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STRUCTURE OF GLASSES CONTAINING TRANSITION-METAL IONS

Progress Report

for Period February 1, 1980 - January 31, 1981

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January, 1981

Prepared for

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STRUCTURE OF GLASSES CONTAINING TRANSITION METAL IONS

Progress Report

for Period February 1, 1980 - January 31, 1981

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Table of Contents

	<u>Page</u>
1.0 Introduction.	1
2.0 Results	2
2.1 STRUCTURE OF HOST GLASSES.	2
2.1.1 Structural Changes in Heated Borosilicate Glass	2
2.1.2 Raman and IR Intensities in Alkali Silicate Glasses	3
2.1.3 Spectra of Alkali Aluminosilicate Glasses	4
2.1.4 Spectra of Gallium-Containing Glasses	6
2.2 TRANSITION METAL IONS IN GLASSES AND MELTS	7
2.2.1 Iron in Alkali Silicate and Phosphate Glasses	7
2.2.2 Nickel in Alkali Alumino-Silicate Glasses	11
2.3 DISSOLUTION MECHANISMS OF GLASSES.	12
2.3.1 Inter-Diffusion Mechanisms.	13
3.0 Management.	15
3.1 COMPLIANCE WITH PROJECT OBJECTIVES	15
3.2 EQUIPMENT PURCHASE AND CONSTRUCTION.	16
3.2.1 Spectroscopic Equipment	16
3.2.2 Sputter-Induced Photon Spectroscopy (SIPS).	16
3.3 PERSONNEL.	17
3.4 PUBLICATIONS AND PRESENTATIONS	17
3.4.1 Continuing Bibliography	18
3.4.2 Papers Published in 1980-1981	19
3.4.3 Papers Submitted for Publication During 1980-1981	19
3.4.4 Papers Presented at Professional Meetings	20
4.0 Appendices	
4.1 Raman Spectroscopic Investigation of Structural Changes due to Heat Treatment of B ₂ O ₃ -SiO ₂ Glasses.	
4.2 Raman Spectroscopic Investigation of the Structure of Silicate Glasses. III. Raman Intensities and Structural Units in Sodium Silicate Glasses.	
4.3 Transition Metal Ions in Silicate Melts. II. Iron in Sodium Silicate Glass.	
4.4 Luminescence of Fe ³⁺ in Metaphosphate Glasses: Evidence for Four and Six-Coordinated Sites.	

1.0 Introduction

This research is concerned with the structure and properties of insulator glasses, particularly as these are modified by transition metal ions in solution. This progress report spans a one-year period and describes the status of the work two-thirds into the sixth contract year.

The format of the report follows the style set in previous years. In the front section are given short accounts of work now in progress. This is followed by a series of appendices which report in detail segments of the work that have been completed. The appendices are intended to be preprints of work already in press or which is ready for submission to the journals. The final section of the main body of the report lists the publication status of material described in earlier annual reports and lists the publications and oral presentations of the current year.

Work on the host glasses has been concentrated on the alkali borosilicate, alkali aluminosilicate and alkali-gallia-silicate glasses. The main interest here is the structure setting for aluminum.

The optical absorption spectra of nickel and iron in a variety of glasses have been examined. Utilization of luminescence in addition to optical absorption spectra has permitted the identification of several iron arrangements in glass.

The investigation of diffusion processes, particularly hydrogen diffusion, by sputter-induced photon spectrometry (SIPS) has moved from qualitative demonstration to quantitative calculation. The counter diffusion of alkali ions and hydrogen in alkali silicate glasses was fitted to a diffusion model and work on ternary glasses is now underway.

2.0 Results

2.1 STRUCTURE OF HOST GLASSES

2.1.1 Structural Changes in Heated Borosilicate Glasses

It has been a common assumption that glasses are structurally similar to the melts from which they formed. Indeed the few Raman and infrared spectroscopic investigations made at high temperatures more or less confirm this hypothesis. One finds few changes in the spectra except for some band broadening which increases with temperature and seems to increase faster above the glass transition temperature.

