# Appendix A

# Review of Raman Spectra in Glasses

Glass is a unique material which forms an interesting topic to study. We can see glass everywhere in our life. The most obvious characteristic of the glass is its transparency to visible light. Glass has been used as a window, in sliding doors, and in various optical devices such as lenses. The windows in the spectrographs are often made of a glass. This non-crystalline and amorphous solid with covalent bonds makes it interesting to study the strength and elastic properties. Silicon oxide (SiO) is one of the well known glasses but researchers found another type of glasses, the chalcogenide glasses that contain one of the chalcogen element in periodic table like sulphur, selenium or tellurium [92]. While fluoride glass and heavy metal oxide also categorized as special glasses that are of interest to study.

The transition of glasses from floppy to rigid state haven been discovered. The floppy mode refers to zero frequency modes in real systems. To describe an elastic property of chalcogenide glass, Thorpe has introduced rigidity percolation exponent [23]. This theory describes the transition from floppy to rigid state. Meanwhile, Thorpe *et al.* [93] also found another phase which is rigid but unstressed. This is different with

rigid stressed phase. It is call intermediate phase that self-organizes between floppy and stressed rigid phases. This system has two transitions, the rigidity transition from floppy to unstressed rigid and floppy to stressed rigid [94]. The self-organization minimizes the stress in the system.

The study of self-organization in random network glasses becomes a major problem for understanding of the intermediate phase. Many papers have been published to explain this finding by using experimental and theoretical techniques. Micoulaut and Phillips [95] in 2007 have shown the existing of intermediate phase both in experimentally and theoretically. The phase occurs when a network is self-organized. The self-organization can avoid stress when network becomes rigid. The transition from rigid-unstress to rigid-stress phase called rigidity transition happens in random networks and found by experiments on chalcogenide glasses [23].

The randomness of the network has been introduced in the early research. The structure is viewed as a network of bonds between atoms that is topologically disordered, yet as implied by the work, the glass has no macro or mesoscopic voids and maybe as dense as the crystalline phase [96]. The randomness of the network is important to understand the structure, but some concern remains. Thorpe [93] has discussed the problem of the randomness in network glasses. Even though glasses form at high temperatures where entropic effects are dominant, it is important to consider the energy that can favor particular local structural arrangements over others. A more subtle effect is the structure of glass. This correlation is referred to as self-organization. The network self-organizes to avoid stress. In the intermediate phase, the network is rigid, but unstressed [96]. The structural changes occurring in the intermediate phase should have a tendency to self-organize the network.

Based on the work of Phillips, Thorpe *et al.* [23, 93, 94] has introduced the concept of rigidity percolation to describe how an elastic network goes from floppy to rigid as constraints are added to it. This section showed only a simple explanation about

rigidity percolation. To describe the mean coordination, Thorpe [23] has used the $Ge_xAs_ySe_{1-x-y}$ to examine a large covalent network with the total number of atoms, N and $n_r$ atoms with coordination r where r = 2, 3 or 4,

$$N = \sum_{r=2}^{4} n_r, \tag{A.1}$$

and the mean coordination can be define as,

$$\langle r \rangle = \frac{\sum_{r=2}^{4} r n_r}{\sum_{r=2}^{4} n_r} = 2 + 2x + y, \tag{A.2}$$

where $\langle r \rangle$ is a mean coordination number ($2 < \langle r \rangle < 4$). In the covalent network, the bond length and bond angles are well defined. Small displacements from the equilibrium structure can be written as

$$V = \frac{\alpha}{2}(\Delta l)^2 + \frac{\beta}{2}(\Delta\theta)^2. \tag{A.3}$$

where, $l$ = bond length, $\Delta l$ = change in the bond length, $\beta$ = bond-bending force, $\alpha$= bond stretching term, $\theta$= angle and $\Delta\theta$ = change in the angle. The solution of the eigen modes of the potential of Eq. A.3 is a problem in classical mechanics. If any eigen modes having zero frequency are present in the system, then the smaller terms in the potential will give these modes a small finite frequency, thus warranting the name floppy modes [96]. The total number of constraints is,

$$N = \sum_{r=2}^{4} n_r[\frac{r}{2} + (2r - 3)], \tag{A.4}$$

Using the total number of constrains, it can estimate the total number of zero-frequency modes. The fraction, $f$, of zero-frequency modes is given by,

$$f = \frac{[3N - N = \sum_{r=2}^{4} n_r[\frac{r}{2} + (2r - 3)]]}{3N}, \tag{A.5}$$

This equation can be simplified,

$$f = 2 - \frac{5}{6}\langle r \rangle. \tag{A.6}$$

The rigidity of the threshold of $\langle r_c \rangle = 2.4$ [96], when $f$ decreases to zero. The network becomes rigid as it goes through a phase transition from floppy to rigid [96].

