SPECTROSCOPIC STUDY OF ANHYDROUS AND HYDROUS SILICATE GLASSES UNDER HIGH PRESSURE AND HIGH TEMPERATURE.

A DISSERTATION SUBMITTED TO THE GRADUATE DIVISION OF THE UNIVERSITY OF HAWAII IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

IN

GEOLOGY AND GEOPHYSICS

May 1996

by

Zifu Wang

DISSERTATION COMMITTEE:

Shiv K. Sharma, Chairman
Li-Chung Ming
David W. Muenow
George P.L. Walker
Paul Lucey
We certify that we have read this dissertation and that, in our opinion, it is satisfactory in scope and quality as a dissertation for the degree of Doctor of Philosophy in Geology and Geophysics.

DISSERTATION COMMITTEE

Chairperson

[Signatures]

[Signatures]

[Signatures]
To
my parents,
my wife Ying
I would like to express my sincere thanks first to my research advisor Shiv Sharma who has always been a constant source of support, guidance and encouragement. I would also like to thank my dissertation committee members for their willingness to help me and their overall support in all stages. David Muenow always provided me with very valuable and constructive comments. The hours of discussion and numerous suggestions supplied by Li-Chung Ming were very important and helpful. The critical review of my dissertation by George Walker greatly enhanced my knowledge of the geological significance of this work. Paul Lucey has always been a source of encouragement and well thought-out ideas. I would also like to extend my thanks to following people. A. Jayaraman's help and instruction were particularly appreciated. Tom Cooney's guidance was always there whenever I needed his help. Sieger van der Laan's encouragement and suggestions were always a source of energy pushing me forward. Shaoyu Wang is greatly appreciated for his constant help. My special thanks go to my wife, Ying, for her wholehearted support of me.

Finally, financial support provided by National Science Foundation grants (EAR 92-06132 and EAR 89-15830), and by the Department of Geology and Geophysics in the form of a Teaching Assistantship are gratefully acknowledged.
ABSTRACT

Modified confocal micro-Raman spectrometry has been used in this study for measuring Raman spectra of anhydrous and hydrous silicate glasses at high temperature both at ambient and reducing atmosphere, and at high pressure and room temperature. Results from high temperature studies indicate that the structures of glasses are similar to that of respective high temperature melts, except some minor changes, e.g., the increase in bond length and bond angle, and occurrence of some disproportionation reactions at high temperatures. We suggest that the distinct differences in the physical properties, e.g., viscosity, are primarily from different dynamic behaviors of cations and anions in the melts relative to that in glasses. High temperature study of iron-bearing silicate glasses under reducing conditions has demonstrated that in our samples Fe$^{2+}$ are basically octahedrally rather than tetrahedrally coordinated. The present study clearly indicates that a decrease in the degree of polymerization of structure is accompanied by the reduction from Fe$^{3+}$ to Fe$^{2+}$. The presence of Fe$^{2+}$ in reduced quenched glasses is demonstrated using Mössbauer spectroscopy.

Our results from high pressure studies on K$_2$Si$_4$O$_9$ glass show that coordination number of Si increases from 4 to higher numbers (5 or 6) at pressures higher than ~6 GPa, which has important implications for the emplacement of
natural magma in the deep earth. The decrease in the viscosity of highly polymerized compositions of silicate melts could result from the shrink in the Si-O-Si bond angle which weakens the interaction between neighboring TO₄ tetrahedra.

Our study of hydrous albite glass at pressure shed new light on the controversial assignments of Raman bands in both hydrous and anhydrous albite glasses. It demonstrates an intrinsic relationship between the distinct 900 cm⁻¹ band and other bands in the Raman spectrum of hydrous albite glass. Our study at high pressure also indicates that OH species have various structural environments when the pressure-induced structural changes occurs. Our results of high temperature studies demonstrate that the introduction of water preferentially affects the structural site of Al cations relative to Si. In addition, strength of hydrogen bonding is found weakened with increasing temperature.
TABLE OF CONTENTS

ACKNOWLEDGMENTS.............................................................. iv
ABSTRACT.................................................................................. v
LIST OF TABLES........................................................................... xii
LIST OF FIGURES......................................................................... xiii
CHAPTER 1. GENERAL INTRODUCTION................................. 1
CHAPTER 2 EXPERIMENTAL METHODS......................... 10
  2.1. Sample synthesis.............................................................. 10
     2.1.1. The K₂Si₄O₉ glass...................................................... 10
     2.1.2. Iron-containing silicate glasses............................ 10
     2.1.3. Hydrous albite glass.............................................. 11
  2.2. Confocal Raman microspectroscopy......................... 12
     2.2.1. Theory and optics................................................... 12
     2.2.2. Modification of micro Raman spectrometry
     for application to silicate glasses
     and melts............................................................. 15
  2.3. In situ high temperature Raman spectroscopic
      measurements............................................................. 20
     2.3.1. K₂Si₄O₉ glass and melt........................................ 21
     2.3.2. Iron-containing glasses and melts..................... 21
     2.3.3. Hydrous and anhydrous albite glasses............ 22
  2.4. In situ high pressure Raman spectroscopic
      measurements............................................................. 23
  2.5. Mössbauer Spectroscopy.............................................. 25

CHAPTER 3 EFFECT OF TEMPERATURE AND PRESSURE ON THE
      RAMAN SPECTRA OF K₂Si₄O₉ GLASS AND MELT.................. 28
3.1. Introduction

3.2. General assignment of observed bands in the Raman spectra of silicate glasses

a. The high-frequency region
b. The mid-rang bands
c. The low-frequency region

3.3. Results

3.3.1. High-temperature Raman spectra of $K_2Si_4O_9$

3.3.2. High-pressure Raman spectra of $K_2Si_4O_9$ glass

3.4. Discussion

3.4.1. The $D_2$ band in $SiO_2$ and $GeO_2$ glasses

3.4.2. Assignment of the 592 cm$^{-1}$ "defect" band and implicates for the structure

3.4.3. Temperature and pressure effect on the structure of $K_2Si_4O_9$

a. Raman spectra of $K_2Si_4O_9$ with increasing temperature and pressure
b. Raman spectra of $K_2Si_4O_9$ in the decompression process

3.4.4. Coordination change in silicate glasses and melts under high temperature, and high pressure

3.4.5. Implications for viscosity of silicate glasses and melts

3.5. Conclusions

CHAPTER 4 STRUCTURAL STUDY OF ALKALI AND IRON-CONTAINING SILICATE GLASSES AT HIGH TEMPERATURE

4.1. Introduction
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.2. Results</td>
<td>65</td>
</tr>
<tr>
<td>4.2.1. Mössbauer spectrum of (Na$_2$O·0.5Fe$_2$O$_3$·3SiO$_2$) NFS1 glass</td>
<td>65</td>
</tr>
<tr>
<td>4.2.2. Raman spectra of oxidized Fe-containing glasses</td>
<td>65</td>
</tr>
<tr>
<td>4.3. Discussion</td>
<td>82</td>
</tr>
<tr>
<td>4.3.1. Mössbauer spectrum of NFS1 glass</td>
<td>82</td>
</tr>
<tr>
<td>4.3.2. Room temperature Raman spectra and band assignments</td>
<td>83</td>
</tr>
<tr>
<td>4.3.3. Fully polymerized Fe-albite (NFS0) glass below and above T$_g$</td>
<td>86</td>
</tr>
<tr>
<td>4.3.4. Nature of the vibrational spectra of glasses</td>
<td>87</td>
</tr>
<tr>
<td>4.3.5. Depolymerized oxidized glasses at temperatures below and above T$_g$</td>
<td>88</td>
</tr>
<tr>
<td>4.3.6. Temperature dependence of the &quot;defect&quot; bands</td>
<td>94</td>
</tr>
<tr>
<td>4.4. Conclusions</td>
<td>95</td>
</tr>
</tbody>
</table>

CHAPTER 5  EFFECTS OF HIGH TEMPERATURE ON THE STRUCTURE OF REDUCED IRON-BEARING SILICATE GLASSES AND MELTS 97

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1. Introduction</td>
<td>97</td>
</tr>
<tr>
<td>5.2. Na$_2$O·FeO·3SiO$_2$ (NFS1-R) glass and melt</td>
<td>98</td>
</tr>
<tr>
<td>5.2.1. Results</td>
<td>98</td>
</tr>
<tr>
<td>a. Mössbauer spectra</td>
<td>98</td>
</tr>
<tr>
<td>b. Raman spectra</td>
<td>99</td>
</tr>
<tr>
<td>5.2.2. Discussions</td>
<td>103</td>
</tr>
<tr>
<td>a. Mössbauer spectra</td>
<td>103</td>
</tr>
<tr>
<td>b. Raman spectra</td>
<td>108</td>
</tr>
<tr>
<td>5.3. Reduced KFS-R (K$_2$O·FeO·3SiO$_2$) glass and melt</td>
<td>111</td>
</tr>
<tr>
<td>5.3.1. Results</td>
<td>111</td>
</tr>
</tbody>
</table>
5.3.2. Discussion................................................. 111
5.4. Conclusions.................................................. 116

CHAPTER 6  TEMPERATURE AND PRESSURE DEPENDENCE OF RAMAN SPECTRA OF HYDROUS AND ANHYDROUS ALBITE GLASSES................. 118

6.1. Introduction.................................................. 118
6.2. Results...................................................... 122

6.2.1. In situ high temperature Raman spectra of anhydrous and hydrous albite glasses 122

6.2.1.1. Anhydrous albite glass (NaAlSi<sub>3</sub>O<sub>8</sub>) at high temperature................................. 123

6.2.1.2. Hydrous albite glass at high temperature......................... 126

a. Raman spectra in the frequency region of 200-1300 cm<sup>-1</sup>......................... 126

b. Raman spectra in the frequency region of 2000-4000 cm<sup>-1</sup>.......................... 130

6.2.2. In situ high pressure Raman spectra of hydrous albite glass (with 10 wt% water) at room temperature............................. 134

a. Raman spectra in the frequency region of 200-1300 cm<sup>-1</sup>.......................... 134

b. Raman spectra in the frequency region of 2500-4000 cm<sup>-1</sup>......................... 137

6.3. Discussion.................................................... 140

6.3.1. Effects of temperature on the structures of hydrous and anhydrous albite glasses 140

6.3.2. Effects of pressure on the structure of hydrous albite glass......................... 142

6.3.3. The assignments for the high frequency envelope (950-1200 cm<sup>-1</sup>)............. 143

6.3.4. The 900 cm<sup>-1</sup> band and its implications for the water dissolution mechanism.... 146
6.3.5. Water species in the hydrous albite glass

- a. Effects of temperature on the water species

- b. Effects of pressure on the water species

6.4. Conclusions

REFERENCES
<table>
<thead>
<tr>
<th>TABLE</th>
<th>Description</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Data of microprobe Analysis of Glass NFS1 (Na$_2$O·0.5Fe$_2$O$_3$·3SiO$_2$)</td>
<td>66</td>
</tr>
<tr>
<td>2.</td>
<td>Mössbauer Parameters for NFS1 Glass</td>
<td>67</td>
</tr>
<tr>
<td>3.</td>
<td>Raman peaks positions (cm$^{-1}$) in the spectra of NFS1 at various temperatures</td>
<td>79</td>
</tr>
<tr>
<td>4.</td>
<td>Raman peaks positions (cm$^{-1}$) in the spectra of NFS2 (1.5Na$_2$O·0.5Fe$_2$O$_3$·3SiO$_2$) at various temperatures</td>
<td>80</td>
</tr>
<tr>
<td>5.</td>
<td>Raman peaks positions (cm$^{-1}$) in the spectra of KFS (K$_2$O·0.5Fe$_2$O$_3$·3SiO$_2$) at various temperatures</td>
<td>81</td>
</tr>
<tr>
<td>6.</td>
<td>Mössbauer parameters for NFS1-R (Na$_2$O·FeO·3SiO$_2$) glasses</td>
<td>101</td>
</tr>
<tr>
<td>7.</td>
<td>Positions (cm$^{-1}$) of certain characteristic Raman bands in the spectra of albite glass at various temperatures</td>
<td>125</td>
</tr>
<tr>
<td>8.</td>
<td>Positions (cm$^{-1}$) of certain characteristic Raman bands in the spectra of hydrous albite glass at various temperatures</td>
<td>128</td>
</tr>
<tr>
<td>FIGURES</td>
<td>PAGE</td>
<td></td>
</tr>
<tr>
<td>---------</td>
<td>------</td>
<td></td>
</tr>
<tr>
<td>Figure 2.1. The principle of confocal Raman microspectrometry</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>Figure 2.2. The principle of modified confocal Raman spectrometry</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td>Figure 2.3. Two Raman spectra of hydrous albite glass in a diamond anvil cell (DAC) measured with and without modified confocal Raman optics, respectively</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td>Figure 2.4. Schematic of diagram of multichannel micro-Raman setup</td>
<td>19</td>
<td></td>
</tr>
<tr>
<td>Figure 2.5. Mao-Bell cell. (a) A cross-sectional view. (b) Shows the long cylinder-piston assembly with the anvil diamonds set in carbide half cylinders</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>Figure 2.6. A schematic diagram of a Mössbauer spectrometer</td>
<td>26</td>
<td></td>
</tr>
<tr>
<td>Figure 3.1. Polarized Raman spectra of SiO2 glass</td>
<td>29</td>
<td></td>
</tr>
<tr>
<td>Figure 3.2. Raman spectra of K2Si4O9 glass and melt at various temperatures</td>
<td>36</td>
<td></td>
</tr>
<tr>
<td>Figure 3.3. Raman spectra of K2Si4O9 glass at various pressures</td>
<td>39</td>
<td></td>
</tr>
</tbody>
</table>
Figure 3.4. Pressure dependence of the band frequency in the Raman spectra of K$_2$Si$_4$O$_9$ glass.......................... 40

Figure 3.5. Raman spectra of K$_2$Si$_4$O$_9$ glass recorded during the decompression process....... 42

Figure 4.1. The Mössbauer spectrum of NFS1 glass is fitted to a single doublet................. 68

Figure 4.2.(a) Polarized Raman spectra of NFS0 glass at room temperature................... 69

(b) Polarized Raman spectra of NFS1 glass at room temperature.......................... 70

(c) Polarized Raman spectra of NFS2 glass at room temperature.......................... 71

(d) Polarized Raman spectra of KFS glass at room temperature......................... 72

Figure 4.3.(a) Unpolarized Raman spectra of NFS0 glass at various temperature................ 74

(b) Unpolarized Raman spectra of NFS1 glass at various temperature..................... 75

(c) Unpolarized Raman spectra of NFS2 glass at various temperature..................... 76

(d) Unpolarized Raman spectra of KFS glass at various temperature..................... 77

Figure 4.4. Unpolarized Raman spectra of NFS0, acamite (NaFeSi$_2$O$_6$), NFS1 and NFS2....................... 85
Figure 4.5. Two-Gaussian-peak fits to the high frequency band envelope of the high temperature spectra of NFS1............ 91

Figure 4.6. The proportion of A1 relative to the area of whole envelope (A=A1+A2) at different temperature................. 92

Figure 5.1. Mössbauer spectrum of NFS1-R glass is fitted to either one or two doublets... 100

Figure 5.2. Temperature dependence of the unpolarized Raman spectra measured under H2 reducing conditions and using NFS1 glass as the initial starting material.............. 102

Figure 5.3. The polarized high frequency spectra of reduced NFS1-R glass at room temperature............................. 104

Figure 5.4. Unpolarized Raman spectra with KFS glass as starting material at various temperatures measured under reducing conditions................................. 112

Figure 5.5. The polarized Raman spectra of reduced KFS-R glass at room temperature........ 115

Figure 6.1. Temperature (K) dependence of the Raman spectra of anhydrous albite glass...... 124

Figure 6.2. Temperature (K) dependence of the Raman spectra of hydrous albite glass....... 127
Figure 6.3. Raman spectra of OH stretching band from the hydrous albite glass at various temperature (K)......................... 131

Figure 6.4. The temperature dependence of the OH band position.......................... 132

Figure 6.5. Raman spectra of glass quenched from the high temperature OH stretching band measurements................................. 133

Figure 6.6. Selected high pressure Raman spectra of hydrous albite glass............... 135

Figure 6.7. Pressure dependence of the positions of several characteristic Raman bands of the hydrous albite glass............. 136

Figure 6.8. Raman spectrum of hydrous albite glass quenched from 10.5 GPa............... 138

Figure 6.9. High pressure Raman spectra of hydrous albite glass with 10 wt% water in the frequency region of 2500-4000 cm⁻¹... 139
CHAPTER 1

GENERAL INTRODUCTION

Viscosity is a property of magma that has an important effect on igneous processes. Bowen (1934) emphasized the importance of viscosity as a dominant controlling factor during the passage of magma through the Earth, the pouring-out of lava upon the surface, and the sinking of crystals and the rise of gases within a magma body. A number of viscosity measurements have been made by both field observations of lava flows and experiments in laboratories (e.g., Kani, 1934; Krauskopf, 1948; Shaw et al., 1968; Bottinga and Weill, 1972; Urbain et al., 1982; Scarfe, 1986). Although viscosity of many melt compositions are reasonably well known at 1 atmosphere, knowledge of the effect of pressure on melt viscosity is more limited. Kushiro (1976, 1977, 1978, 1980) showed that the viscosity of several anhydrous silicate and aluminosilicate melts (e.g., jadeite and albite) decrease when measured isothermally at pressures up to 20 kbar. Kushiro et al. (1976), Fujii and Kushiro (1977a, b) and Scarfe (1981) have also shown that qualitatively similar behavior is exhibited by anhydrous rock melts of andesitic and basaltic composition. In the case of rock melts, sufficient data are available to indicate a viscosity decrease both isothermally and along the liquidus with pressure. Although the decrease in viscosity along the anhydrous liquidus may be due to structural changes in the
melt, brought about by increasing temperature, the decrease in viscosity measured under isothermal conditions must be attributed to structural changes in the melt.

At present the nature of the decrease in viscosity of the polymerized silicate melts (e.g., jadeite and albite) with pressure is not clear yet. It has been suggested that the structural changes of both jadeite and albite may be associated with the shift of Al from 4-fold to 6-fold coordination at high pressures (Kushiro, 1976; Velde and Kushiro, 1978; Kushiro, 1978). Such a coordination change of Al must produce non-bridging oxygens. However, studies by Raman spectroscopy (Sharma et al., 1978a, 1979) do not show a significant increase in number of non-bridging oxygens in glass of jadeite composition with increasing pressure of quenching. Sharma et al. (1979b) conducted viscosity measurements on GeO₂ melt at 1425 °C at various pressures and Raman spectroscopic measurements on the GeO₂ glass quenched from high temperatures and pressures. Similar to the case of aluminosilicate melts, the viscosity of GeO₂ melt underwent a decrease with increasing pressure. The Raman spectroscopic measurements show that the Ge is tetrahedrally coordinated in the glass structure. More recently, Scarfe et al. (1987) carried out viscosity measurements on silicate melts with highly polymerized compositions (NBO/T<1) (NBO/T= the number of non-bridging oxygens per tetrahedrally coordinated cations) and relatively depolymerized compositions (NBO/T>1). The former melts show an isothermal decrease in viscosity
with increasing pressure whereas the latter melts show an isothermal increase in viscosity to 20 kbar indicating a fundamental difference in the behavior of the highly polymerized melts compared to the depolymerized melts. A Raman spectroscopic study (Dickenson et al., 1990) of K$_2$Si$_4$O$_9$ glass quenched isobarically from 1200 °C and 2.1 GPa does not show a significant change in structure, although a minor change is observed which is suggested as a result of presence of Si in high coordination.

In this connection, a knowledge of the structures of silicate melts is essential to accurately model magmatic properties such as viscosity, as well as liquid-liquid immiscibility, volatile solubility and ionic diffusion. Raman spectroscopy has been very useful in investigating the microscopic nature of various materials in different states (solid, liquid and gas). Unfortunately, the chemical complexity of natural magma and the hostile conditions under which they are formed (> 1000°C) make it difficult to conduct direct spectroscopic studies of those naturally occurring silicate melts. Consequently, in the past, high temperature quenched silicate glasses of chemically simple compositions were often used to investigate the structural roles of individual components in disordered silicate network (Stolen and Walraffen, 1976; Brawer and White, 1977; Sharma et al., 1979a; McMillan et al., 1982; Mysen et al., 1982; Brandriss and Stebbins, 1988). The information from these glasses has been extrapolated to the melts from which the glasses were
quenched, and ultimately, to the more complex natural geological melt systems.

There are at least two outstanding problems related to anhydrous silicate melts. Firstly, it has been proposed (e.g., Sharma et al., 1978b; Seifert et al., 1981) that the structures of silicate glasses and melts may not necessarily be identical because a marked break in most physical properties occurs at the glass transition temperature, \( T_g \), where the viscosity attains \( 10^{13} \) poises (e.g., Doremus 1973). In the case of \( B_2O_3 \) glass, it has been demonstrated that the structure of the glass is different to that of the melt (Walrafen et al., 1980). In the \( B_2O_3 \) glass, the \( BO_3 \) triangles form boroxol rings, and above \( T_g \) these rings progressively break-down to form \( BO_3 \) triangles in a random network. In order to provide insight into the differences in the structures between silicate glasses and melts, several in situ high temperature investigations have been conducted on the silicate melts. The studies include an X-ray radial distribution study by Waseda and Toguri (1978) on binary melt system, Raman spectroscopic and infrared reflectance studies on sodium silicate melts (Sweet and White, 1969; Sharma et al., 1978a; Seifert et al., 1981; ), Nuclear Magnetic Resonance (NMR) studies (Liu et al., 1987; Farnan and Stebbins, 1990, McMillan et al., 1992; Mysen and Frantz, 1992, 1994) and an Extended X-ray Absorption Fine Structure (EXAFS) study by Waychunas et al. (1988). Most of these workers have indicated that there is a close correspondence
between the structures of glasses and melts, at least in terms of the short range structural details. In these investigations, however, only limited compositions of glasses and corresponding melts have been examined, e.g., very little work has been done on iron-containing silicate melts.