A more complex behavior is expected for glasses that undergo phase separation and one would expect the spectra to be dependent on the thermal history of the glass. These phenomena were investigated for a series of glasses on the join $\text{SiO}_2\text{-B}_2\text{O}_3$ and for the composition $0.5\text{SiO}_2\cdot 0.5\text{B}_2\text{O}_3$ in particular. The results are given in detail in Appendix 4.1.

Raman spectra were measured on borosilicate glasses that has been heat-treated at various temperatures for different periods of time. It was found that the intensity ratio of the 810 cm^{-1} band (characteristic of boroxo groups) and the 475 cm^{-1} band (characteristic of three-dimensional silicate framework structures) was dependent on both thermal history and composition. The intensity versus heat treatment temperature curve exhibited a maximum in the glass transition temperature range. High temperature Raman spectra were measured on the $0.5\text{SiO}_2\cdot 0.5\text{B}_2\text{O}_3$ composition glasses both with increasing and with decreasing temperatures. Above 300°C with increasing temperature, the intensity of the 810 cm^{-1} band decreased while the intensity of the 475 cm^{-1} band increased. The changes reversed on decreasing the temperature. The reversible change of intensity was interpreted as a reversible formation and decomposition of boroxo rings. The reaction becomes very sluggish below the glass transition temperature so that the intensity ratio stayed constant below 300°C .

2.1.2 Raman and IR Intensities in Alkali Silicate Glasses

Glass compositions extending from SiO_2 to $\text{Na}_2\text{O} \cdot \text{SiO}_2$ have been used extensively as prototypes for glass structural studies. It has been assumed that the only effect of adding alkali to SiO_2 glass is to depolymerize the silica framework resulting in the formation of non-bridging oxygens. Along the compositional sequence the structural units shift from framework structures made of tetrahedra sharing all corners to sheet-like units with an average of one non-bridging oxygen per tetrahedron, to chain-like structures with an average of two non-bridging oxygens per tetrahedron. Beyond the metasilicate composition it is difficult to prepare glasses because of the ease with which the more alkali-rich materials recrystallize and because the materials are very hygroscopic. Thus the expected dimers and monomers that should appear between the metasilicate and orthosilicate compositions are not observed.

The Raman spectra of these glasses have two characteristic intense, broad, polarized bands, one in the $900\text{--}1100\text{ cm}^{-1}$ region and one in the $400\text{--}600\text{ cm}^{-1}$ region which shift with degree of polymerization and which have been assigned empirically to symmetric stretching and bending motions of tetrahedra containing 2, 1, or 0 non-bridging oxygens. However, there has been little theoretical justification for these assignments.

Carefully measured Raman spectra were interpreted by normal mode calculations and by IR and Raman intensity calculations for the silicate anion structural units: SiO_4 isolated tetrahedra, Si_2O_7 dimers, Si_2O_6 chain links, Si_2O_5 sheet units, and Si_2O_4 framework units. According to these simplified models, the polarized high frequency band is due to symmetric stretching of Si-O^- non-bridging bonds and the frequency increases with degree of polymerization of the tetrahedra. The previous assignments of the 1100 cm^{-1} band to the symmetric stretch of tetrahedra containing one non-bridging oxygen and of the 950 cm^{-1}

band to the symmetric stretch of tetrahedra containing two non-bridging oxygens were confirmed. The other main feature of the alkali silicate glasses, an intense polarized band in the range of $400\text{--}600\text{ cm}^{-1}$ was shown to be a mixed stretching bending mode of the Si-O-Si bridging bond. The model also accounts for the loss of intensity of the high frequency band with increasing degree of silica polymerization.

The details of the calculation and of the results are given in Appendix 4.2.

2.1.3 Spectra of Alkali Aluminosilicate Glasses

Raman spectra of potassium aluminosilicate glasses have been measured. Due to the rapid increase in the heat of fusion of potassium silicates as aluminum is added, only glasses containing 10 mole percent or less Al_2O_3 were synthesized (Figure 1).

