensities) are 211(0.124), 343(0.044), 353(0.035), 358(0.085), 416(0.079), 538(0.288), 567(0.291), 586(0.048) cm^{-1} (arb. units). The computed spectrum is shown in Fig. 7. In the ion exchange cluster Si_3Se_2 , the Se-Si bond distance is 0.294 nm and Se-Se

bond distance is 0.242 nm and the calculated frequencies (intensities) are 246 (0.134), 351 (0.046), 419 (0.261), 439 (0.134), 502 (0.112), 561 (0.107), 601 (0.161) and 634 (0.041) cm^{-1} (arb. units) as shown in Fig.8.

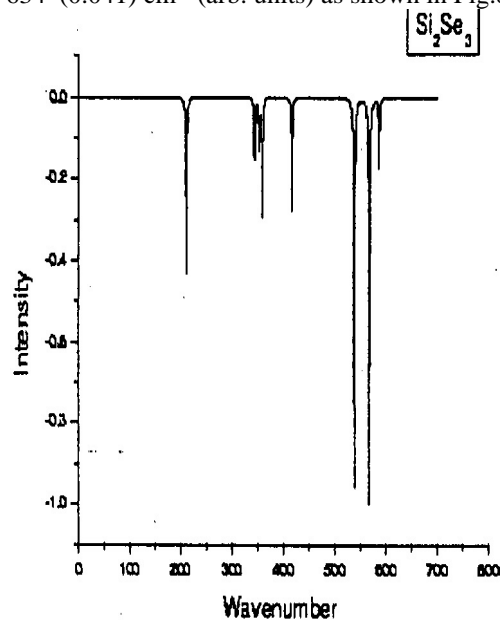


Fig. 7. The ab initio calculated vibrational spectrum of Si_2Se_3 .

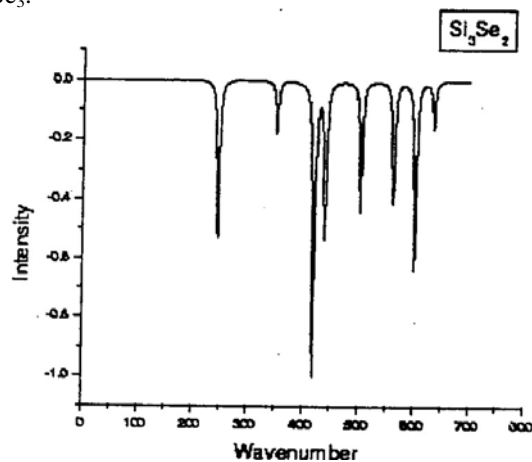


Fig. 8. The ab initio calculated vibrational spectrum of Si_3Se_2 .

(v) The cluster Si_4Se_5 . Some of the glasses have a fibre type structure. Therefore, we make a model of linear chain (CM) model with Si and Se on alternate sites. The CM- Si_4Se_5 gives the following frequencies (intensities): 96 (0.007), 116 (0.073), 156 (0.013), 157 (0.028), 424 (0.044), 457 (0.378), 504 (0.431), 508 (0.015) cm^{-1} (arb. units). The vibrational spectrum calculated from the first principles for this cluster is shown in Fig. 9.

(vi) The cluster Si_2Se_2 . This is a small pyramidal structure with Si-Se bond distance of 0.227 nm, Se-Se distance of 0.243 nm and Si-Si distance 0.218 nm. The calculated frequencies (intensities) are 316 (0.193), 442 (0.506), 515

(0.188), 659 (0.110) cm^{-1} (arb. units) as they should belong to irreducible representations A_1 , A_2 and E with E further split in the C_{2v} point group. The spectrum calculated from the first principles is shown in Fig. 10.

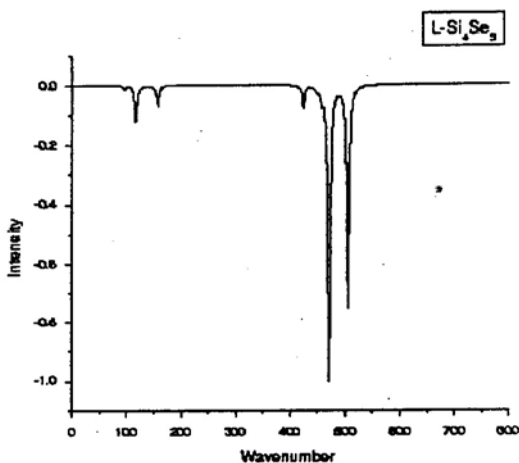


Fig. 9. The ab initio calculated vibrational spectrum of L-Si₄Se₅.