The Raman spectroscopy is important to study the intermediate and short range forces in glasses. Dejus *et al.* [31] has studied the chalcogenide glasses GeSe doped with silver, Ag. The experimental results of Raman spectra show that Ag has destroyed the intermediate range order in GeSe glass. A calculation of AgGeSe have been done from the first principles and have compared the calculated values with those measured by Dejus *et al.* [31] as explained in chapter 2. The substance in the glass changes because of the reaction in the glass, [97]. The resistivity considerably changes upon addition of Ag in the glass. The Ag-Ge-Se material is suitable for use in memory devices of the programmable metallization cell (PMC). The Raman spectroscopy is used to understand the vitreous properties of glasses.

The chalcogenide $GeSe_2$ glasses studied by Lucas [98] showed the presence of rigid $GeSe_2$ phase even with high selenium content. They have used the Raman spectroscopy and nuclear magnetic resonance (NMR) to understand the elastic properties of glasses. From Raman spectra they found peaks at 195, 213 and 255 $cm^{-1}$ in $Ge_xSe_{1-x}$ glasses with 255 $cm^{-1}$ assigned to Se chain mode. The result from NMR and Raman lead to the explanation of bimodal phase percolation of Ge - Se glasses. The description of interatomic interaction is given by Iyetomi *et al.* [99] by using molecular dynamic simulation to understand the Ag-Ge-Se molecule. They found that $GeSe_2$ glass is formed with edge sharing and corner sharing tetrahedral bonds. The combination of silver and $GeSe_2$ glass show that Ag can modify the $GeSe_2$ network because of the low valence of Ag ion.

The vitreous $B_2O_3$ has been studied both experimentally and theoretically. Ferlat

*et al.* [100] reported the first principles calculations of $B_2O_3$. This prototypical glass former has been observed by using x-ray diffraction, Raman spectroscopic and NMR. Using molecular dynamics (MD) simulation, this glass makes an interesting study for the understanding of the vibrational frequencies. They divided the glasses into two models, the boroxol-poor (BP) and the boroxol-rich (BR). The results of calculation show the agreement of BR Raman spectra within 15% errors. For the BP case, the calculated result underestimates and the intensity of calculated spectrum is much lower than the experimental value.

The $As_2O_3$ has been studied for a long time because of the good glass forming substance. The researchers still continue to understand the linkage of the building blocks of $AsO_3$ glass with pyramidal shape. Soignard *et al.* [101] has reviewed the interesting studies done by other researchers related to $As_2O_3$ glass. In their research, they increased the external pressure up to 40GPa to understand the glass forming transition of $As_2O_3$. This glass been characterized by x-ray diffraction and Raman spectroscopy. This glass has arsenolite type of cubic c-$As_2O_3$ and claudetite type of monoclinic m-$As_2O_3$ bonds. The crystalline $As_2O_3$ polymorphs have been made by heating the arsenolite form of $As_2O_3$ at $800^oC$ in vacuum sealed quartz tubes. The sealed quartz tube has been removed from the furnace to let the liquid cool in air and become a glass. The glass was studied by using the Raman spectroscopy as a function of pressure up to 40GPa. A large change in the glass structure and coordination happens at 20-40 GPa but there is no sign of hysteresis in the transition. They conclude that the structure of g-$As_2O_3$ is much more closely related to that cubic c-$As_2O_3$ rather than to m-$As_2O_3$.

Another well known glass material is vitreous silica. The $SiO_2$ glass form has been studied to understand the sharp lines found in the Raman spectrum. The Raman spectroscopy is a central tool to investigate the amorphous material. The Brillioun and x-ray scattering are also used to characterize the low frequency part of the vibrational

dynamics. J. Burgin *et al.* [102] used two methods to study the vitreous glass. The spontaneous Raman and impulsive-stimulated Raman (ISRS)spectra have been used to investigate the sharp lines in the Raman modes. The frequencies from both methods are in excellent agreement. They also found that in Raman scattering, the intensity also provides a mean to identify bonding motion show that it is important to study the intensity of Raman line like how researchers focussed on frequencies and linewidths. The boson peak frequency ($\omega_{BP}$) can be obtained by Raman scattering [103]. Under densification, the low frequency states are distributed in the boson peaks. Zanatta *et al.* [103] report that there is a relation between BP intensity and the density. Another report done by using epoxy-amine mixture consists of diglycidyl ether bisponel-A (DGEBA) and diethylenetromine (DETA) [104]. In the transition from liquid to glass network, the polymer changes the microscopic structures. The low-frequency vibrational density of states show that the scaling of BP does occur. It is also found that the low frequency spectra change the Debye frequency.