The spectra are similar in their overall features to those of the analogous sodium aluminosilicate glasses except that the vibrational modes of the potassic glasses occur at frequencies slightly higher than those in the sodic glasses. The Si-O (non-bridging) stretching mode shifts from 1110 cm^{-1} to 1090 cm^{-1} as aluminum is added to potassium trisilicate, behavior paralleling that of the sodic analogues. At the same time, low frequency bands assigned to Si-O-Si stretching modes also decrease, 535 to 495 cm^{-1} and 595 to 578 cm^{-1} , as aluminum content increases.

While the Raman data imply that the structure of potassium and sodium aluminosilicate glasses are very similar, IR data collected on both sets of glasses show that the IR-active modes in the glasses from the two compositional systems behave quite differently. The frequencies of the longitudinal modes in the sodic glasses decrease slightly upon the initial addition of aluminum to the glass but subsequently remain reasonably constant as aluminum content increases. The two transverse modes observed in soda-rich glasses along the

Figure 1. Compositions studied in the System K₂O-Al₂O₃-SiO₂.

binary $\text{Na}_2\text{O-SiO}_2$ system merge into a single transverse mode in the ternary glasses at a composition having an Al/Si ratio of approximately unity. In contrast, the longitudinal modes in the potassic glasses are more numerous and increase in frequency as aluminum content increases. Some transverse modes in the potassium aluminosilicate glasses increase in frequency as aluminum is added while others decrease.

It is possible that the Raman and IR data are illustrating the structure of the alkali-aluminosilicate glasses from two different perspectives. The Raman spectra seem to indicate that the potassic and sodic glasses contain similar structural units which are generalizations of disordered crystalline compounds. The IR spectra may be recording a more localized effect of composition on the structure which is likely to differ considerably between glasses containing the larger alkali ion and those containing sodium.

2.1.4 Spectra of Gallium-Containing Glasses

Previous studies have shown that aluminum enters any of a large number of compositions in the system $\text{Na}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$ as AlO_4 tetrahedra substituting for SiO_4 tetrahedra in network-forming arrangements. The vibrational modes of the alumina and silica tetrahedra appear to be completely coupled. No new bands appear that might be ascribed to Al-O stretching modes and there is only a small frequency shift as alumina is added. In $\text{Na}_2\text{O-GeO}_2\text{-SiO}_2$ glasses, in contrast, the spectra of intermediate compositions appear as an additive mixture of the characteristic bands of SiO_4 tetrahedra and of GeO_4 tetrahedra. In the language of solid solution spectra, the germania glasses exhibit "two-mode" behavior while the alumina glasses exhibit "one-mode" behavior. These contrasting behaviors are puzzling. Germanium and silica are similar in size and charge except that germanium is much heavier. Aluminum and silica are unlike in charge but of similar mass. Is the strong vibrational coupling observed in the sodium aluminosilicate glasses simply a mass effect?

In an attempt to resolve this riddle, a series of glasses were prepared in the system $\text{Na}_2\text{O}-\text{Ga}_2\text{O}_3-\text{SiO}_2$ (Figure 2). The gallium ion has a size and charge similar to aluminum but with a mass similar to germanium. The spectra shown in Figure 3 are typical of the other results. As Ga_2O_3 is added to sodium metasilicate, the intensity of the high frequency band rapidly diminishes and the strong low frequency band shifts to lower frequency. Although interpretation is still underway, it appears that gallium enters these glasses as GaO_4 tetrahedra substituting into the glass-forming network and that the gallium tetrahedra are strongly coupled to the silica tetrahedra. Gallium, in other words, behaves almost exactly like aluminum, and not like germanium. The two-mode spectra observed in the germanate glasses must have some origin other than the mass differences between the tetrahedral cations.