Secondly, the basic mechanisms of diffusion and viscous flow in high temperature associated liquids are long-standing problems. The diffusion theory of crystalline materials (like metal) has been well established, in which the diffusion is described as a defect controlled process, i.e., the defects like dislocation and vacancies can provide empty spaces for moving atoms. Because of the difference in the structures between the liquids and crystalline materials, however, the concepts of dislocation and vacancies can not be simply generalized to liquid state. Accordingly, several theoretical models had been proposed for high temperature liquids. In 1936, Eyring considered a liquid as a collection of molecules bound to their neighbors and of "dissolved holes" (similar to vacancies in solids). In associated liquids, consisting of complex ions, transport, either by diffusion or viscous flow, is thought to occur by thermally activated jumps of the molecules into the holes. The diffusion coefficient is expressed by Arrhenius law: 

\[ D = D(0) \exp\left(-\frac{E}{RT}\right) \]

where the E is the activation energy corresponding to the potential barrier that the molecules must overcome to jump into the hole. Even though the equation fit the experimental data reasonably good, the microscopic
mechanism of the "dissolved holes" is unclear. Some other models using different mechanism, e.g., free volume and density fluctuations, all reached a Arrhenius law and the value of activation energy can be calculated from the lnD versus 1/T relation, even though here the activation energy does not have any physical meaning. Therefore, the basic mechanisms of the transport of ions and molecules relating to the diffusion and viscous flow in high temperature silicate liquids remain unclear.

Recently, several molecular dynamics computer simulation studies have proposed that certain amount of five-coordinated Si atoms could reside inside the structures of silicate melts (e.g., Angell et al., 1983; Kubicki and Lasaga, 1988). Similar to the defects in crystalline materials, which provide empty spaces for moving atoms, the five-coordinated Si atom is claimed as a corresponding defect in melts because such high coordinated Si atom can provide one more space for in-coming oxygen atoms, and consequently, make the diffusion and viscous flow possible. The evidence of existence of the five-coordinated Si has been clearly demonstrated in several NMR studies on silicate glasses (e.g., Stebbins and McMillan, 1989; Stebbins, 1991). However, several problems still remain. First, because of the fast exchange rate between different species in the silicate melts, high temperature NMR spectra can only provide limited information on the structures of silicate melts. If the species like five-coordinated Si dominate the structure under high temperature,
these cannot be assessed by NMR spectroscopy. Second, the concentration of five-coordinated Si is very small (estimated in fast quenched glasses ~0.1%) (Stebbins, 1991). It can be easily questioned if the five-coordinated Si atoms with such a small concentration are able to provide enough empty spaces for in-coming oxygen atoms because the viscous flow of silicate magma involves simultaneous movement of large amount of atoms, consequently, at the same time a large amount of empty spaces are needed. Third, several in situ high temperature Raman spectroscopic studies on silicate melts have been carried out. Unfortunately, no new Raman peak, which could be related to the five-coordinated Si, is observed in the spectra of silicates at high temperature above respective melting points. Apparently, further investigations are needed.

All natural magmas contain dissolved water and other volatile components. Dramatic changes in physical properties of silicate melts with the introduction of water have been generally attributed to its modifying effect on the structure of melts. Early studies of volatile dissolution in silicate melts were limited to studies of solubility (Hamilton et al., 1964) and the effects on phase relations (e.g., Tuttle and Bowen, 1958). Burnham (1974, 1975, 1979) formulated a general model for the mechanism of dissolution of water based largely on solubility data for glass of albite composition. The main idea of his model is that water is dissolved in silicate melts exclusively, or nearly so, as hydroxyl groups
(X-OH; X≠H) rather than as molecules of water. Hydroxyl (OH\textsuperscript{−}) could break the existing T-O-T linkage (where T is tetrahedrally coordinated cation) and form T-OH structure, resulting in a depolymerization of the previous structure. In the past ten years spectroscopic measurements on hydrous glasses have been widely used to deduce structural features of hydrous silicate glasses. With FTIR spectroscopy Stolper (1982a, b) showed the presence of dissolved molecular water as well as hydroxyl species (OH\textsuperscript{−}) in silicate glasses. In the case of hydrated albite glass, it has been proposed that the OH\textsuperscript{−} group is either attached to tetrahedrally coordinated cations (e.g., Si or Al) or present as [NaOH] complex. Even though several models have been proposed for the structural position of the hydroxyl ions in hydrous silicate glasses, the question still remains open (e.g.; McMillan et al., 1983; Kushiro et al., 1985; McMillan and Remmele, 1986; Mukherjee and Sharma, 1986; Mysen and Vergo, 1986a, b; Kohn et al., 1989; Pandya et al., 1992, 1994; Sykes and Kubicki, 1993). Furthermore, how the application of high pressure will affect the structure of hydrous glasses of albite composition is not known at present.

In this dissertation I present the results of investigations of effects of temperature, oxidation state of iron, which has its significance in the geochemistry and igneous petrology, and pressure on the vibrational spectra of several highly polymerized alkali- and alumino-silicate glasses and melts, which are taken as analogue for granite
magnas; and high pressure or high temperature Raman measurements on hydrous albite glasses. These studies could provide insight into the structures and viscosity as functions of pressure and temperature. The results are presented in the following six chapters.

In Chapter 2, the experimental methods used for measuring the structure of silicate glasses and melts are described.

In Chapter 3, the effect of temperature on the structure of K$_2$Si$_4$O$_9$ glass and melt at 1 atm. and of high pressure on the glass at room temperature are investigated.

In Chapter 4, the high temperature Raman spectra of oxidized iron-bearing K$_2$O·0.5Fe$_2$O$_3$·3SiO$_2$ (KFS), 0.5Na$_2$O·0.5Fe$_2$O$_3$·3SiO$_2$ (NFS0), Na$_2$O·0.5Fe$_2$O$_3$·3SiO$_2$ (NFS1), and 1.5Na$_2$O·0.5Fe$_2$O$_3$·3SiO$_2$ silicate glasses and melts are used to gain insight into their structure.

In Chapter 5, high temperature Raman spectra of reduced iron-bearing Na$_2$O·FeO·3SiO$_2$ and K$_2$O·FeO·3SiO$_2$ glasses and melts are presented, and the effects of change in oxidation state of iron on their structure.

In Chapter 6, high pressure Raman spectra of hydrous albite glasses, and high temperature Raman spectra of both hydrous and anhydrous albite glasses are reported. The data are used to shed light on the effect of pressure and temperature on hydrous aluminosilicate glasses.
CHAPTER 2

EXPERIMENTAL METHODS

2.1. Sample synthesis

2.1.1 The K$_2$Si$_4$O$_9$ glass

The K$_2$Si$_4$O$_9$ glass sample was prepared with dried K$_2$CO$_3$ and SiO$_2$ (produced by dehydration of silicic acid) by decarbonation and partial fusion at 1123 K for 48 hours followed by fusion in air at 1423 K in a platinum crucible for 60 minutes in a Del Tech furnace. The sample was air-quenched by removing the crucible from the furnace. No crystalline phases were observed using a petrographic microscope.

2.1.2 Iron-containing silicate glasses

Oxidized iron-containing silicate glasses of the appropriate compositions were prepared from dried reagent grade Na$_2$CO$_3$, K$_2$CO$_3$, Fe$_2$O$_3$ and SiO$_2$ by decarbonation and partial fusion at 1123 K for 48 hours followed by fusion in air at 1473 K in a platinum crucible that was presaturated with iron for 60 min in a Del Tech furnace. The samples were air-quenched from 1473 K by moving the crucible from the box furnace. No crystalline phases were observed using a petrographic microscope. The chemical compositions of glass
samples were analyzed with electron microprobe and were found to be close to the respective nominal compositions.

2.1.3. Hydrous albite glass

The hydrous albite glass was synthesized by Dr. Van der Laan at the University of Göttingen in Germany and the experimental procedure is described as following.

A cylinder of almost bubble free anhydrous albite glass was ground to fit the inner dimension of a platinum capsule. The glass cylinder was cleaned with alcohol (in an ultrasonic bath) and briefly boiled in water. A capsule was filled with a glass cylinder and heated at 400°C to purge organic contaminants. Then water was added with a microsyringe of 2µl capacity. Water amounts were also checked by weighing the capsule on a Cahn microbalance. After adding the water the capsule was crimped shut and quickly welded. Water losses during welding were negligible.

The capsule was run in an internally heated pressure vessel. Argon gas was used as pressure medium. To avoid bursting of the capsules, an initial pressure of a few hundred bar higher than the final pressure was imposed to allow some water to dissolve. Pressure was then stepwise reduced keeping pace with the amount of dissolved water so that over-pressure inside the capsule was avoided. The final pressure of equilibration was maintained for 100 hrs. The
quenching rate of samples in these experiments was 100 °C per minute.

2.2. Confocal Raman microspectroscopy

In numerous applications, micro-Raman spectroscopy has been shown to be a useful tool in the study of small samples. However, in many applications it is important to have good spatial resolution along the optical axis of the microscope. This can be very useful in the study of thin layers buried in a matrix of other materials, such as multilayer foils or fiber composite materials. It is also useful in the study of small impurities in a sample, in the study of fluid inclusions in minerals, or in the study of the properties of a material as a function of the depth into the material, like mapping the local stress or orientational order in the radial direction of strained fibers or foils.

In optical microscopy, high resolution along the optical axis can not be attained without the so-called confocal arrangement, because light is collected equally from each plane in the sample (Sheppard and Wilson, 1978). It has been shown that by placing a pinhole in the back image of a microscope (the confocal configuration) the spatial resolution can be enhanced, not only in the focal plane, but also along the optical axis (Brakenhoff et al., 1979; Tabaksblat et al., 1992).

2.2.1. Theory and optics
The theoretical performance of a confocal Raman microscope is mainly determined by the optical properties of the microscope objective (numerical aperture, magnification power, and focal length) and by the size of the pinhole placed in the back image plane of the microscope. For simplicity, the microscope is described as a system of two lenses, $L_1$ and $L_2$, with focal length $f_1$ and $f_2$, and with the distance between $L_1$ and $L_2$ equal to $f_2$ (Fig. 2.1). The latter has been done to simplify the derivation of Eq. 2.2, which will be derived later. The $z$-axis is defined along the optical axis, with the origin in the front focal plane of lens $L_1$. A laser spot with diameter $s(f_1)$ in the front focal plane of the lens will be projected on the back image plane of the microscope with diameter $M \cdot s(f_1)$, with $M$ the magnification power of the objective (Fig. 2.1). An out-of-focus laser spot with size $s(f_1+z)$ will be imaged out of the back image plane at a distance

$$b_2 = \left\{1/f_2 - 1/(f_2 - [1/f_1 - 1/(f_1+z)])^{-1}\right\}^{-1} \quad (2.1)$$

from the second lens $L_2$. For our purposes it suffices to approximate the diameter of this image by $M \cdot s(f_1+z)$. This image will be projected on the back image plane of the microscope, and size of this projection will be larger than the size of the image from a laser spot that lies in the focal plane. The diameter of an out-of-focus projection on
Fig. 2.1. The principle of confocal Raman microspectroscopy. A laser spot in the focal plane passes through the pinhole $P$. A laser spot at a distance $z$ from the focal plane is projected in the image plane with size $P'$, and is largely blocked by the pinhole $P$. $L$ = lens; $M$ = beam splitter; $f_1$, $f_2$ = focal length of lens $L_1$ and $L_2$, respectively; $b_2$ = image distance of out-of-focus laser spot.
the image plane $f_2$ is determined by simple geometry, and is equal to

$$P' = \frac{f_2 \cdot M \cdot s(f_1 \tau_z)}{b_2}$$

(2.2)

from Eq. 2.2 it can be seen that these projections $P'$ are larger than the projection caused by a laser spot in the focal plane of lens $L_1$, so that by placing a pinhole with diameter $P < P'$ and $P > M \cdot s(f_1)$ in the back image plane, a large percentage of the light coming from out-of-focus planes is cut off without significantly blocking light from the in-focus planes.

2.2.2. Modification of micro-Raman spectrometry for application to silicate glasses and melts.

Almost all silicate glasses and melts of geologic importance exhibit very weak scattering ability for Raman spectroscopic study. The problem becomes much more serious when a diamond anvil cell is used to conduct high pressure measurements. The signals from glass samples are so weak that they are always buried by the fluorescence background excited from the diamond anvil by the incident laser beam. In order to circumvent the problem of interference from the diamond fluorescence we have used a modified confocal Raman optics (Figure 2.2). Because of the weak scattering cross-sections of silicate glasses, we want to collect as much signal as possible from the samples. In the modified confocal Raman spectroscopic optics we use the aperture of
Fig. 2.2. The principle of modified confocal Raman spectroscopy.
the third lens (l₃) to improve the spatial resolution, which is 6 mm. A lens l₁ with focal length of 16 mm is used to collect scattered signal from sample. After passing lens l₁, the collected signal becomes a parallel beam and this beam becomes very divergent after crossing lens l₂ which has a short focal length of 6 mm. As a result, a laser spot in the focal plane of lens l₁ passes through the aperture BB' of the lens l₃. A laser spot inside diamond anvil defocused from the focus plane of l₁ is projected in the image plane with the size of AA', and is largely eliminated by the lens l₃. The signal passing through the l₃ is then focused by lens l₄ onto the entrance slit S of spectrometer. Figure 2.3 shows two spectra of hydrous albite glass in a diamond anvil cell (DAC). The spectrum collected with modified confocal Raman spectroscopic optics shows much better quality within the region above 500 cm⁻¹ where the interference of fluorescence from diamond is usually very serious.

The system for obtaining micro-Raman spectra is shown in Fig. 2.4. In order to avoid interference from Raleigh scattering of the laser beam, an oblique illumination geometry was used in the experiments. A Spex Triplemate spectrometer equipped with a EG&G liquid nitrogen cooled CCD detector was used to record the Raman spectra. A single lens with a 30 mm focal length was used to focus the exciting laser beam to a spot size of approximately 10 µm. The beam
Fig. 2.3. Two Raman spectra of hydrous albite glass in a diamond anvil cell (DAC) measured with and without modified confocal Raman optics, respectively.
Fig. 2.4 Schematic diagram of multichannel micro-Raman setup
was focused onto the sample at an incident angle of about 55° to the vertical.

2.3. *In situ* high temperature Raman spectroscopic measurements

High-temperature Raman spectra were acquired with the aid of a Leitz model 1350 heating stage coupled with the micro-Raman spectroscopic system. Small fragments of the sample were mounted on a piece of platinum foil placed on a sapphire plate, which was then placed on top of the metal object carrier of the heating stage. The sample environment was isolated by a fused silica window pressed against an O-ring seal on the heating stage to form an air-tight fit. Because the heating stage contains only one thermocouple for controlling the heater, we corrected the temperature reading of this thermocouple to the temperature at the sample position. This correction was done by initially constructing a calibration curve based upon visual microscopic observations of the melting of three standard materials: KNO₃, (nominal melting point 607 K), NaCl (nominal m.p. 1074 K), and Au (nominal m.p. 1336 K). Corrected temperatures determined in this manner are believed to be accurate to ± 10 K. The temperature of the sample during measurement was constant to ± 1 K. The spectra were obtained with either the 457.9 or the 488.0 nm line of an Ar⁺ laser. Parallel and perpendicular components of the scattered radiation (VV and VH) from the sample were recorded separately by changing the
orientation of a polarized filter mounted in front of an optical scrambler. The Raman spectra of glasses were recorded both before heating and after quenching the melt to glass.

2.3.1. K$_2$Si$_4$O$_9$ glass and melt

High temperature micro-Raman studies were carried out using a Leitz model 1350 heating stage as described previously. A Raman spectrometer equipped with CCD detector was used to record the Raman spectrum. The glass sample was heated above 1043 K in order to observe the liquid state properties of the sample. The 457.9 nm line from an Ar$^+$ laser was used for Raman excitation. The laser power at the sample was 60 mw.

2.3.2. Iron-containing glasses and melts

An initial set of experiments was performed on Fe$^{3+}$ containing glasses under ambient oxygen fugacity conditions in the micro-furnace (although the heating stage was sealed below and above, two inlet ports enabled communication with the laboratory atmosphere). Spectra were taken at the oxidized starting glass and at several higher temperatures until visual observation confirmed that the sample had softened and spread out upon the foil. After obtaining a spectrum of this high-temperature melt, the temperature was rapidly (within five minutes) lowered to quench the melt to glass on the stage of the micro-furnace. Result was compared
with spectrum of original glass sample to evaluate if there were any compositional changes during heating.

A second set of measurements was obtained upon a second glass fragment under strong reducing conditions (pure H2 flow over the sample) such that the melt was reduced in situ to the approximate composition Na2O·FeO·3SiO2 during the measurements of Raman spectra. The sample was quenched to room temperature glass as before but with pure H2 continually flowing through the heating stage. After obtaining the room temperature Raman spectrum of the resulting reduced glass, the H2 flow was stopped, and the sample was re-heated under ambient fO2 conditions. The melt was allowed to oxidize for approximate two hours and the color of the melt was observed to change. Subsequent quenching of the oxidized melt allowed Raman spectrum measurements of the re-oxidized glass. On the basis of these experiments, it was possible to observe the effect of the change of fO2 on the structure of the melts and glasses.

2.3.3. Hydrous and anhydrous albite glasses

Raman spectra of hydrous albite glass under high temperature have been obtained in two different spectral regions, i.e., low frequency region (<1500 cm\(^{-1}\)) and high frequency region (2000\textendash 4000 cm\(^{-1}\)). In the low frequency region the temperature dependence of the 900 cm\(^{-1}\) band is observed whereas in the high frequency region the temperature effect on the OH stretching band is studied. As a
comparison, we also measured the high temperature Raman spectra of anhydrous albite glass in the low frequency region.

Because of the introduction of water, the hydrous albite glass may undergo devitrification if the temperature increases rapidly (This has been observed in an experiment by Mrs. Lan Wang). Therefore, in the high temperature experiments for thin plate of hydrous albite, we gradually increased the temperature in steps of 50 °C. At each temperature, integration time for recording a spectrum lasted 20 minutes. The experiments lasted about 6 hours after recording the spectrum of the glass at 800 °C. From both Raman spectra and using a petrographic microscope we found that the glass sample is not devitrified. This shows that the temperature of a thin albite glass is increased slow enough that the sample has long enough relaxation time to keep its structure amorphous during the dehydration process (see chapter 6).

2.4. In situ high pressure Raman spectroscopic measurements

A Mao-Bell type diamond-anvil cell (Fig. 2.5) was used for high pressure measurements at room temperature. Stainless steel 301 foil (250 µm thick) preindented to 100 µm thick was used as gasket material. Glass samples were loaded into the hole of the gasket (diameter of 250 µm) without any
Fig. 2.5. Mao-Bell cell. (a) A cross-sectional view (Mao et al., 1979). (b) Shows the long cylinder-piston assembly with the anvil diamonds set in carbide half cylinders; design features after Mao and Bell (1978).
pressure transmitting medium. Several small (<10µm) ruby chips were scattered in the sample chamber for monitoring pressure. Pressure was determined from the shift of the ruby R1 line (Mao et al, 1978). The Raman spectra were obtained by focusing the 488 nm line of the Ar+ ion laser, at power levels around 60 mW, on a small spot (<20 mm) on the sample. A modified confocal optic system (see section 2.2) equipped with micro-Raman optics was used to eliminate interference from the fluorescence of the diamond anvils.

2.5. Mössbauer Spectroscopy

A schematic diagram of a Mössbauer effect spectrometer is shown in Fig. 2.6. In our experiment, as a first step, several fragments of glass mounted in a crimped gold cup were heated in the micro-furnace under reducing condition and quenched to yield approximate one milligram of sample for Mössbauer analysis. The sample was quenched from high temperature under H2 flow once the Raman spectrum, measured at several points, had become similar to that observed in the second set of experiments. The green glass recovered from the gold cup was crushed under acetone and then spread as a thin film of powder on cellophane tape stretched across a 1.6 mm diameter hole in a lead plate. The lead plate with attached sample was mounted approximately 1 mm from a Mössbauer point source (3 mCi 57Co deposited on the 0.5 mm diameter tip of a Pd rod) attached to an Austin Science Associates Mössbauer spectrometer. Non-mirror-image spectra
Fig. 2.6 A schematic diagram of a Mössbauer effect spectrometer
were collected over 512 channels on a personal computer. The source-to-detector distance was 10 cm. The resulting spectrum baseline corrected and then fit to two doublets using the Mössbauer data reduction program STONE as modified by Dr. M.D. Dyar. Hyperfine parameters were calculated with reference to the four innermost absorption bands of iron foil, which was run both before and after the sample. The Mössbauer spectrum of oxidized glass was obtained in a similar fashion and fitted to a single doublet.
CHAPTER 3

EFFECT OF TEMPERATURE AND PRESSURE ON THE RAMAN SPECTRA OF $K_2Si_4O_9$ GLASS AND MELT

3.1. Introduction

A knowledge of the structure of silica and alkali silicate glasses and melts under high temperature and pressure is fundamental to understanding and predicting the physical and chemical properties of highly polymerized silicate liquids. Because of its importance in both material and earth sciences, $SiO_2$ glass has been investigated extensively both theoretically and experimentally. A widely accepted model known as the CRN (continuous random network) has been used to describe the structure of vitreous silica. Each Si atom is bonded to four O atoms and each O atom is linked to two Si atoms from neighboring tetrahedra in a continuous manner to form a three dimensional network. Raman spectroscopy has been very useful in investigating the microscopic nature of silica glass and melt. The observed Raman bands have been interpreted in terms of bond angle and bond length changes in the fundamental building block, namely the $SiO_4$ tetrahedra. During the past ten years, however, controversy has arisen about the assignment of certain Raman bands, in particular, the 606 cm$^{-1}$ band, which is also called the $D_2$ band (Fig. 3.1). The $D_2$ band has been attributed to a "defect" in the glass structure (Stolen et al., 1970; Bates
Fig. 3.1. Polarized Raman spectra of SiO$_2$ glass. $I_{\perp}$ denote the perpendicular and $I_{\parallel}$ denote the parallel spectra (see text).
et al., 1974) caused by "partially broken" Si-O bonds or the presence of interstitial oxygen (Bates et al., 1974; Sharma et al., 1981; Galeener and Mikkelson, 1981). From the absence of any Raman peaks corresponding to non-bridging oxygen vibration modes, Galeener et al. (Galeener and Mikkelson, 1981; Galeener, 1982a; Galeener, 1982b; Galeener and Geissberger, 1983; Galeener et al., 1984; Galeener and Wright, 1986) assigned the 606 cm$^{-1}$ peak to oxygen breathing modes in rings consisting of three SiO$_4$ tetrahedra. It has also been suggested that the D$_1$ (491 cm$^{-1}$) and D$_2$ bands may arise from Si-O-Si vibrations of linkage with small intertetrahedral angles (Murray and Ching, 1989). Kubicki and Sykes (1993) have recently performed molecular orbital calculations that support Galeener's assignment of the D$_2$ peak to three-member rings. Hemley et al. (1986) carried out an in situ high pressure Raman investigation on SiO$_2$ glass and found that the D$_2$ band increased in relative intensity when decompressed from pressures above 8 GPa. They attributed this result to an increase in the number of three-member rings of SiO$_4$ tetrahedra.