Boson peak has been found in $As_xS_{1-x}$ glasses [105, 106]. The experimental result of Raman spectra has been performed by Chen *et al.* [105] who found the low frequency Raman modes in chalcogenide $As_xS_{1-x}$ glasses. The experimental study was also compared with the first principle calculations to understand the Raman peak for a variety of compositions, (x = 8% - 41%). The boson peaks were also found for 8 to 20 per cent As content in oxide glasses. On the whole it appears that a variety of glasses have been studied by the Raman spectra.

# Appendix B

# List of Publications

1. Ahmad Nazrul Rosli, Noriza Ahmad Zabidi, Hasan A. Kassim, and Keshav N. Shrivastava (2011). Ab initio Calculation of Vibrational Frequencies and Raman Spectra of Barium Peroxide Glass Including Comparison of Tetrahedral $BaO_4$ with $GeO_4$ and $SiO_4$. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy.* (**ISI**)

2. Ahmad Nazrul Rosli, Hasan A. Kassim, and Keshav N. Shrivastava (2010). Ab initio Calculations of Vibrational Frequencies in a Glassy State of Selenium. *Sains Malaysiana*, 39 (2) 281-283. (**ISI**)

3. Ahmad Nazrul Rosli, Noriza Ahmad Zabidi, Hasan A. Kassim, and Keshav N. Shrivastava (2010). Ab initio Calculation of Vibrational Frequencies of AsO Glass. *Journal of Non-Crystalline Solids*, 356 (6-8), 428-433. (**ISI**)

4. Ahmad Nazrul Rosli, Noriza Ahmad Zabidi, Hasan A. Kassim, and Keshav N. Shrivastava (2010). DFT Calculations of Vibrational Frequencies of Carbon-Nitrogen Clusters: Raman Spectra of Carbon-Nitrides. *Journal Cluster of Science*, 21, 197-210 (Springer). (**ISI**)

5. Ahmad Nazrul Rosli, Noriza Ahmad Zabidi, Hasan A. Kassim, and Keshav N.

Shrivastava (2010). Density Functional Theory Adsorption of Atoms on Cytosine, *Malaysian Journal of Science*, 29 (1). 64. ISSN 1394-3065.

6. Ahmad Nazrul Rosli, Noriza Ahmad Zabidi, Hasan Abu Kassim Abu Kassim, Abdul Karim Hj Mohd Arof and Keshav N. Shrivastava (2009). Density Functional Theory Calculation of Adsorption of NaCl on Chlorophyll. *Malaysian Journal of Science*, 28 (1). 99-103. ISSN 13943065.

7. Ahmad Nazrul Rosli, Hasan Abu Kassim, Christopher G. Jesudason and Keshav N. Shrivastava (2009). DFT Calculation Of Vibrational Frequencies in Clusters Of Fe and As Atoms. *AIP Conf. Proc.* 1169, 256.

8. Ahmad Nazrul Rosli, Hasan A. Kassim, and Keshav N. Shrivastava Ahmad Nazrul Rosli, Hasan A. Kassim, and Keshav N. Shrivastava. DFT Determination of Law of Force in Fe and P Clusters of Atoms, *AIP Conf. Proc.* 1150, 376.

9. Ahmad Nazrul Rosli and Keshav N. Shrivastava (2009). Von Klitzing's Constant as a Special Case of Generalized Constants, *AIP Conf. Proc.* 1136, 469.

10. Ahmad Nazrul Rosli, Hasan Abu Kassim and Keshav N. Shrivastava (2009). Ab Initio Calculation of Vibrational Frequencies in $As_xS_{1-x}$ Glass and The Raman Spectra, *AIP Conf. Proc.* 1136, 370.

11. Noriza Ahmad Zabidi, Ahmad Nazrul Rosli, Hasan Abu Kassim, Keshav N. Shrivastava and Devi, V. Renuka (2008). DFT Calculations of Adsorption with Correlations of Atoms on $C_{60}$, *Malaysian Journal of Science*, 27 (1). pp. 111-119. ISSN 13943065.

12. Ahmad Nazrul Rosli, H. A. Kassim and K. N. Shrivastava (2008). DFT ab initio calculation of vibrational frequencies in AsSe glass, *Bull. American Phys. Soc.* 53, 03.6.

13. Ahmad Nazrul Rosli, H. A. Kassim and K. N. Shrivastava (2007). Ab initio calculation of the frequencies of AgGeSe glass, *J. Sci. Tech. Tropics* 3, 129-133.

14. Ahmad Nazrul Rosli, Noriza Ahmad Zabidi, H. A. Kassim, K. N. Shrivastava, P. V. Rao and V. R. Devi (2007). Adsorption of atoms on thymine: Density functional theory, *Malaysian Journal of Science* 26, 99-109.

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