2.2 TRANSITION METAL IONS IN GLASSES AND MELTS

2.2.1 Iron in Alkali Silicate and Phosphate Glasses

There is a certain semantic problem in the glass literature and it pertains to the way in which various ions, transition metals, rare earth ions, or whatever, can be taken into solution in some host glass melt. It is conventional to speak of "network-forming sites" and "network-modifying sites" and to equate these with 4-fold and 6-fold coordination and then to debate which of the two alternatives is followed by some specific ion. The implication is crystallographic. Crystals are said to contain "sites" as specific volumes from which one ion can be removed and another substituted in its place. If one were discussing solutions, however, one would speak of the speciation or complexing of ions taken into solution. One would not picture dissolved ions as occupying some sort of pre-existing "site". Glasses fall somewhere between these two models and there needs to be some adjustment of language to describe the local environment of substituent ions.

Figure 2. Compositions investigated in the system $\text{Na}_2\text{O}-\text{Ga}_2\text{O}_3-\text{SiO}_2$.

Figure 3. Raman spectra of soda-gallia-silica glasses.

The behavior of iron in sodium silicate glasses has been investigated and the complete results are given in Appendix 4.3.

The combination of optical absorption, luminescence, and Raman spectroscopic data provides strong evidence that iron in sodium silicate glasses occurs in at least three distinct environments.

Divalent iron exhibits an optical absorption spectrum consistent with six-fold coordination. As the alkali concentration is increased the effective Fe^{2+} -O bond length decreases. It is argued that in the highly polymerized structure, the Fe^{2+} ion occupies a coordination polyhedron with size dictated by the bonding requirements of the silica framework. Addition of soda increases the number of non-bridging oxygens and the coordination polyhedron adjusts itself to more nearly meet the size and bonding requirements of Fe^{2+} and as a result the optical spectrum of the high sodium glasses is much like the spectrum of Fe^{2+} in crystals.

Most of the iron in these glasses exists as Fe^{3+} which can be shown by luminescence and Raman data to occur in two distinct tetrahedral arrangements. One appears to be an FeO_4 tetrahedron linked into the glass-forming network by Fe-O-Si bridging bonds. The interpretation of the FeO_4 tetrahedron that occurs in high soda glasses is more ambiguous but crystal field parameters and the influence of this entity on the Raman spectrum provides evidence that it is a quasi-molecular complex dissolved in the glass.

A parallel study on the luminescence of ferric iron in sodium and calcium metaphosphate glasses gave different results. Broad emission bands at $16,000\text{ cm}^{-1}$ and $12,000\text{ cm}^{-1}$ were assigned to the ${}^4\text{T}_1 \rightarrow {}^6\text{A}_1$ transition of Fe^{3+} in four-coordinated and six-coordinated arrangements respectively. The complete results are found in Appendix 4.4.

2.2.2 Nickel in Alkali Alumino-Silicate Glasses

Absorption spectra have been measured on glasses ranging in composition from sodium trisilicate to sodium metasilicate which have been doped with one mole percent NiO. The spectra are characteristic of Ni^{++} in octahedral coordination and remain unaffected by the change in base glass composition. There are three major bands at 4800 cm^{-1} , $9000\text{--}10,000\text{ cm}^{-1}$ and $22,000\text{ cm}^{-1}$ from which Dq and the Racah B Parameter can be calculated: 482 cm^{-1} and 1062 cm^{-1} , respectively. While the Racah B parameter is slightly higher than the free ion value (1030 cm^{-1}), the low Dq has been used in the past as an indication of Ni^{++} in tetrahedral coordination. As a whole, the data result in a rather confused perception of the Ni^{++} site.

By comparing data from silicate, germanate, borate, phosphate, tungstate and borosilicate glasses, the optical absorption spectra of Ni^{++} become somewhat more understandable. The values of Dq and B for Ni^{++} in these host glasses have an inverse relationship. The glasses do not fall into discrete groups characteristic of glasses bearing octahedral and tetrahedral Ni^{++} but show a continuous change in both Dq and B.