Likewise the Raman spectra of amorphous germanium dioxide (a-GeO$_2$) and sodium and potassium tetrasilicate glass (Na$_2$Si$_4$O$_9$ and K$_2$Si$_4$O$_9$) exhibit shoulders near 520 cm$^{-1}$ and 600 cm$^{-1}$, respectively. These are believed to be of the same origin as the feature responsible for the 606 cm$^{-1}$ band in pure silica (Wolf et al., 1990; McMillan et al., 1992). Further, the intensity of the 520 and 600 cm$^{-1}$ bands are
enhanced in pressure quenched GeO₂ and Na₂Si₄O₉ glasses. This has been attributed to an increase in the concentration of three-member ring structures, or linkages involving five or six-coordinated Si (Wolf et al., 1990; Durben and Wolf, 1991). The temperature-induced structural change is another constraining factor on the structural model of glass and melts. High temperature Raman spectra of GeO₂ (Seifert et al., 1981), Na₂Si₄O₉ (Frantz and Mysen, 1991), and more recently, Rb₂Si₄O₉ (Sharma et al., 1994) glasses show an enhancement in the intensities of the "D₂" bands when temperature exceeds the respective glass transition temperature T₉ of the glasses. It is significant that both temperature and pressure should favor the same structural unit, providing us with a very important clue to arrive at the correct structure. It has been argued by McMillan et al. (1992) that, because 3-membered siloxane rings are compact and highly strained structures, their concentration should increase with increasing glass or melt density at high pressure, rather than with increasing temperature and lower density in the liquid. Based on their Raman measurements on Rb₂Si₄O₉ glass, Sharma et al. (1994) pointed out that it is extremely unlikely that both high temperature and high pressure would favor the same 3-membered ring structural unit. In order to pursue the study on the nature of this controversial band based on the previous studies, we decide to revisit the in situ high temperature Raman spectroscopic study on the K₂Si₄O₉ glass as a part of present study. A in
situ high pressure measurement is also conducted for providing new information on the structural change of this glass as function of pressure.

The viscosity of silicate melts is also an important parameter in problems related to the generation, evolution, and emplacement of igneous rocks (Bartlett, 1969). Although some silicate melts show a viscosity increase with increasing pressure, as expected from the properties of other inorganic liquids, most silicate and aluminosilicate compositions of geologic interest show a decrease in viscosity with pressure, despite the fact that the density of the melt or the glass increases (Kushiro, 1976, 1977, 1978, 1980). Several hypotheses for this behavior have been advanced, but none of them is really satisfactory (Scarf, 1986; Scarf et al., 1987). The study reported here also addresses these questions and attempts to provide an understanding of the basic mechanism behind the change in viscosity of silicate glasses and melts at high temperatures and at atmosphere pressure, as well as at high pressures.

3.2 General assignment of observed bands in the Raman spectra of silicate glasses.

Most of the Raman studies on the silicate glasses have primarily considered band assignments related to vibrations of the silicate units, which are generally described in terms of tetrahedral SiO$_4$ groups in various states of polymerization by corner-sharing of oxygen between tetrahedra
(e.g., Liebau, 1980). This is consistent with the results of diffraction and other spectroscopic experiments on vitreous and molten silicates (e.g., Urnes, 1969; Mozzi and Warren, 1969; Wright and Leadbetter, 1976; Waseda, 1980) and with the structures of corresponding crystalline phases.

A few polarized (i.e., where parallel (VV) (collected scattered light has same orientation to that of the laser source) and perpendicular (VH) (collected scattered light has an orientation perpendicular to that of the laser source)) spectra have been obtained separately Raman studies have been carried out for the silicate glasses. The depolarization ratio $\rho$ is defined as $I_{VV}/I_{VH}$ (Herzberg, 1945). Only totally symmetric vibrations of systems with cubic point symmetry are completely polarized, with $\rho=0$. Antisymmetric vibrations are fully depolarized, with $\rho=0.75$, while all other vibrations have intermediate depolarization ratios. Doubly and triply degenerate modes give rise to depolarized bands. Lowering of symmetry can cause these modes to show splitting with component bands. These may have different depolarization ratio.

a. The high-frequency region.

It has been concluded that the high-frequency spectra of alkali and alkaline earth silicate glasses or melts could be described in terms of combinations of four major polarized Raman bands; at 1100-1050 cm$^{-1}$, 1000-950 cm$^{-1}$, near 900 cm$^{-1}$, and near 850 cm$^{-1}$, each dominant at the disilicate,
metasilicate, pyrosilicate and orthosilicate compositions, respectively. These are also referred as $Q^3$, $Q^2$, $Q^1$ and $Q^0$ species, where superscript indicates number of bridging oxygens (Engelhardt et al., 1975). These bands have generally been assigned to symmetric silicon-oxygen stretching motions of silicate units containing SiO$_4$ tetrahedra with respectively one, two, three and four non-bridging oxygens. The four dominant Raman bands noted above are highly polarized, and that near 850 cm$^{-1}$ may be completely polarized within experimental error. This typical feature of polarization of these bands indicates that the bands are related to non-bridging oxygens vibration modes.

Vitreous silica itself shows two weak, depolarized high-frequency bands at 1200 and 1060 cm$^{-1}$. Most workers have assigned these two high-frequency bands to anti-symmetric silicon-oxygen stretching vibrations within the framework structure. The presence of a doublet in the high frequency spectra of SiO$_2$ and GeO$_2$ glasses have been attributed to TO-LO splitting (Galeener and Lucovsky, 1976)

b. The mid-range bands

These bands near 800 cm$^{-1}$ appear as weak bands in the room temperature spectrum of silicate glasses. The bands have a high depolarization ratio. It has been suggested that the bands are probably related to intertetrahedral deformation modes within a 3-D network and is referred to as
\(v_b(T-O-T)\) band (Sharma et al., 1984). This band is also active in the infrared spectra.

c. The low-frequency region

All the silicate glasses, except for the orthosilicate glasses, show major polarized Raman bands in the 700-400 cm\(^{-1}\) region. These bands have been suggested to be associated with the presence of bridging oxygens, or Si-O-Si linkages, in the structure (McMillan, 1984; and references therein). The appearance of these bands in the silicate glass spectra has been generally taken as diagnostic of Si-O-Si linkages within the glass structure, or silicate units more polymerized than the orthosilicate. These bands are always highly polarized, suggesting symmetric motions of bridging oxygens.

3.3 Results

3.3.1. High-temperature Raman spectra of \(K_2Si_4O_9\)

Raman spectra of \(K_2Si_4O_9\) glass and melt obtained at different temperatures are presented in Fig. 3.2. The room temperature spectrum of \(K_2Si_4O_9\) glass is very similar to previously published spectra (Matson et al., 1983; McMillan et al., 1992). In the high frequency region there is a strong peak at 1102 cm\(^{-1}\) with a shoulder near 1150 cm\(^{-1}\). Although the final assignment of these two peaks is not yet clear, a generally accepted model suggests that they
Fig. 3.2. Raman spectra of $K_2Si_4O_9$ glass and melt at different temperatures.
originate from Si-O-stretching vibration from two different types of Q\textsuperscript{3} species (three bridging oxygens per tetrahedrally coordinated cation) (Matson et al., 1983). The features of the low frequency envelope of the room temperature Raman spectrum consist of a dominant peak near 520 cm\textsuperscript{-1} and a weaker band at 592 cm\textsuperscript{-1}. The 520 cm\textsuperscript{-1} band is generally assigned to the symmetric vibration of the linkage of Si-O-Si from Q\textsuperscript{3} species, whereas the assignment of the 592 cm\textsuperscript{-1} peak is still controversial and is referred to in this paper as the "defect" band. A weak peak near 700 cm\textsuperscript{-1} is related to inter-tetrahedral deformation modes with a 3-D network and is referred to as the \(v_6\)(Si-O-Si) band (Sharma et al., 1984).

In situ high temperature Raman spectra of K\textsubscript{2}Si\textsubscript{4}O\textsubscript{9} glass have been obtained in previous studies (McMillan et al., 1992; Mysen and Franz, 1992, 1994). Our results are very similar to that of the previous studies. No striking changes occur in the Raman spectra between the room temperature and glass transition temperature (\(T_g=752\) K) (Richet and Bottinga, 1980). Above \(T_g\), the intensity of the 592 cm\textsuperscript{-1} band increases strikingly relative to that of the 520 cm\textsuperscript{-1} band. In the high frequency region, the shoulder around 1150 cm\textsuperscript{-1} moves toward lower frequencies. The two bands merge gradually into a single peak. This change may be attributed to the homogenization of the environment of Q\textsuperscript{3} species. At 1246 K, the highest temperature of our study, the position of the symmetric high frequency peak remains 1102 cm\textsuperscript{-1}. In the low
frequency region, the position of the 592 cm\(^{-1}\) peak does not change with temperature, whereas that of the band relating to Si-O-Si bending from Q\(^3\) species shifts from 520 to 510 cm\(^{-1}\).

3.3.2. High-pressure Raman spectra of K\(_2\)Si\(_4\)O\(_9\) glass

Figure 3.3 shows the high pressure Raman spectra of K\(_2\)Si\(_4\)O\(_9\) glass at different pressures in the range 1 atm to 15.2 GPa. The pressure dependence of the Raman peak frequencies is shown in Fig. 3.4. Between 1 atm and 3.8 GPa, the peak of the high frequency envelope shifts from 1102 to 1134 cm\(^{-1}\), while the intensity of the 591 cm\(^{-1}\) band increases dramatically relative to that of the 520 cm\(^{-1}\) band. Between 3.8 to 6.0 GPa the position of the 591 cm\(^{-1}\) peak gradually moves to 601 cm\(^{-1}\) with relative intensity increasing smoothly. In the high frequency region, the position of the strong shoulder remains almost constant around 1134 cm\(^{-1}\) whereas the strong band at 1102 cm\(^{-1}\) gradually moves to high frequency and merges into 1134 cm\(^{-1}\) band. From 6.0 to 7.7 GPa, the position of the high frequency peak suddenly decreases from 1134 to 1121 cm\(^{-1}\) and its intensity also drops dramatically. At the same time the "defect" band becomes a dominant feature in the low frequency region and its frequency jumps from 601 to 623 cm\(^{-1}\). From 7.7 to 15.2 GPa, the high frequency peak gradually shifts downwards and loses its intensity. At a pressure of 15.2 GPa it becomes a very weak peak located at ~1111 cm\(^{-1}\). The "D\(_2\)" band becomes the main feature in the entire spectrum.
Fig. 3.3 Raman spectra of K$_2$Si$_4$O$_9$ glass at different pressures.
Fig. 3.4. Pressure dependence of the band frequency in the Raman spectra of K$_2$Si$_4$O$_9$ glass
at a pressure of 15.2 GPa and its frequency increases to 663 cm⁻¹.

In Fig. 3.5 the Raman spectra of K₂Si₄O₉ glass recorded during the decompression process are presented to illustrate to what extent the pressure induced deformation mechanisms in this silicate glass are reversible. With decreasing pressure the intensity of the high frequency peak gradually regains its intensity and again becomes a strong peak at 1 atm. Meanwhile, the two peaks in the lower frequency region also recover. The spectrum recorded after complete pressure release is somewhat different from the starting material. The intensity of the "D₂" band in the spectrum of the K₂Si₄O₉ glass is greatly enhanced and its position shifted to 595 cm⁻¹, which is similar to the observed behavior of the D₂ band of SiO₂ glass quenched from high pressure (Hemley et al., 1986) as well as in pressure quenched Na₂Si₄O₉ and Rb₂Si₄O₉ glasses (Wolf et al., 1990; Sharma et al., 1994). The 520 cm⁻¹ peak is also shifted to 526 cm⁻¹. Furthermore, the high frequency peak shifts to 1106 cm⁻¹ and becomes more symmetrical after decompression. Some new features appear on the low frequency side between 950 to 1050 cm⁻¹ (Fig. 3.5).

3.4. Discussion

3.4.1. The D₂ band in SiO₂ and GeO₂ glasses

Before discussing the assignment of the 592 cm⁻¹ peak in K₂Si₄O₉, we briefly review the controversy surrounding the
Fig. 3.5. Raman spectra of K$_2$Si$_4$O$_9$ glass recorded during the decompression process.
assignment of D$_2$ band in SiO$_2$ and GeO$_2$ glasses. From the observed increase in the intensity of the 606 cm$^{-1}$ Raman band of SiO$_2$ glass with increasing exposure to the neutron irradiation, and from the results reported for the silicate glasses (Bates et al., 1974), the said band has been assigned to localized modes of defect represented by a broken Si-O-Si linkage, i.e.

\[
[-\text{Si} \cdots \text{O-Si}]^{-}
\]

It is well known that the addition of Na$_2$O to pure SiO$_2$ will result in breaking of Si-O-Si linkages and formation of SiO$^-$ bonds, where the O$^-$ is a nonbridging oxygen atom. Concurrently, we observe a prominent increase in intensity in the high frequency region around 1100 cm$^{-1}$. The strong and polarized Raman band in this region is known to be due to a Si-O$^-$ stretching mode. In contrast to the behavior of such silicates, no significant change in intensity is observed in SiO$_2$ samples as a result of irradiation. Therefore, the 606 cm$^{-1}$ band has been attributed to a partially broken Si-O bond (Bates et al., 1974).

Amorphous germanium dioxide (a-GeO$_2$) has served as an useful analog for understanding the pressure and temperature induced structural changes in SiO$_2$ glass and has been studied by Raman spectroscopy. The Raman spectrum of GeO$_2$ has a broad high-frequency shoulder to the main Raman peak near 520 cm$^{-1}$. The intensity of this band is enhanced in neutron
irradiated samples (Galeener, 1980) and the behavior is believed to be analogous to the 606 cm\(^{-1}\) "defect" band in a-Si\(\text{O}_2\). The structural origin of the 520 cm\(^{-1}\) band of Ge\(\text{O}_2\) glass is also unclear, as in the case of Si\(\text{O}_2\) glass. One group of studies has assigned the 520 cm\(^{-1}\) band to broken-bond or other bond defects in the network (Sharma et al., 1984; Galeener, 1980) while another ascribes the band to three-member rings embedded in a CRN (Galeener, 1982b; Galeener and Geissberger, 1983). A recent Raman spectroscopic study of Ge\(\text{O}_2\) glass in diamond cell has demonstrated a considerable enhancement of the intensity of the 520 cm\(^{-1}\) band with pressure compared to that before compression (Durben and Wolf, 1991). This behavior is claimed to be consistent with an increase in three-member ring population.

Recently, Murray and Ching (1989) suggested that specific Si-O-Si angles (close to those found in threefold or fourfold rings) could be responsible for the "D\(_2\)" bands. Kubicki and Sykes (1993) pointed out that any assignment of the D\(_2\) peak should be compatible with at least three experimental facts: the frequency of the vibrational mode, the isotopic frequency shifts, and the anomalously narrow width of the peak. In fact, two more constraining factors should also be added to complete the requirements for the assignment of the D\(_2\) peak, namely, the enhancement of its intensity with both temperature and pressure. The fact that the intensity of the D\(_2\) peak of Si\(\text{O}_2\) and Ge\(\text{O}_2\) increases after quenching from high
pressure has been cited as supportive evidence for the three-member ring structure, as such structure would be favored with increasing density of glass or melt under pressure (Hemley et al., 1986; Durben and Wolf, 1991). On the other hand, the intensity increase in the D2 band with temperature (Seifert et al., 1981) contradicts the above assignment because, with increasing temperature, a compact structure such as the three-member ring would not be favored in view of the fact that the density decreases with temperature.

3.4.2. Assignment of the 592 cm\(^{-1}\) "defect" band and implications for the structure

Because of the similarity in the behavior under pressure and temperature of the 592 cm\(^{-1}\) band of K\(_2\)Si\(_4\)O\(_9\) glass to that of the "D2" band of GeO\(_2\) and the 600 cm\(^{-1}\) band in Na\(_2\)Si\(_4\)O\(_9\) glass (Wolf et al., 1990), it is reasonable to assume that the 592 cm\(^{-1}\) peak is related to the same structural feature responsible for the 520 cm\(^{-1}\) band in GeO\(_2\) glass and the 606 cm\(^{-1}\) band in SiO\(_2\) glass.

It is to be noted that for K\(_2\)Si\(_4\)O\(_9\) glass, the density ratio \(\rho/\rho_0\) decreases at first in going from room temperature to the strain point (739 K) and then shows a slight increase between 739 K and 993 K. Above 993 K, the density decreases again (Xu and Manghnani, 1992). Interestingly, our results (Fig. 3.2) show that the intensity of the 592 cm\(^{-1}\) band increases strikingly at temperatures higher than 993 K. This
could be related to the decrease in the density of the K$_2$Si$_4$O$_9$ melt.

As we noted before, the assignments of the 592 cm$^{-1}$ are controversial. McMillan et al. (1992) have pointed out that the concentration of 3-membered rings should not increase with increasing temperature and lower density in the liquid, although the nature of this band still remains open to discussion. Apparently, further work is needed to pursue the previous studies on the assignment of this "D$_2$" band. In order to explain the enhancement of the "D$_2$" band with both increasing pressure and temperature we invoke the model having units with small Si-O-Si angle as proposed by Murray and Ching (1989). The increase in the intensity of the "D$_2$" band (592 cm$^{-1}$ at 1 atm) with pressure (Fig. 3.3) could be attributable to an increase in the population of units with small Si-O-Si bond angle. In addition, the shift of the peak position to higher frequency (665 cm$^{-1}$ at 15.2 GPa) is indicative of a shift in the bond angle of such linkage to smaller values with increasing pressure. This would again be in accord well with both theoretical calculations (Murray and Ching, 1989) and experimental observation (Meade et al., 1992). In the high-temperature Raman spectra (Fig. 3.2) the 520 cm$^{-1}$ band shifts to lower frequency by about 10 cm$^{-1}$, whereas the 592 cm$^{-1}$ peak position remains the same with increasing temperature. If we assume that the red shift of the 520 cm$^{-1}$ band mainly reflects the increase of the Si-O-Si
bond angle and causes the volume increase of the melt at high temperature, we can argue that the increase in bond angle of certain Si-O-Si linkages occur at the expense of some other Si-O-Si linkages. That is to say, some Si-O-Si bond angles decrease while others increase as a result of structural deformation at high temperature. In this event the concentration of the Si-O-Si linkages with smaller intertetrahedral angle might be expected to increase at high temperature. The result that the "defect" band does not move with temperature suggests that the Si-O-Si bond angle associated with the 592 cm⁻¹ mode represents the limit to which the angle of other Si-O-Si bonds can shrink at the high temperature end. It is to be noted that the width of this band increases slightly, which indicates a wider distribution of Si-O-Si angles about the mean value at high temperature.

The above scenario of the generation of structural units with small Si-O-Si bond angle would be consistent with the idea that the "D₂" band is due to "partially broken" Si-O bonds. Bearing this in mind, we now examine the character of the Si-O-Si mode. For the Si-O-Si linkages of silicates in general, the Si-O-Si angle is larger than the critical θₑ (Sen and Thope, 1977). Therefore, one would regard the stretching modes in the high frequency region in terms of coupled Si-O vibrations rather than stretching vibrations of isolated SiO₄ tetrahedra. The character of the mode can be assessed in terms of the relative contribution from two separate Si-O
bonds to the total stretching force on the oxygen atom along the line of one of the Si-O bonds. It can readily be shown that if one Si-O contributes $K_{SiO}$ (the Si-O stretching force constant), then another Si-O contributes $K_{SiO} \cos^2 \theta$, where $\theta$ is the complement of the Si-O-Si angle (McMillan, 1984). Therefore, the smaller the angle of the linkage the weaker is the interaction between two neighboring SiO$_4$ tetrahedra. Consequently, when $\theta$ approaches 90°, the two connected SiO$_4$ tetrahedra are almost completely decoupled. Furthermore, it is known that inverse relationship exit between the change of the band angle at the oxygen atom shared by the two adjacent Si atoms and Si-Obr length (e.g., Taylor, 1972; Gibbs et al., 1977) Therefore, under both situations the Si-O-Si bond is weakened. According to this viewpoint, the linkage with small angle could be regarded as partially broken. This may explain why we do not observe the strong Raman band in 1100 cm$^{-1}$ region when the concentration of such defects increases in the glass and melt.