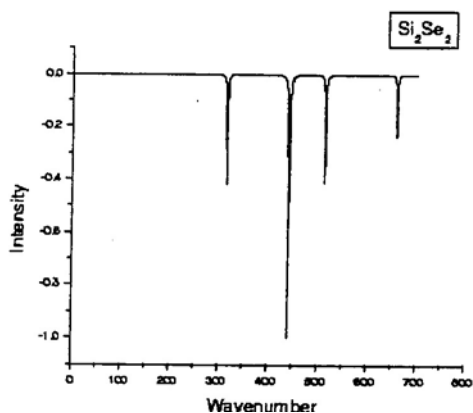


Fig. 10. The ab initio calculated vibrational spectrum of Si₂Se₂.

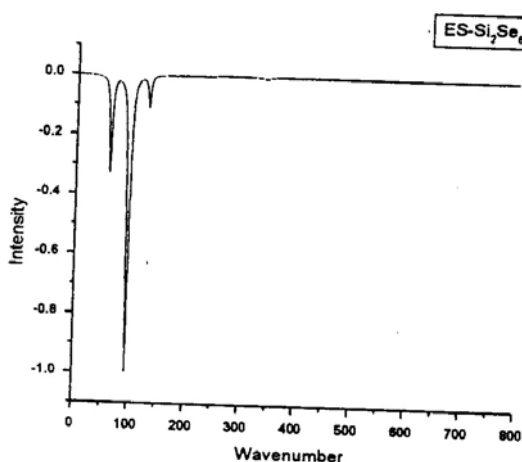


Fig. 11. The ab initio calculated vibrational spectrum of ES-Si₂Se₆.

(vii) The edge sharing model, ES-Si₂Se₆, is made by putting three Se in a line and another three below them. Then two Si are placed in the centres of the two squares formed by six Se. The Se-Se bond distance is 0.238 nm and Se-Si bond distance is 0.393 nm. The frequencies (intensities) calculated for this model are, 60 (0.224), 94 (0.119), 95 (0.584), 129 (0.671) cm^{-1} (arb. units). The modes at 94 and 95 cm^{-1} are obviously generated from the doubly degenerate representation. The modes occurring below 100 cm^{-1} are called “bosons” as they are in the continuum of phonons. The spectrum calculated from the first principles, in this case, is shown in Fig. 11.

Table 1. The ab initio calculated and measured Raman frequencies in a glass of SiSe.

S. No.	Measured cm^{-1}	Calculated cm^{-1}	Model
1	68	56	CS-Si ₄ Se
2	110	116	CM-Si ₃ Se ₄
3	216	211	Si ₂ Se ₃
4	242	246	Si ₃ Se ₂
5	350	358	Si ₂ Se ₃
6	465	464	Si ₄ Se

COMPARISON WITH THE EXPERIMENTAL DATA

The experimental measurements of the Raman spectra of SiSe glass have been carried out several times (Tenhover *et al.*, 1983a, Tenhover *et al.*, 1983b, Griffiths *et al.*, 1984, Sugai 1986, Selvanathan *et al.*, 2000). The vibrations of frequencies (symmetries) 68(E), 110(F₂), 216(A₁^B), 242 (A₁), 350 and 465 (F₂) cm^{-1} are clearly seen in the glassy state. When the value of x in Si_xSe_{1-x} is varied from 0.15 to 0.22 most of the Raman activity is found near 210, 225 and 260 cm^{-1} and there is a stiffness transition. We now have a method to identify the clusters which are present in the glass. We compare the experimental values of the Raman frequencies with those calculated and hence identify the clusters. Such a comparison is given in Table 1. We see that we have found a new method to identify the clusters present in the glass. The frequencies calculated from the first principles are useful for the study of experimental Raman spectra. We also find the ion exchange effect as well as the variations in the symmetries. Selvanathan *et al.* (2000), by varying the relative concentrations of Si:Se report that major Raman activity is near 210, 225 and 260 cm^{-1} . These frequencies are near the calculated values of 211, 233(pyramidal Si₄Se) and 246 (Si₃Se₂). The importance of linear mode is also quite clear in terms of providing the required strength to the glass. However, the glass tends to shatter so that small clusters are surely present. It may be

noted that clusters are not the crystallites or microcrystals. These clusters are smaller than the unit cell of a crystal. The glass is thus composed of sub-crystallographic objects and fibre like linear chains of atoms.

CONCLUSIONS

We have performed the first principles calculations of several clusters containing Si and Se atoms. We have successfully calculated the vibrational frequencies and compared them with those measured by the Raman spectra. We have identified the clusters present in the glass. We are able to find the effect of "ion exchange" as well as that of symmetries. It may be noted that in the fundamental exchange only the electrons are exchanged but in the present case an ion as a whole, is exchanged.

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