To examine the relationship between the optical parameters of Ni^{++} and the different host glasses, the average field strength, $\overline{\text{FS}}$, of each host structure was calculated as

$$\overline{\text{FS}} = \sum_i x_i \left(\frac{Z_c}{(r_c + r_0)^2} \right)_i$$

where: Z_c = charge on the cation of component, i.

r_c = radius of the cation of component, i.

r_0 = radius of oxygen ion = $1.26\text{ \AA}$

x_i = mole fraction of component, i.

Plots of $\overline{FS}$ versus Dq (Figure 4) show that as $\overline{FS}$ increases, Dq increases. Dq is proportional to $1/(Ni-O)^5$ where $Ni-O$ is the interatomic distance between Ni^{++} and the coordinating oxygens. Thus, as $\overline{FS}$ increases, the glass network tightens so that the available Ni^{++} site becomes smaller.

The Racah B parameter is inversely proportional to $\overline{FS}$. At high $\overline{FS}$, the Ni^{++} in the small site experiences greater orbital overlap of the 3d electrons with the 2p electrons on the coordinating oxygens. In silicate glasses the network is expanded and the Ni^{++} behaves essentially as an isolated ion.

While the results of the field strength calculations do not indicate whether Ni^{++} occupies an octahedral or a tetrahedral site in glass, they do show that a change in coordination is unnecessary to explain the range of Dq and B values observed. Since octahedral sites are known to exist in glass structures from the optical spectra of other transition metal ions, Ni^{++} can be expected to prefer those sites due to a high resultant crystal field stabilization energy.

2.3 DISSOLUTION MECHANISMS OF GLASSES

2.3.1 Inter-Diffusion Mechanisms

Work is continuing on the sodium-calcium-silicate glasses. During the past year, a great deal of time has been devoted to learning to operate the new Secondary Ion Mass Spectrometer (SIMS) -- Sputter Induced Photon Spectrometer (SIPS) unit. Data from the old SIPS unit had to be corrected for edge effects caused by a spatially non-uniform beam, a process which can be very time consuming. The new unit has a smaller beam spot which is rastered to form a flat-bottomed crater. The signal is then gated so that only the signal from the central flat region of the crater is collected; this virtually eliminates the need for edge correction. The SIMS unit of this instrument is capable of detecting secondary ions from hydrogen to uranium with isotope information.

Figure 4. Crystal field strength, Dq as a function of average field strength.

Figure 5. Racah B parameter as a function of average field strength.

Due to the durability of sodium-calcium-silicate glasses and to the slower sputtering rate of the new instrument, the thickness of the leached layers now being studied are typically less than one micron. Therefore, there is increasing concern for the effects that surface preparation and surface damage may have on the diffusion profiles. Samples have been prepared of 20 mole % Na_2O , 10 mole % CaO , 70 mole % SiO_2 glass with fracture surfaces, surfaces polished to a one micron diamond paste finish, and surfaces polished and then etched in 8% HF solution for five minutes. The results of this study have so far been inconclusive and more samples are being prepared.

A new glass-melting furnace was built during the past year. The maximum temperature obtained was not as high as desired. The furnace is presently being revised and redesigned.

Samples of a variety of glasses ranging from a simple sodium-silicate to commercial glasses were hydrated. Data was taken at Oak Ridge National Laboratory using a nuclear reaction technique which can measure the absolute number of hydrogen atoms in a solid. The objective of this experiment was to determine the number of hydrogen atoms going into the surface for each sodium leached out. A 3:1 ratio would lend support to a hydronium-alkali exchange hypothesis, i.e.,

whereas a 1:1 ratio will support a hydrogen-alkali exchange hypothesis, i.e.,

We are still in the process of analyzing the nuclear reaction data.

3.0 Management

3.1 COMPLIANCE WITH PROJECT OBJECTIVES

The proposed technical scope given in the 1980 renewal proposal was:

"Continuation is proposed for a study of transition metal ion-containing glasses utilizing Raman, optical absorption and luminescence spectroscopy. Thrusts are (i) structure and phase separation of gallium-containing and borosilicate glasses; (ii) local environment and thermodynamics of mainly Fe and Ni, in glasses and (iii) dissolution and diffusion processes in glasses utilizing SIPS and IR reflectance spectroscopy."