3.4.3. Temperature and pressure effect on the structure of K$_2$Si$_4$O$_9$

In the following, we examine the effect of increasing temperature and pressure on the Raman spectra of K$_2$Si$_4$O$_9$ glass sample.

a. Raman spectra of K$_2$Si$_4$O$_9$ with increasing temperature and pressure
As discussed in the previous section, the behavior of the low frequency spectra at different temperatures (shown in Fig. 3.2) can be interpreted in terms of a temperature effect, which increases the bond angle of Si-O-Si linkage of the Q⁳ species, while causing another group of Si-O-Si linkages to undergo a decrease in their bond angle as a result of distortion of the glass and the melt structure at high temperature. On the other hand we observed that an increase in pressure decreases the angle of Si-O-Si linkages (Fig. 3.3). From the changes in the strong Raman bands in the high frequency region involving the Si-O⁻ stretching vibrations, it is evident that the bond length of Si-O⁻ is sensitive to the initial increase in temperature and pressure. The high frequency features have been considered as Si-O⁻ bonds in two different types of Q³ species (Matson et al., 1983; Dickinson et al., 1990; McMillan et al., 1992). Here we simply assume that the Si-O⁻ bonds in the Q³ and Q³' species have different bond lengths. In Fig. 3.2, the shoulder around 1150 cm⁻¹ gradually merges into the main peak at 1102 cm⁻¹, indicating the Si-O⁻ bond with shorter bond length extends more with temperature and finally, at higher temperatures above T_g, the both types of Q³ species have the same environment, which is represented by a single symmetric Gaussian peak at 1102 cm⁻¹. On the other hand, as pressure is increased to 3.8 GPa, the position of the stronger peak due to Q³ species shifts to 1134 from 1102 cm⁻¹, indicating a relatively larger decrease in bond length of Si-O⁻ in the
main Q³ species, that has longer Si-O⁻ bond (Fig. 3.3). This demonstrates the different response of the Si-O-Si linkage and Si-O⁻ bond to the external constraints. Most theoretical and experimental work on SiO₂ (Murray and Ching, 1989, Meade et al., 1992) indicate that, under relatively low pressure (<10 GPa), the Si-O bond barely changes within the experimental error of x-ray diffraction techniques, whereas the average Si-O-Si bond angle decreases with pressure. Because of the absence of nonbridging oxygen atoms in SiO₂ glass, however, the response of Si-O⁻ bond cannot be assessed. In fact, the difference in viscosity-pressure relations between highly polymerized and depolymerized compositions (Scarf et al., 1987) may originate from the difference in the characteristics of Si-O-Si and Si-O⁻ bonds.

Above the T⁰ the main high frequency band of Q³ species is still stable and its position remains at 1101 cm⁻¹ (Fig. 3.2). This indicates the stability of the Si-O⁻ bond length of the Q³ tetrahedral structural unit over the temperature range of our present study. In the high pressure spectra, between 3.8 to 6.0 GPa, the position of the high frequency band at 1134 cm⁻¹ due to the Q³ species shifts only slightly. Meanwhile in the low frequency region, the intensity of the "defect" band gradually increases relative to the 520 cm⁻¹ band and its frequency changes smoothly from 595 cm⁻¹ at 3.8 GPa to 603 cm⁻¹ at 6.0 GPa. From 6.0 to 7.7 GPa, abrupt changes occur in both positions and intensities of Raman bands. At 7.7 GPa,
the "defect" band becomes a dominant peak in the low frequency region and its position jumps from 603 cm$^{-1}$ at 6.0 GPa to 623 cm$^{-1}$ at 7.7 GPa. In the high frequency region, the peak position decreases dramatically from 1133 to 1121 cm$^{-1}$ when pressure is increased from 6.0 to 7.7 GPa, and the intensity drops significantly. The changes in the Raman spectra of K$_2$Si$_4$O$_9$ glass between 6 and 7.7 GPa may be similar to the changes observed in SiO$_2$ (≈ 8 GPa) and GeO$_2$ (≈ 6.6 GPa) glasses, which have been attributed to coordination increase of Si and Ge in the glass structure (Meade et al., 1992; Itie et al., 1989). The decrease in frequency of the high frequency band, may be related to an increase in the bond length accompanying the possible increase in the coordination, viz five or six-fold for Si. The observed decrease in the intensity of the high frequency band of the Q$^3$ species may result from the interaction between non-bridging oxygen and neighboring silicon atom.

b. Raman spectra of K$_2$Si$_4$O$_9$ in the decompression process

Figure 3.5 illustrates the Raman spectra of K$_2$Si$_4$O$_9$ glass under decompression. The original main characteristics of the spectrum at 1 atm. are retained after quenching to ambient pressure. Some changes are noticeable, however. In the low frequency region, the "defect" band gains intensity relative to that of the peak at 526 cm$^{-1}$. This indicates that in the compressed glass, the concentration of Si-O-Si linkages with smaller intertetrahedral angle increases
relative to that before compression. The frequency change from 520 to 526 cm$^{-1}$ suggests an even smaller angle for the Si-O-Si linkages. In the high frequency region, the main Raman band occurs at 1106 cm$^{-1}$, several wave numbers higher than before compression. This indicates the presence of compressive strain in the glass. The shoulder at 1134 cm$^{-1}$ is no longer seen, indicating that the environments of Q$^3$ species have become more homogenous after compression and that the bond length of Si-O$^-$ is slightly shorter than the bond length before compression. In Fig. 3.5 some new features can be seen around 950 to 1050 cm$^{-1}$ on the low frequency side of the 1106 cm$^{-1}$ peak. The positions of these weak features usually reflect those of the more depolymerized structural units, e.g., Q$^2$ species. It has been suggested that they may result from a disproportionation reaction (Wolf et al., 1990) or from SiO$_5$ and SiO$_6$ groups (Xue et al., 1991). Here we present another possible mechanism. After compression, the angles of Si-O-Si linkages in Q$^3$ species become smaller and the coupling between SiO$_4$ tetrahedra in adjacent Q$^3$ species is weakened. This may cause redistribution of K$^+$ ions, thus creating Q$^2$ species.

3.4.4. Coordination change in silicate glasses and melts under high temperature and pressure

Recently much attention has been focused on the structural change of silicate glasses and melts in terms of changes in coordination of Si under high pressure and
temperature. Molecular dynamics simulations predict that
defect complexes consisting of silicon with five oxygen
neighbors (Si (V)) are of importance in the mechanism by
which viscous flow takes place (Angell et al., 1983; Brawer,
1985; Kubicki and Lasaga, 1988). The coordination changes of
Si and Al cation from four to six fold have been suggested as
a possible mechanism for the drastic increase of melt density
(Waff, 1975). This is supported by molecular dynamics
simulations (Rigden et al., 1984; Stolper and Ahrens, 1987)
and IR vibrational spectra (Williams and Jeanloz, 1988).

Specifically for K$_2$Si$_4$O$_9$ glass, significant results have
been drawn from previous studies. Stebbins (1991) has clearly
shown from $^{29}$Si NMR studies of K$_2$Si$_4$O$_9$ glass that Si (V) does
exist in silicate liquids at low pressure and the abundance
of this species increases with temperature. Stebbins and
McMillan (1989) demonstrated five and six coordinated Si in
K$_2$Si$_4$O$_9$ glass quenched from 1.9 GPa and 1473 K. After
quenching from 6 GPa, Xue et al. (1991) observed evidence for
both Si (V) and Si (VI) in NMR spectra of K$_2$Si$_4$O$_9$ glass and
that their intensities increased with pressure. It is
interesting to note, however, that to the best of our
knowledge, most direct, clear evidences supporting the five
coordinated Si in either organic molecules (Laine et al.,
1991; Heereos et al., 1994) or silicate glasses and melts
(Stebbins and McMillan, 1989; Angell et al., 1983) is derived
from $^{29}$Si NMR studies. The same is true for sixfold Si with
the exception of a few X-ray studies (Meade et al., 1992;
Itie et al., 1989) and one IR vibrational spectral study (Williams and Jeanloz, 1988). Raman studies, unfortunately, have not yet produced clear evidence for the existence of five and six coordinated Si, except in an indirect way from changes in position and intensity of Raman bands (Durben and Wolf, 1991; Xue et al., 1991; Kubicki et al., 1992). Similarly, in the present study, we do not see any new peak appearing at either high temperature or pressure which can be clearly assigned to five or six coordinated Si. There could be two reasons for this. First, although the Raman technique is a very sensitive tool to detect the local structure of materials, the concentrations of species like Si (V) and Si (VI) may be very low (e.g., ~0.1±0.02% of Si (V) in fast-cooled K2Si4O9 glass (Stebbins, 1991)) and therefore beyond the detection limit of the Raman technique. For Na2Si4O9 quenched from 12 GPa, however, even though the concentrations of Si (V) and Si (VI) have been calculated to be 8.5% and 6.3%, respectively (Xue et al., 1991), no new peak at pressures as high as 50 GPa assignable to Si (V) or Si (VI) (Wolf et al., 1990) has been found. In the case of SiO2 and GeO2 glasses, coordination changes from fourfold to sixfold have been claimed by x-ray technique, starting from 8 and 6.6 GPa (Meade et al., 1992; Itie et al., 1989). Raman studies of compressed SiO2 and GeO2 at above 30 and 50 GPa did not show any direct evidences of V and VI-coordinated Si or Ge (Hemley et al., 1986; Durben and Wolf, 1991).
Second, it has been suggested that the Raman intensities from vibrations of ionic bonds are about two orders of magnitude weaker than that of the vibrations of covalent bonds (George et al., 1953; Hester, 1967). On the basis of our results, we can conclude that the fifth or sixth oxygen atoms may be geometrically close to the Si cation but the bonds between them are basically ionic. From the point of view of charge density, there is little or no oriented overlaps of electronic cloud between these extra oxygen atoms and Si cations. Therefore, even though those Si atoms are five or six fold coordinated, they are not really five or six fold bonded. Consequently, such special units will not produce new bands in the Raman spectra and the tetrahedral structural units remain their main feature in the spectra. The decrease in the intensity of the Si-O\textsuperscript{-} stretching modes may be attributable to the deformation of the tetrahedral units at high pressure (Kubicki et al., 1992) and the decrease in frequency of such modes due to the increase in the bond length when the coordination number of Si atoms increases (Itie et al., 1989). Recent molecular dynamic simulations on larger ensembles of particles (Rustad et al., 1990) indicates that factors other than coordination number may be important in determining the nature of diffusive atomic motions, consistent with our assumption of non-covalently bonded five coordinated Si, because such Si (V) does not really provide one more space for coming oxygens.
The coordination of Si in the high pressure $\text{K}_2\text{Si}_4\text{O}_9$ glass may be similar to that of Mo ions in $\text{HgMoO}_4$ in Wolframite ($\text{NiWO}_4$) structure. According to x-ray diffraction data the structure of $\text{HgMoO}_4$ (space group $\text{I2}/\alpha$, $Z=2$) consists of edge-sharing molybdate octahedra (Sleight, 1972). The six Mo-O distances are, however, very different, viz 1.722 Å, 1.944 Å, and 2.228 Å. Because of two rather long Mo-O bonds the Raman spectrum of $\text{HgMoO}_4$ is dominated by tetrahedrally coordinated Mo ions (Blasse, 1975). Blasse (1975) has shown that the vibrational spectra of $\text{HgMoO}_4$ can be analyzed by considering the crystal structure as packing of $\text{MoO}_4$ tetrahedra and $\text{Hg}^{2+}$ ions, and Mo cation occupying $\text{C}_2$ symmetry. The fact that two other oxygens at 2.228 Å are approaching a tetrahedrally coordinated Mo ion is reflected only indirectly by the observed large splitting of the antisymmetric stretching Mo-O mode (i.e., 855, 825 and 694 cm$^{-1}$). The potential of Raman spectroscopy to be able to distinguish between covalent and ionic bonds is not fully appreciated in glass literature. It is interesting to note here that the average Mo-O bond in $\text{HgMoO}_4$ is 1.965 Å, which is longer than the expected average Mo-O bond for tetrahedrally coordinated oxygen even though all the oxygens are not in the first coordination sphere of Mo cation. The results of a x-ray diffraction study of Si$\text{O}_2$ glass at high pressure (Meade et al., 1992) show that increase in average Si-O bond length with pressure may reflect a situation similar to that of the HgMoO$_4$ crystal. As the Si atoms tend to achieve six fold
coordination by edge-sharing of SiO₄ tetrahedra, the two additional oxygen will approach the four coordinated Si. This will cause bond length of Si (IV)-O bonds to increase because of electrostatic repulsion between the oxygen atoms. There will, however, be an intermediate structure over a pressure range when the additional one or two oxygens in Si (V) or Si (VI) type units are not in the first coordination sphere of four-fold coordinated Si but are close enough to distort and influence the SiO₄ tetrahedra.

3.4.5. Implications for viscosity of silicate glasses and melts

Although several models have been proposed, the basic mechanism for the decrease of viscosity of some geologically important silicate and aluminosilicate compositions with pressure is not yet well understood (Dickinson et al., 1990). It has long been recognized that the decrease of Si-O-Si bond angles with pressure could weaken the network structure (Sharma et al., 1979b). Observed anomalous decrease in viscosity of GeO₂, NaAlSi₂O₆ is most likely related to three dimensional network structure of these materials (Sharma, et al., 1979a; Kushiro, 1976) The disproportionation reaction between different species at high temperature and pressure may also contribute to the decrease of viscosity (Dickinson et al., 1990). Some authors have suggested that pressure-induced coordination change may be responsible for the decrease of viscosity (Kushiro, 1978; Waff, 1975). Because
the phenomena are usually observed at relatively low pressure (<40 kbar), such coordination changes are unlikely to happen in highly viscous melts with 3-D network below 40 kbar (Sharma et al., 1979a).

As we mentioned earlier, a decrease in the Si-O-Si bond angles could weaken the network structure and may be one of the possible mechanisms. However, the question of how it weakens the network structure remains open. As discussed earlier, the decrease in the intertetrahedral angle may cause the Si-O-Si linkage of some units to get elongated and even be partially broken. These defects in the network give rise to a Raman band at ~592 cm\(^{-1}\). Therefore, we conclude that the pressure effect on highly polymerized glass or melt structures is to depolymerize the network structure by creating defects in the network and, consequently, the viscosity decreases.

In contrast to highly polymerized glasses and melts, those of relatively depolymerized composition show a viscosity increase with pressure in the pressure range 0 to 4.0 GPa (Scarf et al., 1987). This difference in response to pressure may be attributed to the nature of the Si-O\(^-\) bond, where O\(^-\) is a nonbridging oxygen atom. Figure 3.3 shows that, between 1 atm to 3.8 GPa, the Si-O (O is bridging oxygen atom) bond length does not change but the bond length of Si-O\(^-\) (O\(^-\) is non-bridging oxygen atom) does shorten. This is reflected in the increase in the frequency of the Raman
band in the high frequency region. The frequency increase of the Raman band relating to Si-O\(^-\) stretching in Q\(^3\) species has also been observed in previous studies on Na\(_2\)Si\(_4\)O\(_9\) glass (Wolf et al., 1990) and Rb\(_2\)Si\(_4\)O\(_9\) glass (Sharma et al., 1994) to 5.0 GPa. It is obvious that when the bond length decreases, the Si-O\(^-\) bond will become stiffer, and the activation energy for breaking Si-O\(^-\) bond will increase as well. As a result, the relative depolymerized silicate melts, in which there are many Si-O\(^-\) bonds, will exhibit an increase in viscosity with pressure within 5.0 GPa. This is also consistent with the free volume theory. Free volume inside the glass sample will decrease with increasing pressure, and the viscosity will increase.

The \(\text{d}v/\text{d}P\) of the high frequency envelope in the pressure range of 0 to 3.8 GPa is 0.809 cm\(^{-1}\) per kilobar, close to the value of 1.07 for the corresponding peak in the Rb\(_2\)Si\(_4\)O\(_9\) glass (Sharma et al., 1994). This result indicates that the alkali cations may only have a slight effect on the structure. From the shift in the Raman band it appears that decrease in the Si-O\(^-\) bond stops beyond 5.0 GPa (Fig. 3.4). This observation is in agreement with the results of studies on Na- and Rb-tetrasilicate glasses by previous workers (Wolf et al., 1990 and Sharma et al., 1994). It is possible that, for those relatively depolymerized compositions, after reaching a maximum value the viscosity may actually decrease or remain constant with pressure above 5.0 GPa. This needs further investigation.
3.5. Conclusions

We have measured the Raman spectra of K$_2$Si$_4$O$_9$ glass and melt at high temperature and at 1 atm, as well as under high pressure at room temperature. We observed an increase in the intensity of the "defect" 592 cm$^{-1}$ band with both temperature and pressure. Our results do not support the assignment of the "defect" band to small ring structure as previously proposed. Instead, a model of Si-O-Si linkage with small bond angle appears to be consistent with our experimental results and also with an earlier model of "partially broken" Si-O bonds.

From the observed changes in the Raman spectra at high temperatures we conclude that the increase in volume of silicate melts at high temperatures results from an overall increase in Si-O-Si bond angle. On the other hand, our high pressure data are consistent with the previous conclusion that the Si-O-Si bond angle decreases with increasing pressure. It is interesting to note that the Si-O$^-$ bond responds to change of temperature and pressure differently compared to the Si-O-Si bond. In the former the bond length decreases with increasing pressure while in the latter it probably gets elongated slightly. No direct evidence for Si (V) and Si (VI) has been found in our Raman spectra of K$_2$Si$_4$O$_9$ glass either at high temperature or under high pressure. We suggest that there may be two reasons for this result. First, the concentration of these species is so low that it
is beyond the detection limit of the Raman technique. Second, the fifth and sixth oxygen atoms may only connect the Si cation through ionic bonds, which would make detection difficult for the Raman technique. Therefore, we propose that those Si (V) and Si (VI) atoms are only geometrically five or six fold coordinated, but not really five or six fold bonded, i.e. the additional atoms are not in the first coordination sphere of Si atoms.

We have proposed the following mechanism for the decrease in viscosity of certain highly polymerized compositions with increased pressure. The decrease of Si-O-Si angles weakens the coupling between neighboring SiO₄ tetrahedra and creates defects in the network, which is equivalent to decreasing the degree of polymerization, and the viscosity will decrease. For the depolymerized composition, viscosity increases with increased pressure. We attribute this to the shortening of Si-O- bond length. The viscosity increase with pressure has been experimentally tested in the 0-5.0 GPa range. Our pressure Raman studies suggest that a viscosity maximum centered around 5.0 GPa is a good possibility for these depolymerized compositions.
CHAPTER 4
STRUCTURAL STUDY OF ALKALI AND IRON-CONTAINING SILICATE GLASSES AT HIGH TEMPERATURE

4.1 Introduction

Iron is an important component of natural magmatic liquids. A knowledge of the structure of iron-containing melts and its dependence on composition, temperature, pressure and oxygen fugacity is fundamental to understanding the physical, chemical and thermodynamic properties of magmas. Raman spectra of silicate melts are weak and presence of strong black body radiation at high temperatures poses some experimental difficulties for Raman spectroscopy. For this reason, in the past most studies were carried out on glasses quenched from their melts, and the results are extrapolated to the liquid structure. However, melts and glasses are not necessarily identical because a marked break in most physical properties occurs at the glass transition temperature $T_g$ where the viscosity attains $10^{13}$ poises (e.g., Doremus, 1973; Volf, 1988).

Raman, infrared and magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy have been used extensively in structural studies of silicate glasses in order to avoid the difficulties associated with carrying out in situ high temperature experiments (e.g., Brawer and White, 1975; Furukawa and White, 1980; Galeener and Mikkelsen, 1981;
Sharma et al., 1981; Mysen et al., 1982; McMillan, 1984; Domine and Piriou, 1983; Stebbins, 1987). To date, several in situ high temperature studies have been conducted for alkali silicate and aluminosilicate glasses and melts (Sharma et al., 1978; Seifert et al., 1981; McMillan et al., 1992; Stebbins and Farnan, 1992). A considerable amount of information on the average structural variation (e.g., the temperature dependence of coordination environments of Si$^{4+}$ and Al$^{3+}$) and the dynamic behavior (e.g., the rate of exchange of oxygen ions between different anionic species which has been suggested to be related to the change of viscosity with increasing temperature) of silicate glasses and melts has been obtained through the combination of vibrational and NMR spectroscopy. Unfortunately, a very limited number of studies of iron-containing silicate glasses above $T_g$ has been carried out because of experimental difficulties (Wang et al., 1993). As a counterpart of Al$^{3+}$ ions, fourfold-coordinated Fe$^{3+}$ ions may have similar influence upon the anionic structure of the silicate glasses (e.g., Dingwell and Virgo, 1987; Mysen and Virgo, 1989). Because of the prominent difference in the chemical affinity and electronegativity between Al$^{3+}$ and Fe$^{3+}$ ions, however, the structural role of Fe$^{3+}$ under high temperature may be different from that of Al$^{3+}$. The paramagnetic properties of Fe$^{3+}$ seriously limit the application of NMR spectroscopy to the iron-containing silicate glasses and melts. Thus, in situ high temperature Raman spectroscopy can play a very
important role in understanding the structure and properties of iron-containing glasses below and above $T_g$ as well as of iron-containing melts.