As documented in this progress report, all work has been within the scope described in the proposal, and substantial progress has been accomplished on all items. All work undertaken follows the guidelines set forth in the proposal. There has been no redirection of effort.

3.2 EQUIPMENT PURCHASE AND CONSTRUCTION

3.2.1 Spectroscopic Equipment

In spite of increasing equipment obsolescence, the spectroscopic facility at MRL struggled on with little change during the past year. Efforts to replace the Raman spectrometer with a new apparatus are underway but have not yet produced anything.

The new Perkin Elmer Model 283 infrared spectrometer installed in the Mineral Constitution Laboratory last year has seen heavy usage. A reflectance attachment has been added so that specular reflectance spectra can be obtained. The computer program for performing the Kramers-Kronig analysis necessary to extract absorption spectra from reflectance spectra has been re-written to allow incorporation of the wider frequency range available on the new instrument. All seems to be functioning well.

3.2.2 Sputter-Induced Photon Spectrometry (SIPS)

The facility of sputter-induced photon spectrometry was completely renovated

last year with the arrival of the long-expected commercial instrument. The new device has the capability of secondary ion mass spectrometry (SIMS) in addition to the primary SIPS capability. The new instrument is the primary device for the study of surface dissolution processes.

3.3 PERSONNEL

This project is directed by Dr. William B. White, Professor of Geochemistry. Dr. White devotes 15% of his time over the 12-month year to this project.

The development and experimentation with the sputter-induced photon spectrometry instrumentation is under the direct supervision of Dr. I.S.T. Tsong. Dr. Tsong devotes 10% of his time over the 12-month year to this project.

The principal technical person on the project has been Dr. Toshiharu Furukawa, Project Associate. Dr. Furukawa devoted 100% of his time to the project and was responsible for most of the Raman spectroscopic work. He left the project in January, 1981 to accept a position in industry.

The graduate students on the project are Miss Carolyn Nelson, Miss Cheryl Houser and Ms. Janet Herman. Ms. Nelson and Ms. Houser receive half-time graduate assistantship and their research on the thermodynamics of melts and on dissolution mechanisms respectively will be the subjects of their Ph.D. theses. Ms. Herman holds a fellowship but has been involved with the theoretical end of the diffusion and dissolution studies.

Ms. Karen Fox, an undergraduate student at The University of Waterloo, has again worked on the project for a 4-month period as part of a special work-study program for a degree in applied physics.

3.4 PUBLICATIONS AND PRESENTATIONS

The output from this project has been divided into four categories listed separately below. First is compiled a continuing bibliography of the work

supported by the project which had appeared in print before the last Annual Report. These papers are accumulated here for ready reference. Secondly are listed the papers, mostly "in press" in last year's report which have appeared in print during the current year. Thirdly are listed the papers submitted this year. These are the same publications that are included in manuscript form as appendixes to this report. Finally are listed the papers presented at technical meetings during the year.

3.4.1 Continuing Bibliography

1. S.A. Brawer and W.B. White. Raman spectroscopic study of hexavalent chromium in some silicate and borate glasses. *Mat. Res. Bull.* 12, 281-287 (1977).
2. S.A. Brawer and W.B. White. Optical properties of trivalent chromium in silicate glasses: A study of energy levels in the crossing region. *J. Chem. Phys.* 67, 2043-2055 (1977).
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8. S.A. Brawer and W.B. White. Structure and crystallization behavior of $\text{Li}_2\text{O}-\text{Fe}_2\text{O}_3-\text{SiO}_2$ glasses. *J. Mat. Sci.* 13, 1907-1920 (1978).
9. I.S.T. Tsong, C.A. Houser, N.A. Yusuf, R.F. Messier, W.B. White and J.W. Michels. Obsidian hydration profiles measured by sputter-induced optical emission. *Science* 201, 339-341 (1978).
10. C. Houser, I.S.T. Tsong and W.B. White. Characterization of leached surface layers on simulated high-level waste glasses by sputter-induced optical emission. *Scientific Basis for Nuclear Waste Management*, G.J. McCarthy, ed., Plenum Press, NY, 131-139 (1979).