High-temperature Raman studies can also provide insight into the shift of anionic disproportionation reactions with temperature. In alkali and alkaline earth silicate glasses, certain distributions of silicate species $Q^n$ (where $n$ refers to the number of bridging oxygens per tetrahedrally coordinated, $T$, cation) should exist within specific composition regions. The $Q^n$ distributions depend upon composition through changes in the quantity $NBO/T$, the average ratio of nonbridging oxygens to the tetrahedrally coordinated cations, (e.g., Mysen et al., 1980; Matson et al., 1983; Murdoch et al., 1985). Thus, for the range $(4>NBO/T>2)$, silicate glass structures are usually dominated by $Q^0$, $Q^1$, and $Q^2$ species; for $(2>NBO/T>1)$ $Q^1$, $Q^2$, and $Q^3$ species dominate; for $(1>NBO/T>0)$ $Q^2$, $Q^3$, and $Q^4$ species coexist; and for $NBO/T=0$, only $Q^4$ species are present. A model of disproportionation reaction between these species, when temperature is higher than the glass transition $T_g$, has been suggested as

$$2Q^n = Q^{n+1} + Q^{n-1} \quad (4>n>0) \quad (4.1)$$

The change in the relative abundance of various species with increasing temperature above $T_g$ indicates the direction of the change in the equilibrium.
In this study, we present the results of our investigation of the temperature dependence of Raman spectra of iron-containing silicate glasses below and above $T_g$. We have examined glasses with the compositions of $K_2O\cdot0.5Fe_2O_3\cdot3SiO_2$ (KFS), $0.5Na_2O\cdot0.5Fe_2O_3\cdot3SiO_2$ (NaFeSi$_3$O$_8$, Fe-albite; NFS0), $Na_2O\cdot0.5Fe_2O_3\cdot3SiO_2$ (NFS1) and $1.5Na_2O\cdot0.5Fe_2O_3\cdot3SiO_2$ (NFS2). These results of the present study are anticipated to be useful in evaluating the response of the structure to the systematic change in composition and increasing temperature. The NFS1 glass was also investigated with Mössbauer spectroscopy and the compositions of glasses were analyzed using electron-microprobe (Table 1).

4.2 Results

4.2.1. Mössbauer spectrum of NFS1 glass

Table 2 reports Mössbauer parameters derived by least-squares curvefits to the data of NFS1. The spectrum of NFS1 is fitted to a single doublet and is illustrated in Fig. 4.1.

4.2.2. Raman spectra of oxidized Fe-containing glasses

The polarized spectra of oxidized iron-silicate glasses recorded at room temperature (Fig. 4.2a, b, c, d) show strongly polarized features in the low frequency range (400-
Table 1. Data of Microprobe Analysis of Glass NFS1
\((N_2O \cdot 0.5Fe_2O_3 \cdot 3SiO_2)\)

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. of analyses</td>
<td>17</td>
</tr>
<tr>
<td>Ave. wt% (ls)(^a)</td>
<td></td>
</tr>
<tr>
<td>(Na_2O)</td>
<td>19.2 (0.31)</td>
</tr>
<tr>
<td>(Fe_2O_3)</td>
<td>23.3 (0.52)</td>
</tr>
<tr>
<td>(SiO_2)</td>
<td>57.0 (0.75)</td>
</tr>
<tr>
<td>Total</td>
<td>99.5</td>
</tr>
<tr>
<td>Renom. mol%(^b)</td>
<td></td>
</tr>
<tr>
<td>(Na_2O)</td>
<td>22.0</td>
</tr>
<tr>
<td>(Fe_2O_3)</td>
<td>10.4</td>
</tr>
<tr>
<td>(SiO_2)</td>
<td>67.6</td>
</tr>
<tr>
<td>No. of ions in formula(^c)</td>
<td></td>
</tr>
<tr>
<td>(Na^+)</td>
<td>3.98</td>
</tr>
<tr>
<td>(Fe^{3+})</td>
<td>1.88</td>
</tr>
<tr>
<td>(Si^{4+})</td>
<td>6.10</td>
</tr>
<tr>
<td>(O^{2-})</td>
<td>17.00</td>
</tr>
<tr>
<td>(NBO/T)(^d)</td>
<td>0.26</td>
</tr>
</tbody>
</table>

Analytical parameters: 32 \(\mu\)m spot size, 10 nA beam current, 20 s counting time, \(K_\alpha\) line detected for all cations, oxygen calculated by stoichiometry. All iron calculated as \(Fe^{3+}\).

Standard: Amelia albite (Na), microcline (K, Si), magnetite (Fe).

\(^a\) Sampling standard deviation (S) in parentheses.

\(^b\) Individual analyses each normalized to 100%. Weight percentages of each oxide then averaged before making this calculation.

\(^c\) Number of oxygens assumed at listed value.

\(^d\) Bulk non-bridging oxygens per tetrahedral cation calculated from stoichiometry assuming all iron as network-forming \(Fe^{3+}\) and charge balanced by an equal ionic fraction of \(Na^+\).
### Table 2

Mössbauer Parameters for NF51 glass

<table>
<thead>
<tr>
<th>Cation Parameters</th>
<th>(Fe$^{3+}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>δ</td>
<td>0.28 (0.02)</td>
</tr>
<tr>
<td>Δ</td>
<td>0.85 (0.008)</td>
</tr>
<tr>
<td>% Area</td>
<td>50 (1), 50 (1)</td>
</tr>
<tr>
<td>% Gauss</td>
<td>46 (5), 44 (5)</td>
</tr>
<tr>
<td>Γ</td>
<td>0.57 (0.01), 0.59 (0.01)</td>
</tr>
</tbody>
</table>

Notes: Symbols: δ, isomer shift; Δ, quadrupole splitting; Γ, halfwidth (FWHM). Units: δ, Δ, Γ in mm/sec; Baseline in counts. Standard deviations (s.d.) in parentheses after each quantity; s.d. of 0 indicates quantity constrained at listed value. Two quantities in an individual category, separated by commas, refer to low-velocity and high-velocity band, respectively. Misfit after Ruby (1973). See text for further discussion.
Fig. 4.1. The Mössbauer spectrum of NFS1 glass is fitted to a single doublet.
Fig. 4.2.(a). Polarized Raman spectra of NFSO glass at room temperature. VV denote parallel and VH denote perpendicular spectra, respectively.
Fig. 4.2.(b). Polarized Raman spectra of NFS1 glass at room temperature. VV denote parallel and VH denote perpendicular spectra, respectively.
Fig. 4.2.(c). Polarized Raman spectra of NFS2 glass at room temperature. VV denote parallel and VH denote perpendicular spectra, respectively.
Fig. 4.2.(d). Polarized Raman spectra of KFS glass at room temperature. VV denote parallel and VH denote perpendicular spectra, respectively.
600 cm$^{-1}$). It is generally believed that, in this range, the spectra consist of both the bands from the symmetric stretching vibration $v_s(T-O-T)$ of bridging oxygens relative to the nearly stationary tetrahedrally coordinated T cations, and so-called "defect" bands (e.g., Galeener and Mikkelson, 1981; Matson et al., 1983; Bunker et al., 1989). In the case of glasses containing non-bridging oxygens, the T-O-T bending mode contribute to the low-frequency envelope (e.g., Furukawa et al., 1981; Kubicki et al., 1992). The depolarized bands in the intermediate range (700-800 cm$^{-1}$) are related to inter-tetrahedral deformation mode within a 3-D network and refereed to as the $v_6(T-O-T)$ modes (Sharma et al., 1984). In the high frequency region the depolarized dominant peaks can be related to the bridging oxygens involved in the T-O-T antisymmetric stretching vibration within the glass network $v_{as}(T-O-T)$. In the spectra of all the Fe$^{3+}$ containing glasses, with the exception of the spectrum of iron albite glass (NFS0), there is a shoulder to the dominant depolarized band at higher frequency side (~1050 cm$^{-1}$) in the spectra of all the glasses. Because the shoulder is strongly polarized, we attribute it to the symmetric stretching vibration of nonbridging oxygens.

Temperature corrected unpolarized Raman spectra of oxidized samples at various temperatures are presented in Fig. 4.3 (a, b, c, d). The frequency positions of the Raman peaks at various temperatures in the spectra of NFS1, NFS2
Fig. 4.3. (a). Unpolarized Raman spectra of NFS0 glass at various temperatures.
Fig. 4.3. (b). Unpolarized Raman spectra of NFS1 glass at various temperatures.
Fig. 4.3. (c). Unpolarized Raman spectra of NFS2 glass at various temperatures.
Fig. 4.3. (d). Unpolarized Raman spectra of KFS glass at various temperatures.
and KFS are tabulated in Table 3, 4 and 5. We note that, at room temperature, the positions of the Raman peaks in these unpolarized spectra (Fig. 4.3a, 4.3b, 4.3c and 4.3d) are somewhat different to that in the polarized spectra in Fig. 4.2a, 2b, 2c and 2d. In the polarized spectra, because of the changes in the intensity of the bands due to different degree of polarization of each individual band component, the overall shape of the envelope could be changed even though it is only to a small extent. This change could result in the difference in the peak summits compared to that in the unpolarized spectra. The intensities of these spectra were temperature corrected to 0 K according to the following equation given by Sverdlov et al. (1974).

\[ I = \frac{2^{8} \pi^{5}(\nu + \nu_{1})^{4}}{9c^{4}} \frac{h}{8\pi^{2}m_{1}v_{1}}(5b'_{1}^{2}+13g'_{1}^{2}) \frac{1}{e^{\frac{h\nu_{1}}{kT}}} \]  

(4.2)

where the \( m_{1} \) is the mass of a harmonic oscillator of frequency \( \nu_{1} \), \( b' \) is the trace and \( g' \) is the anisotropy of the tensor of the polarizability derivatives of a molecule. The tensor of the polarizability derivatives with respect to the normal coordinates \( \frac{\partial \alpha_{uv}}{\partial Q_{1}} = \alpha'_{uv} \), is symmetrical:

\[ \alpha'_{uv} = \begin{bmatrix} \alpha'_{xx} & \alpha'_{xy} & \alpha'_{xz} \\ \alpha'_{yx} & \alpha'_{yy} & \alpha'_{yz} \\ \alpha'_{zx} & \alpha'_{zy} & \alpha'_{zz} \end{bmatrix} \]  

(4.3)

The trace of a tensor is the sum of its diagonal elements:

\[ b_{1} = \alpha'_{xx} + \alpha'_{yy} + \alpha'_{zz} \]  

(4.4)
Table 3

Raman peaks positions (cm\(^{-1}\)) in the spectra of NFS1 at various temperatures

<table>
<thead>
<tr>
<th>T(K)</th>
<th>300</th>
<th>664</th>
<th>854</th>
<th>973</th>
<th>1044</th>
</tr>
</thead>
<tbody>
<tr>
<td>453(s)</td>
<td>477</td>
<td>504</td>
<td>489</td>
<td>502</td>
<td></td>
</tr>
<tr>
<td>535(sh)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>752(w)</td>
<td>745</td>
<td>736</td>
<td>721</td>
<td>720</td>
<td></td>
</tr>
<tr>
<td>943(s)</td>
<td>933</td>
<td>923</td>
<td>920</td>
<td>918</td>
<td></td>
</tr>
</tbody>
</table>

Note: Experimental errors are ±5 cm\(^{-1}\) for strong peaks and ±10 cm\(^{-1}\) for weak peaks. s=strong, sh=shoulder, w=weak.
Table 4

Raman peaks positions (cm$^{-1}$) in the spectra of NFS2 at various temperatures

<table>
<thead>
<tr>
<th>T (K)</th>
<th>300</th>
<th>664</th>
<th>854</th>
<th>1044</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>488(s)</td>
<td>483</td>
<td>512</td>
<td>508</td>
</tr>
<tr>
<td></td>
<td>545(s)</td>
<td>541</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>756(w)</td>
<td>749</td>
<td>742</td>
<td>739</td>
</tr>
<tr>
<td></td>
<td>913(s)</td>
<td>904</td>
<td>904</td>
<td>918</td>
</tr>
<tr>
<td></td>
<td>1061(sh)</td>
<td>1055</td>
<td>1041</td>
<td>1036</td>
</tr>
</tbody>
</table>

Note: Experimental errors are ±5 cm$^{-1}$ for strong peaks and ±10 cm$^{-1}$ for weak peaks. s=strong, sh=shoulder, w=weak.
Table 5

Raman peaks positions (cm\(^{-1}\)) in the spectra of KFS at various temperatures

<table>
<thead>
<tr>
<th>T (K)</th>
<th>300</th>
<th>664</th>
<th>854</th>
<th>1044</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>484(s)</td>
<td>480</td>
<td>517</td>
<td>521</td>
</tr>
<tr>
<td></td>
<td>535(s)</td>
<td>524</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>744(w)</td>
<td>728</td>
<td>723</td>
<td>723</td>
</tr>
<tr>
<td></td>
<td>913(s)</td>
<td>903</td>
<td>910</td>
<td>915</td>
</tr>
<tr>
<td></td>
<td>1057(sh)</td>
<td>1041</td>
<td>1036</td>
<td>1028</td>
</tr>
</tbody>
</table>

Note: Experimental errors are ±5 cm\(^{-1}\) for strong peaks and ±10 cm\(^{-1}\) for weak peaks. s=strong, sh=shoulder, w=weak.
The anisotropy of a tensor is defined as:

$$g_1 = \frac{3}{2} \sum_{u,v} (\alpha_{uv})^2 - \frac{1}{2} (\sum_u \alpha_{uu})^2 =$$

$$= \frac{1}{2} [(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{xy} - \alpha_{yx})^2 + (\alpha_{zz} - \alpha_{zz})^2] + (\alpha_{xy} + \alpha_{yx} + \alpha_{zx} + \alpha_{xz})^2$$

The high-temperature spectra of these glasses before heating and after quenching do not show any appreciable changes, indicating that there is no significant crystallization or compositional change in the samples. At temperatures above 949K (NFSo, NFSl and NFS2) and 664 K (KFS), the samples were observed to soften and flow. This indicates that the glass transition, $T_g$, had already been exceeded. The comparison between the spectra of glasses below and above $T_g$ (>949K) shows that the overall shape of the spectra did not change with temperature.

4.3 Discussion

4.3.1. Mössbauer spectrum of NFSl glass

Mössbauer spectrum of NFSl (Fig. 4.1) is well modeled using a single doublet and the fit results yield component bands having nearly identical area, halfwidth and degree of Gaussian character (Table 2). This strongly suggests that the proportion of Fe$^{2+}$ is negligible in NFSl glass. The symmetry of the spectrum precludes incorporation of a second Fe$^{3+}$ doublet. The isomer shift, $\delta$, value of 0.28 mm/sec for Fe$^{3+}$ in NFSl glass is in a general range, 0.19-0.3 mm/sec.
(Mysen et al., 1980), consistent with fourfold coordination, as determined by comparison with results from Mössbauer studies of crystalline materials (Hafner and Huckenholz, 1971; Annersten and Halenius, 1976; Mysen et al., 1980; Dyar, 1984). The hyperfine parameters determined for Fe$^{3+}$ in NFS1 glass are similar to those which have been assigned to tetrahedral Fe$^{3+}$ for Mössbauer spectra of other glasses in the Na$_2$O-Fe$_2$O-SiO$_2$ system (Mysen et al., 1980; Fleet et al., 1984; Virgo and Mysen, 1985). Fleet et al. (1984) observed a band attributable to a small amount of Fe$^{2+}$ in the Mössbauer spectrum of NaFeSi$_3$O$_8$ glass. The lack of such a band in NFS1 glass can probably be attributed to the less polymerized character and lower synthesis temperature, since both such factors tend to favor a lower Fe$^{2+}$/Fe$^{3+}$ ratio (Mysen et al., 1984, 1985; Lange and Carmichael, 1989).

4.3.2. Room temperature Raman spectra and band assignments

The spectra of the Fe-containing glasses show variable features in the high-frequency range (Fig. 4.2a, b, c, d). These variations in the high frequency region are related to the variation in the number of non-bridging oxygen atoms present in these glasses. Assuming that all Fe$^{3+}$ ions occupy fourfold coordinated positions, the glasses of NFS0 has bulk NBO/T=0, whereas NFS1, NFS2 and KFS have NBO/t=0.25, 0.5 and 0.25, respectively. Therefore, all the oxygens in NFS0 should be bridging oxygens. In the high frequency range (900-1200 cm$^{-1}$), such bridging oxygens are associated with a
depolarized envelope resulting from the anti-symmetric stretching vibration \( \text{vas} (T\text{-O-T}) \). The high frequency spectra of NFS1, NFS2 and KFS glasses consist of a dominant depolarized peak located at -940 and 913 cm\(^{-1}\) respectively with a strong polarized shoulder at higher frequency at -1050 cm\(^{-1}\). The depolarized bands in the polarized spectra of Fe-albite (NFS0) glass (963 cm\(^{-1}\) in Fig. 4.2a) and at -913 cm\(^{-1}\) in the spectra of NFS1, NFS2 and KFS glasses (Figs. 2b, 2c and 2d) corresponds to the antisymmetric coupled mode of FeO\(_4\) and SiO\(_4\) tetrahedra. The fact that this band is depolarized in the spectra of Fe\(^{3+}\) containing glasses indicates that the local symmetry of T cations is close to \( T_d \). This is contrast to weakly polarized high frequency band observed in the spectra of Al- and Ga-albite glasses (Matson and Sharma, 1985).

The strong polarized shoulder at -1050 cm\(^{-1}\) is attributed to the Si-O\(^-\) stretching mode in the Q\(^3\) units. To justify this assignment, we show the Raman spectra of NFS0, acamite (NaFeSi\(_2\)O\(_6\)), NFS1 and NFS2 in Fig. 4.4. It is obvious that, when the number of nonbridging oxygens increase, the shoulders become stronger. In addition, all these shoulders observed in the spectra of depolymerized glasses are strongly polarized. Therefore, it is reasonable to assign these shoulders to the vibrations of non-bridging oxygens from Q\(^3\) species.
Fig. 4.4. Unpolarized Raman spectra of NFS0, acamite (NaFeSi$_2$O$_6$), NFS1 and NFS2 glasses.
4.3.3. Fully polymerized Fe-albite (NFSO) glass below and above \( T_g \)

We have estimated \( T_g \) for Fe-albite from the following equation of Dingwell and Virgo (1988).

\[
\log(\eta) = \log(\eta_0) + \left(\frac{E_t}{2.303}\right) \times R(T - T_0) \tag{4.5}
\]

Where \( \log(\eta_0) = 2.46 \), \( E_t = 27 \times 10^3 \) calories, \( R = 1.9872 \) cal/k-mol and \( T_0 = 427 \) K. Assuming \( T = T_g \) at \( \eta = 10^{13} \) poise, we get a value of 808 K for the glass transition temperature. We realize that \( T_g \) depends upon \( \text{Fe}^{3+}/\text{Fe}^{2+} \) ratio but in the oxidized glasses we could not detect any \( \text{Fe}^{2+} \) using the Mössbauer technique. This indicates that the amount of \( \text{Fe}^{2+} \) must be small and below the detection limit of the Mössbauer technique.

The Fe-albite glass show strong similarities between its spectra below and above 854K (4.3a), which suggests very similar structures between high and low viscosity states. We note that the linewidths of Raman bands become greater with increasing temperature, which can be seen more clearly in the high-frequency envelope. Because NFSO is fully polymerized, the change in linewidth reflects the increase of disorder of the structure of the sample as well as the contribution from anharmonicity. The linewidth of the peaks in the Raman spectra of glasses or melts mainly reflects the T-O-T angle distribution. The increase in linewidth may therefore indicate a wider bond angle distribution in glasses above \( T_g \), which contributes to the degree of disorder in glasses and
melts. It is also interesting to note that with increasing temperature the low frequency envelope shifts to higher frequency (from 452 to 466 cm\(^{-1}\)) whereas the high frequency bands shift to lower frequency (from 963 to 944 cm\(^{-1}\)). Because of thermal expansion, one would expect that all the Raman bands should shift to lower frequency in the entire frequency range. Because this is not entirely obeyed by the NFS0 spectra, other factors must be considered. The low-frequency bands result from T-O-T linkages and smaller angles would result in the increase in the bending modes frequency (McMillan, 1984). Therefore, we suggest that the change in peak positions in the low-frequency region may be attributed to the decrease of the average T-O-T angle with increasing temperature.

4.3.4 Nature of the vibrational spectra of glasses

Before we further analyze the spectra of these Fe-containing glasses, it is important to recall the nature of the vibrational spectra of glasses. Bell and Dean (1970) have discussed the theory of the vibrational spectra of SiO\(_2\) and GeO\(_2\) glasses. According to these authors, the vibrational spectra of glasses represent phonon-density-of-states rather than phonons at the center of Brillouin zone (i.e., \(k=0\), as is the case with ordered solids) because of disorder. Bell and Dean (1970) have shown that in the case of polymerized SiO\(_2\) and GeO\(_2\) glasses the low frequency bands are highly delocalized. In the medium and high frequency
regions the localization is only significant near the band edges, however, it involves motion of about half a dozen molecules. On the other hand, the vibrations of non-bridging oxygen atoms are strongly localized with the effective motion being restricted to no more than one or two molecules. The points outlined above regarding the nature of the vibrational spectra of glasses are of fundamental importance. We must recognize that the molecular description of the vibrational spectra of silicate glasses is a poor approximation and must be applied with great caution. At high temperatures, anharmonic contributions and collision induced broadening of the Raman bands above $T_g$ in the glass will also contribute to the band shapes and their frequencies. In the following section we have applied mathematical curve fitting techniques in the high-frequency spectral region only to examine any systematic changes that may occur with change in composition and temperature. We recognize, of course, that the fitting of Gaussian peaks in the glass spectra is not unique because of the delocalized nature of the vibration modes.

4.3.5 Depolymerized oxidized glasses at temperatures below and above $T_g$.

The most prominent variations of the high-temperature Raman spectra of NFS1, NFS2 and KFS are the changes in the relative intensities of the two components in the high-frequency envelope (Figs. 4.3b, 4.3c and 3d). The dominant depolarized peaks at 943 cm$^{-1}$ (NFS1) and 913 cm$^{-1}$ (NFS2 and
KFS glasses) originate from antisymmetric vibration modes involving bridging \((Q^4)\) oxygen, \(v_{as}(T-O-T)\). Because the NBO/T ratio for these samples are 0.25, 0.5 and 0.25 respectively, nonbridging oxygens from \(Q^3\) species are also present. Therefore, the polarized high-frequency shoulders in the spectra of these glasses can be assigned to \(v_s(T-O^-)\) mode of the \(Q^3\) species. We investigated the structural changes of the sample in terms of these two prominent components in the high frequency envelope assigned to the \(Q^3\) and \(Q^4\) species, respectively. This analysis is needed because the relative change in proportion of these species can significantly influence the structure and physical properties (e.g., viscosity) of the sample. In addition, according to equation (4.1), there should be some \(Q^2\) species existing within the structure of the glass sample. It is possible that the weak \(Q^2\) species is buried on the low frequency side of the dominant \(Q^4\) bands.

With increasing temperature, the intensity of \(Q^3\)-related band increases relative to that of the dominant \(Q^4\)-related peak. In the absence of quantitative information about the Raman scattering cross-sections of various Raman bands from glasses, the interpretation of the abrupt increase of intensities (area) of \(Q^3\) bands with temperature (Figs. 4.3b, 4.3c and 3d) is not straightforward. One possibility is that the increase in the rotational degree of freedom of some T-O-T linkages above the glass transition may affect the stretching vibration and enhance the Raman cross-section.
causing the "jump" in the intensities of Q$^3$ bands in Raman spectra at high temperatures.

The second possibility (if the rotations do not appreciably affect the stretching vibration properties, and the temperature effect on the Raman cross-section is similar to that below the glass transition), is that the anomalous increase of intensity in the Q$^3$ shoulder could be attributed to a net increase of the abundance of Q$^3$ species. This would be consistent with a shift of equilibrium in equation (4.1) to the left side. In order to evaluate the contribution from Q$^3$, we used the curvefit program in the Spectra-Calc software to produce two-Gaussian-peak fits to the high frequency band envelopes of the high-temperature Raman spectra of NFS1 (Fig. 4.5). In these fits, $A_1$ denotes the area of the fitted peak attributed to Q$^3$ species whereas $A_2$ denotes the contribution from species other than Q$^3$. The proportion of $A_1$ relative to the area of whole respective envelope ($A=A_1+A_2$) at different temperatures is plotted in Fig. 4.6. The associated curve is a simple spline fit to the data. It can be seen that the ratio $A_1/A$ increase gradually from room temperature to 664 K, then increase dramatically between 664 and 854 K, and again slowly increases with temperature to 1044 K. The anomalous change between 664 and 854 K may be related to the glass transition.

Another factor which might relate to the temperature effects on the NFS1, NFS2 and KFS Raman spectra and would
Fig. 4.5. Two-Gaussian-peak fits to the high frequency band envelope of the high temperature spectra of NFS1.
Fig. 4.6. The proportion of $A_1$ relative to the area of whole respective envelope $(A = A_1 + A_2)$ at different temperatures.
lead to bulk melt depolymerization is temperature-dependent reduction (i.e., $\text{Fe}_2\text{O}_3 \leftrightarrow \text{FeO}+\text{1/2O}_2$), which must be favored at high temperature because of entropy considerations. It is highly unlikely that this occurred to a sufficient degree to influence our spectra for two reasons. First, according to an empirical models (Sack et al., 1980, Kilinc et al., 1983) the extent of reduction is very small (less than 1% within the temperature range of this study). Second, the starting glass was quenched from a liquid at a higher temperature (1473 K) than used for any of the Raman experiments. Thus any re-equilibration during the Raman measurements should be exactly opposite to that shown above.

For these iron-bearing glasses the overall similarity of spectra of oxidized iron-silicate glasses at various temperatures corresponding to below and above $T_g$ suggests no appreciable structural change other than the relative intensity variations noted above. We thus conclude that the majority of ferric ions remain in four-coordinated positions at all temperatures, which is consistent with the results of previous studies (Fleet et al., 1984; Danckwerth and Virgo, 1987; Dingwell and Virgo, 1988). There is, however, a small change in $T$-$O$-$T$ bond angles as well as $T$-$O^-$ and $T$-$O^+$ bond lengths with temperature. Changes in these parameters and an increase in the number of species in vibrationally excited state at high temperature will decrease the activation energy for viscous flow with temperature. In addition, some minor structural changes, e.g. the occurrence of highly (>4)
coordinated silicon (Stebbins, 1991) or ferric ions which may be below the detection limit of Raman technique, may play an important role in changing the viscosity of melts.

4.3.6. Temperature dependence of the "defect" bands

As we mentioned in the chapter 3, the bands occurring at around 600 cm\(^{-1}\) in silica and alkali-tetrasilicate glasses are believed to be related to certain vibration units even though the nature of such units is still unclear. In this connection, they are called "defect" bands. Similar to the spectra of those glasses, in these iron-containing silicate glasses we also observed that, in the spectra of the fully polymerized NFS0 glass, at the higher frequency side of the dominant low frequency band there is a shoulder at about 540 cm\(^{-1}\) which we may attribute it to the so-called "defect" band. In the other depolymerized compositions (NFS1, NFS2 and KFS) peaks at about 540 cm\(^{-1}\) are observed which could be reasonably related to the "defect" bands as in the case of NFS0.

Our assignments of these "defect" bands are also consistent with the observed temperature dependence of the intensity of these bands. The intensity of the bands shows an enhancement with increasing temperature which is also true for the claimed "defect" bands in all other composition in previous works (e.g., Seifert et al., 1981; McMillan et al., 1992; Sharma et al., 1994). In the previous chapter, we have conducted a detailed discussion on the nature of this well known peak in silicate glasses. The experimental results of
these iron-containing glasses under high temperature is consistent with the model for the nature of the "defect" band proposed in chapter 3. The increase in intensity of the D2 bands with increasing temperature indicates a close correlation between the concentration of the structural unit related to the "defect" band and viscosity of the glasses and melts under high temperature. Consequently, we may suggest that the structural unit relating the "defect" band plays an important role in deciphering the basic mechanism of viscous flow of magma in nature.

4.4 Conclusions

Observations of the Raman spectra of the oxidized iron-containing silicate glasses and liquids at various temperatures demonstrate that there is subtle change in the position of the \( v_8(T-O-T) \) band in relative intensity of the high frequency band with temperatures. The overall spectral topology of the glasses as a function of temperature, however, remain the same. These results show that the structure of the glasses remains approximately the same within the temperature range of our experiments and the coordination environments of Fe\(^{3+}\) remains tetrahedral. Evidence for the existence of appreciable amount of silicon and iron with higher (>4) coordination number has not been found in the present study. Concentrations of the high coordinated Si and Fe species if present must be very low.
For fully polymerized NFS0 (Fe-albite) composition, the observed increase in linewidth of Raman bands (especially for the high frequency peak) with increasing temperature may be related to the wider T-O-T angle distribution at higher temperature. The observation that Raman peaks at low and high frequencies shift in opposite direction with increasing temperature probably indicates a decrease in the average T-O-T angle. For the partially depolymerized compositions of NFS1, NFS2 and KFS, the intensities of the band associated with the Q^3 species increase with temperature relative to that of Q^4 species band. Lacking quantitative information for Raman cross sections of the various bands, we present two possible interpretations to the experimental phenomena, which can be attributed to either the change of cross section of Raman band or the net increase in Q^3 species above T_g.
CHAPTER 5

EFFECTS OF HIGH TEMPERATURE ON THE STRUCTURE OF REDUCED IRON-BEARING SILICATE GLASSES AND MELTS

5.1 Introduction

As discussed in the previous chapters, the relationship between the structure of iron-containing silicate glasses and liquids in relation to their bulk properties is of geochemical significance. Understanding the structural role of iron in silicate glasses and melts provides constraints for the establishment of thermodynamic models. In addition, the change between the two oxidation states of iron as a function of composition, temperature, and oxygen fugacity also has a significant influence upon the physical and chemical properties of iron-containing magmas.

Natural magmatic liquids commonly have appreciable amounts of both ferric (Fe$^{3+}$) and ferrous (Fe$^{2+}$) ions. The Fe$^{3+}$ ions in such melts may act both as a network former and a network modifier (Mysen, 1987). It is generally believed that the Fe$^{2+}$ ions occur as network modifier in octahedral coordination (e.g., Mao et al., 1973; Nolet et al., 1979). Consequently one might expect that the reduction of network-forming Fe$^{3+}$ to Fe$^{2+}$ ion will result in changes in degree of polymerization of silicate melts. Recently, however, through combined X-ray absorption and Mössbauer work, Waychunas et al. (1988) argued that Fe$^{2+}$ ions act as four-coordinated network former in silicate glasses and melts of composition
near $\text{Na}_2\text{FeSi}_3\text{O}_8$ and $\text{K}_2\text{FeSi}_3\text{O}_8$. Cooney and Sharma (1990) measured polarized micro-Raman spectra for glasses rich in fayalite component. They have also suggested that the feature in the mid-to-low frequency range may imply that $\text{Fe}_2\text{SiO}_4$ glass is at least as polymerized as metasilicate composition in other systems. They, therefore, proposed that the polymerization results from adoption of a network forming role by some proportion of $\text{Fe}^{2+}$ ions. In the present work the compositions of $\text{Na}_2\text{FeSi}_3\text{O}_8$ and $\text{K}_2\text{FeSi}_3\text{O}_8$ studied by Waychunas et al. (1988) have been chosen for high-temperature Raman structural analysis under both oxidizing and strongly reducing conditions. As Raman spectroscopy acts as a good discriminator between bridging and non-bridging oxygens, we should observe from the spectra of the completely reduced glass and melt whether $\text{Fe}^{2+}$ behaves as a network former or as a network modifier.

In this study we present the results of our investigation of the temperature dependent Raman spectra of iron-bearing silicate glass melts of $\text{Na}_2\text{O} \cdot \text{FeO} \cdot 3\text{SiO}_2$ (NFS1-R) and $\text{K}_2\text{O} \cdot \text{FeO} \cdot 3\text{SiO}_2$ (KFS-R) compositions. The former glass is also characterized with Mössbauer spectroscopy.

5.2. $\text{Na}_2\text{O} \cdot \text{FeO} \cdot 3\text{SiO}_2$ (NFS1-R) glass and melt

5.2.1 Results

a. Mössbauer spectra
Mössbauer spectrum for NFS1-R glass is shown in Fig. 5.1. The Mössbauer parameters, baseline counts, isomer shift ($\delta$), quadrupole splitting ($\Delta$), and peak half-width ($\Gamma$) is reported in Table 6. The spectrum of NFS1-R is fitted to either one or two doublets.

b. Raman Spectra

Unpolarized Raman spectra measured under $H_2$ reducing condition and using NFS1 glass as the initial starting material are shown for various temperatures in Fig. 5.2. Unlike the spectra taken in the atmosphere environment, significant changes occurred at 973 K. These spectral changes were concurrent with a distinctive color change (from yellow to dark green) in the sample. In the high frequency range the shape of the envelope at 973 K is much different from that at 873 K. At 973 K, the peak at about 1053 cm$^{-1}$ becomes dominant with a shoulder at ~937 cm$^{-1}$, while in spectra obtained at temperatures $\leq$ 873 K the reverse is true. In low frequency range, the broad envelope located about 450-550 cm$^{-1}$ disappears and is replaced by a new sharper peak appeared at ~587 cm$^{-1}$, which indicate decrease in the degree of the polymerization of the sample. We also note that at temperatures lower than 973 K the intensity of low frequency envelope ($<600$ cm$^{-1}$) increases relative to that of the high frequency bands ($>800$ cm$^{-1}$) with increasing temperature.
Fig. 5.1. Mössbauer spectrum of NFS1-R glass is fitted to either one or two doublets.
Table 6. Mössbauer Parameters for NFS1-R glasses

<table>
<thead>
<tr>
<th></th>
<th>NFS1-R (Fit 1)</th>
<th>NFS1-R (Fit 2)</th>
<th>NFS1-R (Fit 3)</th>
<th>NFS1-R (Fit 4)</th>
<th>NFS1-R (Fit 5)</th>
<th>NFS1-R (Fit 6)</th>
<th>NFS1-R (Fit 7)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fe^{2+}(I)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>δ</td>
<td>1.01 (.01)</td>
<td>0.69 (.02)</td>
<td>0.75 (.02)</td>
<td>1.05 (.02)</td>
<td>1.01 (.02)</td>
<td>0.93 (.02)</td>
<td>0.94 (.02)</td>
</tr>
<tr>
<td>Λ</td>
<td>1.92 (.01)</td>
<td>1.44 (.02)</td>
<td>1.61 (.02)</td>
<td>1.68 (.03)</td>
<td>1.57 (.05)</td>
<td>1.86 (.02)</td>
<td>1.90 (.01)</td>
</tr>
<tr>
<td>%Area</td>
<td>48.0 (.6)</td>
<td>6.4 (.4)</td>
<td>8.6 (.8)</td>
<td>24 (2.10)</td>
<td>17 (2.5)</td>
<td>32 (2.6)</td>
<td>39 (.6)</td>
</tr>
<tr>
<td>%Gauss</td>
<td>75 (4)</td>
<td>100 (0)</td>
<td>50 (0)</td>
<td>100 (0)</td>
<td>50 (0)</td>
<td>100 (0)</td>
<td>50 (0)</td>
</tr>
<tr>
<td>Γ</td>
<td>0.58 (.01)</td>
<td>0.38 (.02)</td>
<td>0.42 (.02)</td>
<td>0.83 (.01)</td>
<td>0.64 (.03)</td>
<td>0.50 (.01)</td>
<td>0.47 (.01)</td>
</tr>
<tr>
<td>%Misfit</td>
<td>0.53</td>
<td>0.37</td>
<td>0.42</td>
<td>0.16</td>
<td>0.28</td>
<td>0.10</td>
<td>0.22</td>
</tr>
<tr>
<td><strong>Fe^{2+}(II)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>δ</td>
<td>1.04 (.02)</td>
<td>1.06 (.02)</td>
<td>1.04 (.02)</td>
<td>1.06 (.02)</td>
<td>1.15 (.03)</td>
<td>1.22 (.02)</td>
<td></td>
</tr>
<tr>
<td>Λ</td>
<td>1.92 (.01)</td>
<td>1.94 (.01)</td>
<td>2.09 (.02)</td>
<td>2.12 (.02)</td>
<td>1.80 (.04)</td>
<td>1.80 (.02)</td>
<td></td>
</tr>
<tr>
<td>%Area</td>
<td>43.6 (.4)</td>
<td>41.4 (.8)</td>
<td>28 (2.10)</td>
<td>34 (2.6)</td>
<td>18 (2.6)</td>
<td>11 (.6)</td>
<td></td>
</tr>
<tr>
<td>%Gauss</td>
<td>100 (0)</td>
<td>50 (0)</td>
<td>100 (0)</td>
<td>50 (0)</td>
<td>100 (0)</td>
<td>50 (0)</td>
<td></td>
</tr>
<tr>
<td>Γ</td>
<td>0.65 (.01)</td>
<td>0.58 (.01)</td>
<td>0.47 (.01)</td>
<td>0.48 (.01)</td>
<td>0.71 (.03)</td>
<td>0.46 (.02)</td>
<td></td>
</tr>
<tr>
<td>%Misfit</td>
<td>0.53</td>
<td>0.37</td>
<td>0.42</td>
<td>0.16</td>
<td>0.28</td>
<td>0.10</td>
<td>0.22</td>
</tr>
</tbody>
</table>

Notes: Symbols: δ, isomer shift; Λ, quadruple splitting; Γ, halfwidth (FWHM). Units: δ, Λ, Γ in mm/sec; Standard deviations (s.d) in parentheses after each quantity; s.d. of 0 indicates quantity constrained at listed value. Two quantities in an individual category, separated by commas, refer to low-velocity and high-velocity band, respectively. Misfit after Ruby (1973). See text for further discussion.
Fig. 5.2. Temperature dependence of the unpolarized Raman spectra measured under H$_2$ reducing conditions and using NFS1 glass as the initial starting material.
Furthermore, similar to the spectra of NFS1 we observed that the frequencies of the Raman bands decrease with increasing temperature. Such changes of the band positions in frequency may due to the thermal expansion effects.

The polarized high frequency spectra of reduced quenched NFS1-R at room temperature are shown in Fig. 5.3. It is clear that the whole envelope is strongly polarized, in contrast to the high frequency band in NFS1 spectra, where the dominant band is depolarized (see chapter 4, Fig. 4.2b). The strong polarization of the high frequency envelope indicates the dominant role of non-bridging oxygen in the reduced sample.

5.2.2 Discussions

a. Mössbauer spectra

Table 6 reports Mössbauer parameters derived by least-squares curvefits to the NFS1-R Mössbauer data. The spectrum of NFS1-R glass has been fit both to one doublet (fit #1; Table 6) and to two doublets (fit #2-#7; Table 6). Figure 5.1 illustrates the results of three selected fits (fits #2, #5, and #7 of Table 6) to the NFS1-R Mössbauer spectrum. The single-doublet fits are unconstrained; the two-doublets fits (fit #2-7; Table 6) to the NFS1-R data have been constrained in various ways. Fit #2 and #3 were obtained with the halfwidths, $\Gamma$, and areas of the low and high velocity components of each doublet constrained to be equal and with
Fig. 5.3. The polarized high frequency spectra of reduced NFS1-R glass at room temperature.
the percentage of Gaussian character of all bands constrained at 100% and 50%, respectively. For fits #4 and #5, the area equivalence constraints were relaxed, the halfwidth constraints were retained, and the position of one band (the low velocity component of the most intense absorption doublet) was constrained to occur at the transmission minimum (approximately 0 mm/sec relative to Fe foil). The areas of component bands within doublets for fits #6 and #7 were constrained to be equal, the halfwidth constraints were relaxed, and the position of one low-velocity band was constrained as in fits #4 and #5. This latter constraint was imposed under the assumption that the position of the transmission band envelope minimum is largely controlled by the strongest of two closely overlapping Mössbauer bands.

The percentage of Gaussian character was once again constrained at 100% and at 50% for all bands of fits #4 and #6, and #5 and #7, respectively. Relaxation of this constraint produced non-meaningful results (>100% Gaussian character) probably from slightly incorrect initial modeling of the baseline. As outlined in Table 6, changing the Gaussian versus Lorenzian character of the bands only slightly changes the calculated isomer shift ($\delta$) and quadruple splitting ($\Delta$) values but significantly changes the relative contributions of the two doublets when the areas are not constrained (fits #4 and #5 to the NFS1-R spectrum). Pure-Lorentzian two-doublet models, analogous to those
reported in Table 6, were attempted but yielded poor fits to the data.

Because of the close equivalence of the areas of low and high velocity band envelopes (fit #1) for the Mössbauer spectrum of NFS1-R glass, inclusion of additional Fe$^{3+}$ bands does not seem justified. The one-doublet fit (Fig. 5.1) is clearly not adequate, either, because of the appearance of a partially resolved shoulder near +1.4 mm/sec. This shoulder is also apparent in the Mössbauer spectrum reported by Waychunas et al. (1988), and cannot reasonably be attributed to Fe$^{3+}$. The presence of this shoulder is reflected in the broader linewidth for the high velocity component of the one-doublet fit to the spectrum of NFS1-R glass. The low-velocity mate to the partially resolved high velocity shoulder must closely overlap the low velocity band component of the stronger doublet.

The high-velocity shoulder in the NFS1-R spectrum is more readily modeled in the two-doublet fits (#2-#7). A problem occurs, however, in the location of the low-velocity bands. If both bandwidths and areas are forced to be equal between components of each doublet (fit #2 and #3), the results indicate Fe$^{2+}$ doublets with $\delta$ values near 0.72 and 1.05 mm/sec. If the area constraint is relaxed (but a constraint on one band position added; i.e., fits #4 and #5 of Table 6), then both $\delta$ values are near 1.05 mm/sec and only the $\Delta$ values vary. If the halfwidth constraint is relaxed
and the area constraint re-imposed (and the band-position constraint retained, i.e., fits #6 and #7 of Table 6), then the fit yields two doublets with δ values near 0.94 and 1.18 mm/sec, respectively.

If the assumptions (constraints) used in fits #2 and #3 are correct, then the Fe2+ doublet with the less δ may be taken as evidence for at least a small proportion (~15%) of fourfold coordinated Fe2+. Although the calculated δ values of 0.69 and 0.75 are lower than generally found for tetrahedral Fe2+ in crystals (Clark et al., 1967; Dyar, 1984; Waychunas et al., 1988), isomer shift values in this range have occasionally been reported for Fe2+ in silicate glasses (e.g., Mysen and Virgo, 1978; Fleet et al., 1984). If fits #4 and #5 are considered, the greater (and nearly equivalent) δ values for both doublets are most reasonably interpreted as two sixfold-coordinated Fe2+ sites (Dyar, 1985). The different quadrupole splitting values between these two sites would then suggest different degrees of distortion (Hawthorne, 1988). However, fits #4 and #5 are not considered to be accurate models of the spectrum, because the difference in calculated area between component bands of each doublet is unreasonably large. When the area constraints are re-imposed (fits #6 and #7), the halfwidth vary in such a way that the inherent asymmetry of the whole band envelope is largely incorporated into the doublet with the lesser isomer shift (Fig. 5.1). In these cases, partitioning of Fe2+ would...
between fourfold and sixfold sites may once again be inferred.

b. Raman spectra

From the results of Mössbauer spectra, it is clear that the proportions of Fe$^{2+}$ in the oxidized glass and of Fe$^{3+}$ in the reduced glass are both negligible. Therefore, the abrupt changes occurring in the Raman spectra at 973 K are evidently related to the replacement of Fe$^{3+}$ ions by Fe$^{2+}$ ions. In addition, the abrupt changes also reflect the appearance of new species and disappearance of old species.

Because the NFS1-R glass is almost completely reduced, its composition is very close to that studied by Waychunas et al. (1988). If the conclusion of Waychunas et al. (1988) of network-forming Fe$^{2+}$ in this sample is true, one would expect low frequency envelope to move to even lower frequencies, and the bands at high frequency to become weaker and even more strongly depolarized than those in the Raman spectra of oxidized spectra. The spectra of reduced NFS1-R, however, show completely different features. First of all, the new band which appears at ~590 cm$^{-1}$ implies that the sample becomes more depolymerized. As is well-known, this band can be attributed to the symmetric vibration of bridging oxygens. Compared to the other types of glasses with different degrees of depolymerization (i.e., different NBO/T), for low frequency bands located in the range of 590-600 cm$^{-1}$, the degree of the depolymerization is such that 2>NBO/T>1 (e.g.,
If all Fe$^{2+}$ ions act as network modifier, then the value of NBO/T is 1.33, which falls in the above range. Even more convincingly, the polarized spectra of NFS1-R glass (Fig. 5.3) are extremely similar to those of Na$_2$O·1.5SiO$_2$ glass (Furukawa et al., 1981) which also has a nominal NBO/T of 1.33.

Furthermore, let's consider the behavior of the high frequency bands at different temperatures. At first glance, both the high frequency envelope of the oxidized sample and of the reduce sample consist of two components whose positions are very close. The abrupt change in the spectra initially observed at 973 K, however, can by no means be simply interpreted as a change in the relative intensity of the two components. The high frequency band envelope in the spectra of the reduced sample (NFS1-R) is strongly polarized (Fig. 5.3) whereas the dominant peak in the envelope in the spectra of oxidized glass (NFS1) is depolarized (Fig. 4.2b). This observation indicates that the components of the high frequency envelopes result from different origins in the two samples. As discussed earlier, the structure of NFS1 is expected to consist of Q$^2$, Q$^3$ and Q$^4$ species, with Q$^4$ species predominating. When the NBO/T=1.33, however, the coexisting species will be Q$^1$, Q$^2$ and Q$^3$, with Q$^3$ predominating. Thus, the band envelope in the spectra of NFS1-R contains a strong contribution from non-bridging oxygen stretching vibrations. This argument can be justified by the well-known fact that
the symmetric stretching from $Q^1$ species gives rise to a polarized band in the range of 905-920 cm$^{-1}$, that from $Q^2$ species produced a polarized band in 950-970 cm$^{-1}$, and that $Q^3$ species produce polarized band in 1050-1100 cm$^{-1}$ in silicate glasses and melts. In the NFSI-R spectra, we thus assign the dominant band at ~1060 cm$^{-1}$ to $Q^3$ species, and the shoulder at ~950 cm$^{-1}$ to $Q^2$ species. The component form $Q^1$ is probably too weak to observe directly from the spectra.

The yellow color of NFSI (and other glasses rich in Fe$^{3+}$) results from encroachment of the UV absorption edge into the blue-green region of the visible spectrum. This absorption edge advances farther into the visible region with increasing temperature but retreats into the UV under reducing conditions (Bell et al., 1976; Dyar and Burns, 1981). Combined with increased black-body emission, the temperature effect explains why NFSI melt changes color from straw yellow to amber at high temperature. In glasses in which most iron is Fe$^{2+}$, the absorption edge is almost entirely in the UV and has minimal influence on perceived color. This effect is in accord with molecular orbital calculations (Loeffler et al., 1974) which predict that the lowest-energy oxygen-iron charge transfer bands involving Fe$^{3+}$ (oct), Fe$^{2+}$ (oct), and Fe$^{2+}$ (tet) are at approximately 25 000 cm$^{-1}$, 29 000 cm$^{-1}$ and 37 000 cm$^{-1}$, respectively. The green color of NFSI-R (and other glasses rich in Fe$^{2+}$) results from (in addition to retreat of the UV absorption edge) the encroachment of the edge of the 1.0 μm (octahedral)
absorption into the orange-red region of the visible spectrum. The change from amber to dark green during heating in a reducing atmosphere is thus correlated with the valence change of iron and is strong evidence for the presence of sixfold-coordinated Fe$^{2+}$, as indicated by the Mössbauer spectra.

5.3. Reduced KFS-R glass and melt

5.3.1 Results

Figure 5.4 shows unpolarized Raman spectra at various temperatures measured with KFS as initial material and under reducing conditions created by flowing H$_2$ on the sample. Unlike the spectrum of KFS glass taken in air, significant changes occurred in the spectrum of this sample as the reduction reaction proceeded. In the presence of hydrogen, the Raman spectrum of KFS glasses changed at temperatures as low as 664 K, indicating initiation of reaction with hydrogen (Fig. 5.4). In the spectrum of KFS-R glass at 949 K, the peak at approximately 1054 cm$^{-1}$ becomes the dominant feature with a shoulder at ~940 cm$^{-1}$. In the low frequency range, the broad envelope located about 450-550 cm$^{-1}$ in the spectra at <854K disappears and is replaced by a new sharper peak at ~590 cm$^{-1}$ at 949K.

5.3.2 Discussion

The Raman spectra of KFS (Fig. 5.4) under high-temperature reducing conditions are very similar to the
Fig. 5.4. Unpolarized Raman spectra with KFS glass as starting material at various temperatures measured under reducing conditions.
corresponding spectra of reduced glasses and liquids Na₂O·FeO·3SiO₂ (NFSl-R) discussed previously (section 5.2). The NFSl and NFSl-R glasses were examined using Mössbauer spectroscopy and the results show that iron was almost completely reduced to Fe²⁺ by reaction with H₂. Because of the compositional and spectral similarity between NFSl glass, which has been examined both before and after the Raman experiments (Wang et al., 1993), and KFS glass, we may reasonably conclude that the KFS-R is likewise largely reduced. As a result, its composition is very close to that of the glass investigated by Waychunas et al. (1988).

As discussed before, if the conclusion of Waychunas et al. (1988) of network-forming Fe²⁺ in the KFS-R sample is correct, one would expect the low-frequency envelope to move to even lower frequencies (relative to these in the KFS spectra), and the bands at high frequency to become weaker and even more strongly depolarized than those in the Raman spectra of KFS spectra. The spectra of KFSl-R glass and liquid, however, show completely different features. In the low frequency region a new band appears at ~590 cm⁻¹ indicating that the sample became more depolymerized during reduction. A band in this range can be attributed to the symmetric stretching vibration of bridging oxygens. By comparison with other types of glasses with different degrees of depolymerization (i.e., different NBO/T), low frequency bands located in the range of 590-600 cm⁻¹ imply that the degree of the depolymerization is such that 2 >NBO/T>1 (e.g.,
McMillan, 1984; Mysen et al., 1982; Matson et al., 1983; Xue et al., 1991). If all Fe$^{2+}$ ions act as network modifiers, then the value of NBO/T is 1.33, which falls in the above range. Therefore, a network modifier role for Fe$^{2+}$ is consistent with our experimental results.

Similar to our earlier interpretations of NFS1 and NFS1-R spectra (Wang et al., 1993), the polarization characteristics indicate that the abrupt change in the spectra, initially observed at 949 K cannot simply be interpreted as a change in the relative intensities of the Q$^{3}$ and Q$^{4}$ components assigned on the basis of NFS2 and KFS spectra. The high frequency band envelope in the spectra of the reduced sample (KFS-R) is again strongly polarized (Fig. 5.5), whereas the dominant peak in the envelope of the spectra of oxidized glass (KFS) is depolarized (Fig. 4.1d). This shows that the components comprising the high frequency envelopes result from different origins in the two samples. With NBO/T of 0.25, the structure of KFS is expected to consist of Q$^{2}$, Q$^{3}$ and Q$^{4}$, with Q$^{4}$ species predominating. When the NBO/T is 1.33, however, the coexisting species will be Q$^{1}$, Q$^{2}$ and Q$^{3}$ according to the equation (4.1), with Q$^{3}$ predominating. Thus, the band envelope in the spectra of KFS-R contains a strong contribution from nonbridging oxygens. The 952 cm$^{-1}$ band can be attributed to the Q$^{2}$ species and the 1043 cm$^{-1}$ peak could be assigned to the Q$^{3}$ species. The band related to the Q$^{1}$ species may be too weak to be detected. Therefore, we
Fig. 5.5. The polarized Raman spectra of reduced KFS-R glass at room temperature.
conclude that Fe$^{2+}$ is a network modifier in both NFS1-R and KFS-R glasses and liquids.

On the basis of Raman evidence in the spectra of glasses of olivine compositions (Cooney and Sharma, 1990), it has been suggested that tetrahedrally coordinated Fe$^{2+}$ ions coexist with SiO$_4$ tetrahedra. In the present study, however, we don't find evidence of tetrahedrally coordinated Fe$^{2+}$ despite the fact that a small proportion of Fe$^{2+}$ may be tetrahedrally coordinated as indicated on the basis of Mössbauer results. It is, however, possible that the four-fold coordinated iron may be acting as network modifier similar to the role of four-fold coordinated Mg$^{2+}$ in the crystalline akerwanite (Ca$_2$MgSi$_2$O$_7$). As the Raman spectra are sensitive to T-O-T and T-O$^-$ bonds, it will not be able to discriminated between two types of network modifiers.

5.4 CONCLUSIONS

Raman spectra of Na$_2$·FeO·3SiO$_2$ (NFS1-R) and K$_2$·FeO·3SiO$_2$ (KFS-R) glasses and melts have been measured as functions of temperature. We find typical features suggesting that the reduced sample becomes more depolymerized relative to the oxidized sample. By comparison with previous studies, our experimental results for this composition are completely consistent with a bulk NBO/T=1.33, calculated assuming all Fe$^{2+}$ is a network modifier. Mössbauer spectra suggest, however, a mixture of fourfold and sixfold-coordinated sites.
in the NFS1-R glass. Based upon the similarity between the Raman spectra of those glasses and melts, we conclude that mixed Fe$^{2+}$ coordination environments also exist in the melt and that, regardless of coordination type Fe$^{2+}$ behaves as a network-modifier in silicate glasses with composition close to Na$_2$FeSi$_3$O$_8$ and K$_2$FeSi$_3$O$_8$. Such conclusion is consistent with the results of previous study on the effect of oxidation state on the viscosity of melts in the system Na$_2$O-FeO-Fe$_2$O$_3$-SiO$_2$ (Dingwell and Virgo, 1986), which showed that the viscosity basically decrease with reduction of Fe in the melts.
CHAPTER 6
TEMPERATURE AND PRESSURE DEPENDENCE OF RAMAN SPECTRA
OF HYDROUS AND ANHYDROUS ALBITE GLASSES

6.1. Introduction

Explanation of water solubility mechanisms in silicate melts commonly invokes the interaction of dissolved H$_2$O with bridging oxygens, resulting in the disruption of the extended network structure (Stolen and Walrafen, 1976; McMillan and Remmele, 1986; Mysen and Virgo, 1986a). One indication that such a mechanism operates in hydrous silicate melts is the observed strong decrease in the viscosity of fully polymerized melts with addition of H$_2$O (Dingwell and Mysen, 1985; Dingwell, 1987). Furthermore, a peak at 970 cm$^{-1}$ in the Raman and infrared spectra glass and a peak near -100 ppm in the $^{29}$Si NMR spectra of hydrous SiO$_2$ glasses appear and are ascribed to Si-(OH) bonds (Stolen and Walrafen, 1976; Mysen and Virgo, 1986a,b; Farnan et al., 1987). Isotopic substitution of D$_2$O for H$_2$O shifts the Raman peak maximum to 950 cm$^{-1}$, leading to the assignment of the 970 cm$^{-1}$ peak to an Si-(OH) stretching mode (Galeener and Geils, 1977).

In fully polymerized aluminosilicate glasses, such as NaAlSi$_3$O$_8$, introduction of water in the glass results in the appearance of a peak near 900 cm$^{-1}$ in the Raman and infrared spectra (Mysen et al., 1980; McMillan et al., 1983; Mysen and Virgo, 1986b; Silver and Stolper, 1989). Assignment of this
peak to specific structural feature is not as straightforward as in the H$_2$O-SiO$_2$ glass system. Freund (1982) and McMillan et al. (1983) proposed that the 900 cm$^{-1}$ band could result from a mixture of Al-O-H stretching and bending modes analogous to that found in H$_2$O-SiO$_2$ glasses. Mysen and Virgo (1986b) argued against this because of the lack of a detectable H/D isotopic shift of the 900 cm$^{-1}$ shoulder. Instead, they propose that the 900 cm$^{-1}$ band originated from Si Q$^2$ site and suggested the formation of NaOH and Al(OH)$_3$ "complexes" as the water solubility mechanism.

Kohn et al. (1989) measured NMR spectra of hydrous albite glass and concluded that H$_2$O does not interact with the network cations (i.e., Al$^{3+}$ and Si$^{4+}$). Kohn et al. (1989) argued against the Mysen and Virgo (1986b) model because there is no evidence in the MAS NMR spectra for a coordination change in Al$^{3+}$ or for the formation of Si Q$^2$ sites as predicted by Mysen and Virgo (1986b). Instead, Kohn et al. (1989) proposed exchange of H$^+$ for Na$^+$ in the network throughout the entire solubility range of water in these melts with concomitant formation of NaOH. The H$^+$ cations act as charge balancing cation for Al$^{3+}$ ions in the network and O$_{br}$ remains bonded to two tetrahedral cations (Kohn et al., 1992). Recent NMR spectra have been interpreted to indicate that water does depolymerize silicate melts (Merwin et al., 1991; Kummerlen et al., 1992) and that volatile species such as F$^-$ interact preferentially with Al$^{3+}$ over Si$^{4+}$ and Na$^+$ (Schaller et al., 1992). Merwin et al. (1991) concluded that
the NMR spectra of Kohn et al. (1989) should be re-interpreted based on their NMR spectra of H₂O-Na₂Si₄O₉ glasses.

Sykes and Kubicki (1993) conducted infrared spectroscopy and molecular orbital calculations on the albite glasses. Infrared spectra of H₂O- and D₂O-NaAlSi₃O₈ (albite) glasses were measured and contain two major differences from the anhydrous glass spectra. The first is the presence of a number of bands above 3000 cm⁻¹ arising from O-H stretching modes. The second change in hydrous glass spectra is the appearance of a shoulder at approximately 900 cm⁻¹. No frequency shift of the 900 cm⁻¹ shoulder was detected with H-D substitution. Based on their infrared spectra and molecular orbital calculations as well as previous NMR (Kohn et al., 1989) and Raman (Mysen and Virgo, 1986a) spectra, they concluded that the 900 cm⁻¹ band in the vibrational spectra of H₂O-albite glass arises from an Al-(OH) stretching vibration in an Al Q³ site. Furthermore, they proposed a model for the water solubility mechanism in hydrous albite glass and melt. Below 30 mol% [H₂O]ₜₒₜ, molecular water interacts with the network Al³⁺ to produce Al-(OH) and a minor concentration of Si-(OH) bonds. Above 30 mol% [H₂O]ₜₒₜ, the dominant species is molecular H₂O, and H⁺ exchanges with Na⁺ at the charge-balancing site to produce molecular NaOH or hydrated Na⁺(H₂O)ⁿ complexes in the melt.
McMillan et al. (1993) conducted another Raman spectroscopic study of H/D isotopically-substituted hydrous aluminosilicate glasses and attributed the lack of isotopic shift upon deuteration for the peak at 900 cm$^{-1}$ in the Raman spectra to strong vibronic coupling within the silicate framework and pointed out that this observation does not preclude the presence of Si-OH or Al-OH groups.

Pandya et al. (1992) studied a group of submarine volcanic glasses ranging in composition from basalt to dacites from a variety of tectonic settings for their total (H$_2$O+OH$^-$) and molecular water contents using combined high-temperature mass spectrometric and Fourier-transform infrared spectroscopic techniques. For their samples they obtained a value of 61±1 l/mol·cm for the extinction coefficient of the fundamental OH stretching band at 3550 cm$^{-1}$. This value is low compared to (77-168 l/mol·cm) for those with high content of SiO$_2$. They proposed that such a variation in the value of the extinction coefficient for the 3550 cm$^{-1}$ band reflects a competition among tetrahedral (Si, Al) and non-tetrahedral cations (e.g., Na) for hydroxyl in the melt. If all OH groups are associated with silicon, then one mole of water will produce two moles of OH, giving rise to a higher value of extinction coefficient. On the other hand, if the OH group are associated with Na, then one mole of H$_2$O will only produce one mole of OH, consequently, a lower value of the extinction coefficient.
Keppler and Bagdassarov (1993) carried out a high-temperature FTIR study on a rhyolite melt containing 300 ppm by weight of water. Their study indicates that with increasing temperature a large part of the strongly H-bonded species disappear. At the highest temperature of this study (1300°C) the protons become highly mobile and the high mobility of protons means that a distinction between OH groups and molecular H2O in a H2O-rich melt is probably impossible at these temperatures.

In this chapter, I present the results of our in situ high temperature Raman spectroscopic study on both hydrous and anhydrous albite glasses, and high pressure Raman study on the hydrous albite glass at room temperature. From these comparative studies we are able to provide new information on the structural changes of these glasses with respect to changes in the external conditions.

The hydrous albite glass was synthesized under 1397 K and 500 bar for 100 hours. Water amount was determined to be 10 wt%.

6.2. Results

6.2.1. In situ high temperature Raman spectra of anhydrous and hydrous albite glasses
6.2.1.1. Anhydrous albite glass (NaAlSi$_3$O$_8$) at high temperature

Figure 6.1 shows the temperature dependence of Raman spectra of anhydrous albite glass. The frequency of the Raman bands as a function of temperature is shown in Table 7. The high temperature Raman spectra of anhydrous albite glass with emphasis on low frequency bands have been reported previously (Sharma et al., 1994). In order to compare with the high temperature behavior of hydrous albite glass we repeated this experiment and results are reported here. At room temperature, the spectrum of albite glass shows a intense peak at about 480 cm$^{-1}$ with a shoulder at higher frequency around 588 cm$^{-1}$. A relatively weak band is located at about 800 cm$^{-1}$. In the high frequency region, there is a broad envelope with two components. The feature with higher intensity is located around 1100 cm$^{-1}$ and the shoulder is at about 1000 cm$^{-1}$. In this study the highest temperature is 1173 K. As is observed in the previous high temperature study on albite glass (Sharma et al., 1994) and all the other in situ high temperature Raman studies on silicate glasses, the overall topology of the Raman spectra are very similar at the temperatures both below and above glass transformation, $T_g$ (1018 K, Weil et al., 1980). However, certain changes in the spectra with increasing temperature occur which may provide some information on the both structural and dynamic properties of the glass at high temperatures. First of all, with increasing temperature all
Fig. 6.1. Temperature (K) dependence of the Raman spectra of anhydrous albite glass.
Table 7. Positions (cm\(^{-1}\)) of certain characteristic Raman bands in the spectra of albite glass at various temperatures

<table>
<thead>
<tr>
<th>T (K)</th>
<th>300</th>
<th>473</th>
<th>673</th>
<th>873</th>
<th>1073</th>
<th>1173</th>
<th>300 (quenched)</th>
</tr>
</thead>
<tbody>
<tr>
<td>477(s)</td>
<td>473</td>
<td>463</td>
<td>462</td>
<td>461</td>
<td>460</td>
<td>475</td>
<td></td>
</tr>
<tr>
<td>580(sh)</td>
<td>578</td>
<td>573</td>
<td>573</td>
<td>573</td>
<td>573</td>
<td>578</td>
<td></td>
</tr>
<tr>
<td>794(w)</td>
<td>786</td>
<td>778</td>
<td>778</td>
<td>777</td>
<td>775</td>
<td>790</td>
<td></td>
</tr>
<tr>
<td>1000(sh)</td>
<td>996</td>
<td>992</td>
<td>986</td>
<td>n.d.</td>
<td>n.d.</td>
<td>999</td>
<td></td>
</tr>
<tr>
<td>1101(w)</td>
<td>1094</td>
<td>1090</td>
<td>1086</td>
<td>1083</td>
<td>1083</td>
<td>1100</td>
<td></td>
</tr>
</tbody>
</table>

Note: Experimental errors are ±5 cm\(^{-1}\) for strong peaks and ±10 cm\(^{-1}\) for weak peaks. s=strong, sh=shoulder, w=weak. n.d.=not determined.
the Raman bands shift to lower frequencies. At the highest temperature of this study (1173 K), the dominant band located at about 480 cm\(^{-1}\) at room temperature shifts to 460 cm\(^{-1}\), while the summit of the high frequency envelope shift from around 1100 to 1080 cm\(^{-1}\). The "D\(_2\)" band at around 580 cm\(^{-1}\) does not move prominently and its relative intensity to the main peak at low frequency side becomes stronger at 1173 K compared to that at room temperature. Another effect of temperature on the spectra we would like to point out in this study is the change in the shape of the high frequency envelope. At low temperature, the high frequency envelope clearly consists of two components located at about 1000 and 1100 cm\(^{-1}\), respectively. With increasing temperature, the two components gradually merge into one band. At 1073 K, there is only one symmetrical band in the high frequency region. When the glass was quenched back to room temperature, the original feature of the spectrum were retained showing an almost identical structure of this quenched glass with that of the starting sample.

6.2.1.2. Hydrous albite glass at high temperature

a. Raman spectra in the frequency region of 200-1300 cm\(^{-1}\)

The Raman spectra of hydrous albite glass with 10 wt\% H\(_2\)O at various temperatures are shown in the Fig. 6.2 and the Raman bands positions are shown in Table 8. The spectrum at room temperature is very similar to those published in
Fig. 6.2. Temperature (K) dependence of the Raman spectra of hydrous albite glass.
<table>
<thead>
<tr>
<th>T (K)</th>
<th>300</th>
<th>373</th>
<th>473</th>
<th>673</th>
<th>873</th>
<th>1073</th>
<th>300 (quenched)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>487(s)</td>
<td>483</td>
<td>483</td>
<td>473</td>
<td>468</td>
<td>464</td>
<td>475</td>
</tr>
<tr>
<td></td>
<td>784(w)</td>
<td>780</td>
<td>780</td>
<td>780</td>
<td>775</td>
<td>774</td>
<td>785</td>
</tr>
<tr>
<td></td>
<td>895(w)</td>
<td>893</td>
<td>890</td>
<td>880</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td></td>
<td>1000(sh)</td>
<td>998</td>
<td>996</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>993</td>
</tr>
<tr>
<td></td>
<td>1101(w)</td>
<td>1098</td>
<td>1094</td>
<td>1081</td>
<td>1077</td>
<td>1072</td>
<td>1091</td>
</tr>
</tbody>
</table>

Note: Experimental errors are ±5 cm\(^{-1}\) for strong peaks and ±10 cm\(^{-1}\) for weak peaks. s=strong, sh=shoulder, w=weak. n.d.= not determined.
previous studies (Mysen et al., 1986a, b; McMillan et al., 1983, 1993). The main features of the Raman spectrum of anhydrous albite glass are retained in the spectrum of hydrous albite glass, except that there is a new peak occurring at around 895 cm\(^{-1}\), which is usually refereed as 900 cm\(^{-1}\) peak in the vibrational spectroscopy community.

With increasing temperature, all the peaks shift to lower frequency, similar to that shown by the anhydrous albite glass at high temperatures. The so-called "defect" band at around 580 cm\(^{-1}\) gains intensity with increasing temperature. Also, we note the change in the shape of the high frequency envelope with temperature. The relative intensity of the shoulder at around 1014 cm\(^{-1}\) decreases. At 673 K, compared to the 1073 K for anhydrous albite glass, the two components merged into one symmetrical envelope.

At the highest temperature (1073 K) in this study, the spectrum looks very much like the anhydrous counterpart at same temperature, indicating very similar structural features between the two samples at this temperature, and the amount of water species must be very minor in the hydrous sample. After quenching back to room temperature, the spectra shows features very similar to that of the anhydrous glass at room temperature.
b. Raman spectra in the frequency region of 2000-4000 cm\(^{-1}\)

Fig. 6.3 shows the temperature dependence of Raman spectra of OH stretching band within the range of 2000 to 4000 cm\(^{-1}\). In this region an O-H stretching peak appears with its maximum at 3544 cm\(^{-1}\). This band is asymmetric and has a low frequency shoulder. Similar spectra of hydrous albite glass in this region have been obtained in previous studies (e.g., McMillan et al., 1983, 1993).

With increasing temperature, the changes in the spectra show several prominent features. First, the position of the OH stretching band increases in frequency, i.e., the position at 873 K is higher than 3600 cm\(^{-1}\) relative to that (3544 cm\(^{-1}\)) at room temperature. A temperature dependence of the band position is plotted in the Fig. 6.4. Second, the shoulder on low frequency flank of the stretching band disappears gradually with temperature. At 823 K, the band shape becomes symmetrical. Third, the intensity of this band decreases constantly with temperature. At 873 K, only a very weak feature exists in the spectrum. Above this temperature, we are not able to see any detectable features in this region, indicating that the concentration of water species is too weak to be detected.

After we quenched the sample from 873 K, we went back to low frequency region to see how the spectrum change in this region (Fig. 6.5). It is clearly shown in Fig. 6.5 that the
Fig. 6.3. Raman spectra of OH stretching band from the hydrous albite glass at various temperatures (K).
Fig. 6.4. The temperature dependence of the OH band position.
Fig. 6.5. Raman spectra of glass quenched from the high temperature OH stretching band measurements.
900 cm⁻¹ band disappears and the overall features of the spectrum look very much like that of anhydrous albite glass.

6.2.2. *In situ* high pressure Raman spectra of hydrous albite glass (with 10 wt % water) at room temperature

a. Raman spectra in the frequency region of 200-1300 cm⁻¹

Several selected spectra of hydrous albite glass at different pressures are plotted in Fig. 6.6. The pressure dependence of several characteristic Raman bands are plotted in Fig. 6.7. Several prominent changes have taken place with increasing pressure.

In the low frequency region, the band at 490 cm⁻¹ at 1 atmosphere moves to higher frequency and finally reaches 560 cm⁻¹ at 10.5 GPa, the highest pressure of this study. The intensity of this band decreases constantly with increasing pressure, and at 10.5 GPa it become ten times weaker. We also note that the bandwidth of this band becomes much wider at 10.5 GPa than that at 7.5 GPa.

The 900 cm⁻¹ band also shifts to higher frequency with pressure. Its intensity drops gradually with pressure and become undetectable at pressures higher than 6.3 GPa. As far as the two components in the high frequency envelope (within 950 and 1200 cm⁻¹) are concerned, the changes with pressure are very interesting. Initially, both components move to higher frequency with pressure and the intensity of the
Fig. 6.6. Selected high pressure Raman spectra of hydrous albite glass a.
Fig. 6.7. Pressure dependence of the positions of several characteristic Raman bands of the hydrous albite glass.
shoulder at lower frequency flank decreases relative to its partner in this envelope at same time. At a pressure of 7.5 GPa, the shoulder is not resolved and a broad symmetrical envelope is observed in this region with summit at around 1095 cm\(^{-1}\), which is lower than its original position at 1100 cm\(^{-1}\). With increasing pressure, the position of the envelope summit moves to lower frequency while its intensity drops prominently. Above 10.5 GPa, this band becomes too weak to be detected. We also note the 900 cm\(^{-1}\) band disappears at the same pressure as the low frequency shoulder of the high frequency envelope indicating an intrinsic relation between the two Raman features.

Figure 6.8 shows the spectrum obtained from the glass decompressed from 10.5 GPa to 1 atm. The topology of the spectrum is very similar to the original one obtained from starting material. However, there are some minor differences between the spectra of decompressed and original glasses. There is a slight change in the band positions of the Raman peaks and the intensity of the 900 cm\(^{-1}\) band is slightly higher relative to the high frequency envelope (Fig. 6.8).

b. Raman spectra in the frequency region of 2500-4000 cm\(^{-1}\)

In Fig. 6.9 we present the changes with pressure in the Raman spectra of the hydrous albite glass containing 10 wt% water within the frequency region of 2500 to 4000 cm\(^{-1}\). At 1 atm., a band centered at about 3548 cm\(^{-1}\) with a tail at the lower frequency side is very similar to that we observed in the
Fig. 6.8. Raman spectrum of hydrous albite glass quenched from 10.5 GPa.
Fig. 6.9. High pressure Raman spectra of hydrous albite glass with 10 wt% water in the frequency region of 2500 to 4000 cm$^{-1}$. 
previous section. From 1 atm. to 0.9 GPa, the band does not move prominently considering the accuracy of ±10 cm\(^{-1}\) in determining the band summit. A dramatic change happens when the pressure increases to 2.1 GPa, where the original one band splits to two locating at around 3481 and 3562 cm\(^{-1}\), respectively. With pressure increased to 4.2 GPa, the one at 3481 cm\(^{-1}\) moves to a lower frequency of 3474 cm\(^{-1}\) and the one at 3562 cm\(^{-1}\) moves to a higher frequency of 3566 cm\(^{-1}\). Concomitantly, a weak broad feature appears at around 3080 cm\(^{-1}\) at 4.2 GPa. At pressure of 6.8 GPa, the peak at lower frequency (3474 cm\(^{-1}\) at 4.2 GPa) disappears and the one at higher frequency (3566 cm\(^{-1}\) at 4.2 GPa) moves to 3577 cm\(^{-1}\). The weak feature emerged from 4.2 GPa at about 3080 cm\(^{-1}\) becomes stronger and its position shifts to a lower frequency of about 3036 cm\(^{-1}\). At the same time, weak features around 3270 starts to emerge. At highest pressure of this study (10.1 GPa) the high frequency band (>3500 cm\(^{-1}\)) moves to 3581 cm\(^{-1}\), whereas the low frequency band (3080 cm\(^{-1}\) at 4.2 GPa) further moves to a lower frequency of 2995 cm\(^{-1}\). The features centered around 3270 cm\(^{-1}\) become more prominent.

6.3. Discussion

6.3.1. Effects of temperature on the structures of hydrous and anhydrous albite glasses

The changes in the Raman spectra of both glasses in the frequency region of 200 to 1200 cm\(^{-1}\) with temperature reflect the changes in the internal structures of these glasses.
From Figs. 6.1 and 6.2, it is clear that the overall topology of the features in the Raman spectra of the glasses at high temperature remains very similar to that at room temperature. No new bands for higher coordinated Si or Al could be observed. This means that the structures of the glasses do not change prominently at temperatures below and above glass transformation temperature.

As is observed in the previous study for anhydrous albite glass (Sharma et al., 1994), all the bands except the "D2" band show clear red shift of their positions. This can be explained in terms of thermal expansion of the structure in the glasses with increasing temperature, which result in the increase of the bond angle and bond lengths. This is also consistent with all the other high temperature Raman measurements on other silicate glasses and melts. The so-called "D2" band located at around 580 cm\(^{-1}\) in anhydrous albite glasses shows an initial shift to lower frequency from room temperature to 673 K (i.e., from 580 to 573 cm\(^{-1}\)). At higher temperature, this band is stable at 573 cm\(^{-1}\) until the highest temperature (1173 K) of this study. A similar behavior is observed for the "D2" band in the K\(_2\)Si\(_4\)O\(_9\) composition under high temperature (McMillan et al., 1992; Mysen and Frantz, 1992; Chapter 3 of this dissertation). In the Chapter 3 we have given a detailed discussion on the nature of this band in terms of Murray and Ching's model (Murray and Ching, 1989).
6.3.2. Effects of pressure on the structure of hydrous albite glass

From Fig. 6.6 and Fig. 6.7, we observe a constant increase in the frequency of the strong Raman band from 490 cm\(^{-1}\) at 1 bar to 530 cm\(^{-1}\) at 7.5 GPa. It is generally accepted that this band is related to the symmetric stretching vibration of T-O-T linkages (McMillan, 1984). The increase in frequency of this band indicates smaller angle of the T-O-T linkages at high pressure. This is consistent with previous theoretical calculations and X-ray experimental studies on SiO\(_2\) glass under high pressure (Murray and Ching, 1989; Meade et al., 1992). Within this pressure range, we also observe a gradual change in the shape of high frequency envelope (900-1200 cm\(^{-1}\)). As we discussed in previous sections, there are two components in this envelope, one stronger band at about 1100 cm\(^{-1}\) and a lower frequency shoulder at about 1000 cm\(^{-1}\). With increasing pressure the intensity of the lower frequency shoulder gradually decreases and, at 7.5 GPa, a symmetric Raman band occurs as a result of vanishing of the lower frequency shoulder.

At pressure higher than 7.5 GPa, the intensity of Raman bands within the entire frequency region (200-1300 cm\(^{-1}\)) drops dramatically and the bandwidths become much wider relative to that at lower pressure. The band at low frequency region moves from 530 cm\(^{-1}\) to higher frequency of 561 cm\(^{-1}\) at 10.5 GPa, whereas the high frequency band shifts back to 1080 cm\(^{-1}\).
All these changes in the spectra at high pressure indicate a prominent structural change which we may be related to higher coordination (5- or 6-) of Al^{3+} and Si^{4+} in the network. Because of the distortion of original tetrahedra units, the intensity of Raman band will decrease with increase in the ionic character of the bonds, as a result, the related Raman bands become weaker with pressure (Kubicki et al., 1992). Due to the increase in the coordination number, the T-O bond length increases and bond angle decrease which result in the decrease in frequency of the Raman band in higher frequency region (Hemley et al., 1986; Meade et al., 1992).

6.3.3. The assignments for the high frequency envelope (950-1200 cm\(^{-1}\))

At room temperature, the high frequency envelope (950-1200 cm\(^{-1}\)) in the spectra of both hydrous and anhydrous glasses clearly consist of two components at around 1000 and 1100 cm\(^{-1}\), respectively. It is generally believed that these two components result from the antisymmetric stretching vibration of T-O-T linkages, where T represents the tetrahedrally coordinated cations (e.g., Si, Al, \ldots etc.) (see Wang et al., 1995 and references therein). However, the assignments for this two components are still controversial (e.g., Mysen et al., 1980; McMillan et al., 1982; Matson and Sharma, 1985). Mysen et al. (1980) proposed that the two components originate from two types of three-dimensional structures in the glass with the structure relating to the highest frequency band.
having largest proportion of T cations. McMillan et al. (1982) suggested that the bands in the high-frequency envelope are due to vibrations with a predominant character of silicon-oxygen stretching, with aluminum acting only as a perturbation on these. Matson and Sharma (1985) argued that most of the Si$^{4+}$ cations in pure SiO$_2$ glass likely maintain approximately T$_d$ site symmetry, and the $u_3$(F$_2$) antisymmetric stretching mode of TO$_4$ molecules probably retains its F character even when the TO$_4$ units are bound in a tetrahedral network (see also Phillips, 1982). The addition of small amounts of NaAlO$_2$ results in the formation of Si-O-Al bridges and consequently lowers the site symmetries of SiO$_4$ tetrahedra from T$_d$ to C$_{3v}$ in the network, resulting in a splitting of the triply degenerated F mode into A$_1$ and E modes. The A$_1$ mode is assigned to the higher frequency component whereas the E mode to the lower frequency component.

Here we would like to present a explanation to further the discussion on the nature of the two components in the Raman spectra of albite glasses. We would like to invoke MS model proposed by Matson and Sharma (1985). This model is consistent with our high temperature data. From Fig. 6.2 we can see that the intensity of the E mode gradually decreases, resulting in a symmetric band at high temperature. This could be due to the relaxation of environments of TO$_4$ tetrahedra as a result of thermal expansion. The distortion of the tetrahedral structure is relaxed at high temperature,
leading to the disappearance of original splitting of the Raman bands.

On the other hand, with increasing pressure the symmetry of the structure of sample will also change. As the symmetry changes, the number of the Raman bands may decrease. A good example in this concern is the mineral of fosterite (Mg$_2$SiO$_4$) which is of geologic importance. At low pressure phase fosterite has an orthorhombic crystallographic structure which give rise to 36 Raman active modes. More recent Raman measurements on fosterite clearly shows 21 bands (Wang et al., 1993). The high pressure phase of fosterite is called spinel (or $\gamma$-Mg$_2$SiO$_4$) with cubic structure. By factor group analysis five Raman modes ($A_{1g}+E_g+3F_{2g}$) are expected. Apparently, high pressure phase of fosterite has much fewer modes relative to that possessed by the low pressure phase counterpart. Our high pressure results could be interpreted in terms of symmetry change with pressure. With increasing pressure, the low frequency shoulder at 1000 cm$^{-1}$ disappears gradually. Finally, very similar to the results in our high temperature results, a symmetric band is produced at high pressure, which indicates that the environments of the tetrahedra in the glass framework changes with pressure, resulting in the disappearance of the band around 1000 cm$^{-1}$.

6.3.4. The 900 cm$^{-1}$ band and its implications for the water dissolution mechanism.
Considering that the introduction of water could further lower the regularity of TO₄ tetrahedra, we propose that further splitting of the mode of the stretching vibration of TO₄ tetrahedra occur, resulting in the appearance of the 900 cm⁻¹.

With increasing pressure, the intensity of the shoulder at around 1000 cm⁻¹ decreases indicating a increase in the regularity of TO₄ tetrahedra. At the same time, the intensity of the 900 cm⁻¹ band also drops with pressure. It is interesting to note that the 900 cm⁻¹ band disappears at the same pressure as the 1008 cm⁻¹ band does. This indicates an intrinsic relation between the two Raman bands and both of them could be strongly related to AlO₄ tetrahedra.

The drop of the intensity of the 900 cm⁻¹ band is accompanied by the change in the shape of the high frequency envelope leading to a symmetric band at high temperature. Considering that the introduction of water could further lower the site symmetry of TO₄ tetrahedra, we propose that further splitting of E mode of the stretching vibration of TO₄ tetrahedra occur, resulting in the appearance of the 900 cm⁻¹. Our assignment for the 900 cm⁻¹ band is consistent with the H/D substitution experimental results in which no isotope-induced frequency shift is observed, indicating no hydrous species involved in the 900 cm⁻¹ band.

As we discussed before, the low frequency shoulder at around 1008 cm⁻¹ (Fig. 6.6) is E mode splitted from F mode as
a result of lower site symmetry. With increasing pressure, the intensity of this shoulder decreases indicating an increase in the site symmetry of $\text{TO}_4$ tetrahedra. At the same time, the intensity of the 900 cm$^{-1}$ band also drops with pressure. It is interesting to note that the 900 cm$^{-1}$ band disappears at the same pressure as the 1008 cm$^{-1}$ band does. This indicates an intrinsic relation between the two Raman bands, which support the assignment of the 900 cm$^{-1}$ to one component of the E mode.

6.3.5 Water species in the hydrous albite glass

a. Effects of temperature on the water species

Figure 6.3 and Fig. 6.4 show an prominent increase in frequency of the OH stretching band with increasing temperature. Because the OH stretching frequency generally decreases with increasing hydrogen bond strength (Nakamoto et al., 1955), the above observations indicate that all hydrous species in the glass structure network are in an environment involving strong hydrogen bonding, and such hydrogen bonding environments become much weaker at high temperature which can be seen from the large difference in the positions between room temperature and 873 K. The low frequency tail of this band assigned as OH groups involved stronger hydrogen bonding (McMillan and Remmele, 1986) gradually disappears with temperature, which is consistent with the previous study on hydrous rhyolite glass at high temperature results (Keppler
and Bagdassarov, 1993) and again indicates much weaker hydrogen bonding environments at high temperature.

b. Effects of pressure on the water species

Unexpected results of pressure dependence of OH stretching band demonstrate complex environments of OH species in the albite framework (Fig. 6.9). The initial increase in pressure (<1 GPa) does not change the band position prominently. However, as pressure is increased to above 2 GPa, a splitting of original envelope occurs, i.e., a new peak appears at lower frequency (~3481 cm⁻¹). Considering the coexistence of two different hydrous species (H₂O molecule and OH hydroxyl), the two bands may represent different environments of the two hydrous species at high pressure. It is also possible that there are two different OH groups with different orientation, resulting in a different response to external pressure. With increasing pressure, the 3481 cm⁻¹ band shifts to lower frequency whereas the one at 3562 cm⁻¹ at 2.1 GPa shifts to higher frequency. It has been observed that OH species with different orientation will show different behavior at high pressure (Pandya, dissertation, 1992), as the formation of hydrogen bond critically depends on the relative orientations between neighboring hydrous species. An interesting change in the spectra is the appearance of a weak feature at around 3080 cm⁻¹. Considering the distortion of Al polyhedra at about 4 to 5 GPa which implies a change in the coordination number of
Al, the new feature around 3080 cm\(^{-1}\) could result from the hydrous species in a new environment as a result of the structural change in the glass at the pressure. With increasing pressure, the intensity of this feature increases and its position shifts to lower frequency, indicating a strong hydrogen bond environment surrounding the hydrous species. At pressure above 6.8 GPa, only one band could be observed. Taking into account of the structure change involving 4-to 6 coordination change very near this pressure region, a homogenous environments of OH species could be created as a results of the structural change.

6.4. Conclusions

The temperature and pressure dependence of Raman spectra of hydrous albite glass (200-1300 cm\(^{-1}\) and 2000-4000 cm\(^{-1}\)) have been obtained. A high temperature Raman investigation of anhydrous albite glass was re-investigated within the region of 200-1300 cm\(^{-1}\).

The concomitant disappearance of the shoulder at 1000 cm\(^{-1}\) of the high frequency envelope and 900 cm\(^{-1}\) band at high pressure indicate that there is a intrinsic relation between the two bands. We presented a discussion to explain the changes in the Raman spectra of these glasses. According to the Maston and Sharma's model, with the introduction of NaAlO\(_2\), the site symmetry of TO\(_4\) tetrahedra is lowered resulting in splitting of original F mode. The low frequency shoulder at 1000 cm\(^{-1}\) is assigned to be closely related to
AlO₄ as previous studies discussed. The introduction of water could further lower the site symmetry of the TO₄ tetrahedra, resulting in a further splitting of the F mode, leading to the appearance of 900 cm⁻¹. Both the 900 cm⁻¹ band and the 1000 cm⁻¹ shoulder in the hydrous albite glass gradually disappear with increasing temperature and pressure. We attribute it to the change in the site symmetry of TO₄ tetrahedra as a function of external environments. As a result, the splitting of the F mode disappears.

High temperature effects on the OH stretching band show that most OH species are involved in strong hydrogen bonds. On the other hand, high pressure measurements on this band indicate different environments of H₂O molecule and OH species.

The present results have shown that high pressure and temperature Raman studies of glasses could provide important information about the structural role of water dissolution mechanism in the glass framework and difference in the environments of molecular H₂O and OH species.
References


Cooney T. F. and Sharma S. K. (1990) Structure of glasses in the systems Mg2SiO4-Fe2SiO4, Mn2SiO4-Fe2SiO4, Mg2SiO4-CaMgSiO4, and Mn2SiO4-CaMnSiO4. J. Non-Cryst. Solids, 122, 10-32.


Fleet M. E., Herzberg C. T., Henderson G. S., Crozier E. D., Osvorbe M. D., and Scarfe C. M. (1984) Coordination of Fe, Ga and Ge glasses in high pressure by Mössbauer,


George J.H.B., Rolfe J.A. and Woodward L.A. (1953) Raman effects and the nature of undissociated parts of


analytical techniques on derived partial volumes.


Mao H.K., Bell P.M., Shaner J.W. and Steinberg D.J. (1978) Specific volume measurements of Cu, Mo, Pd and Ag and calibration of the ruby R$_1$ fluorescence pressure gauge from 0.06 to 1 Mbar. J. Appl. Phys., 49, 3276-3283.

Mao H.K., Bell P.M., Dunn K.J., Chrenko R.M., and Devries R.C. (1979) Absolute pressure measurements and analysis
of diamonds subjected to maximum static pressures of 1.3-1.7 Mbar. Rev. Sci. Instrum., 50, 1002-1009.


Merwin L., Keppler H. and Sebald A. (1991) 29Si MAS NMR evidence for the depolymerization of silicate melts by water. Eos, 72, 573 (abstr.)


Mysen B.O. and Virgo D. (1986a) Volatiles in silicate melts at high pressure and temperature. 1. Interaction between OH groups and Si$^{4+}$, Al$^{3+}$, Ca$^{2+}$, Na$^{+}$ and H$^+$. Chem. Geol., 57, 303-331.

Mysen B.O. and Virgo D. (1986b) Volatiles in silicate melts at high pressure and temperature. 2. Water in melts along the join NaAlO$_2$-SiO$_2$ and a comparison of solubility


Sharma S.K., Virgo D., and Kushiro I. (1979b) Relationship between density, viscosity and structure of GeO$_2$ melts