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12. T. Furukawa, S.A. Brawer and W.B. White. Raman and infrared spectroscopic studies of the crystalline phases in the system $\text{Pb}_2\text{SiO}_4\text{-PbSiO}_3$. J. Amer. Ceram. Soc. 62, 351-356 (1979).

3.4.2 Papers Published in 1980-1981

13. Furukawa, T. and W.B. White. Raman spectroscopic study of B_2O_3 and alkali borate glasses at high temperature. Phys. Chem. Glasses 21:85-90 (1980).
14. Nelson, C. and W.B. White. Transition metal ions in silicate melts. I. Manganese in sodium silicate melts. Geochim. Cosmochim. Acta 44: 887-893 (1980).
15. Furukawa, T. and W.B. White. Vibrational spectra and glass structure. J. Non-Cryst. Solids 38/39:87-92 (1980).
16. Tsong, I.S.T., C.A. Houser, W.B. White, G.L. Power and S.S.C. Tong. Glass leaching studies by sputter-induced photon spectrometry (SIPS). J. Non-Cryst. Solids 38/39:649-654 (1980).
17. Furukawa, T. and W.B. White. Raman spectroscopic investigation of the structure and crystallization of binary alkali germanate glasses. J. Mat. Sci. 15:1648-1662 (1980).
18. Houser, C.A., J.S. Herman, I.S.T. Tsong, W.B. White and W.A. Lanford. Sodium-hydrogen interdiffusion in sodium silicate glasses. J. Non-Cryst. Solids 41:89-98 (1980).

3.4.3 Papers Submitted for Publication During 1980-1981

- Furukawa, T., and W.B. White. Raman spectroscopy investigation of borosilicate glass structure. J. Mat. Sci. (submitted).
- Furukawa, T., and W.B. White. Raman spectroscopic investigation of structural changes due to heat treatment of $\text{B}_2\text{O}_3\text{-SiO}_2$ glasses. J. Amer. Ceram. Soc. (submitted).
- Fox, K.E., T. Furukawa and W.B. White. Luminescence of Fe^{3+} in metaphosphate glasses: Evidence for four and six-coordinated sites. J. Amer. Ceram. Soc. (accepted).
- Furukawa, T., K.E. Fox and W.B. White. Raman spectroscopic investigation of the structure of silicate glasses. III. Raman intensities and normal modes of sodium silicate glasses. J. Chem. Phys. (submitted).
- Fox, K.E., T. Furukawa and W.B. White. Transition metal in silicate melts. II. The environment of iron in sodium silicate glasses determined by luminescence, optical absorption, and Raman spectroscopy. Phys. Chem. Glasses (submitted).

3.4.4 Papers Presented at Professional Meetings

- I.S.T. Tsong, C.A. Houser and W.B. White: Ionic Interdiffusion in Leached Glasses. Amer. Ceram. Soc., Chicago, IL.
- T. Furukawa and W.B. White: Raman Spectroscopic Investigation of Structural Changes due to Heat Treatment of B_2O_3 - SiO_2 Glasses. Amer. Ceram. Soc., Chicago, IL.
- T. Furukawa and W.B. White: Vibrational Spectra and Glass Structure. 7th Internat. Glass Congress, Albuquerque, NM.
- I.S.T. Tsong, C.A. Houser, W.B. White and S.S.C. Tong: Glass Leaching Studies by Sputter-Induced Photon Spectrometry (SIPS). 7th Internat. Glass Congress, Albuquerque, NM.
- C. Nelson and W.B. White: Optical spectra of nickel in soda-silicate glasses. Glass Div., Amer. Ceram. Soc., Bedford Springs, PA.
- K.E. Fox, T. Furukawa and W.B. White: Absorption and Luminescence of Iron in Sodium Silicate Glasses. Glass Div., Amer. Ceram. Soc., Bedford Springs, PA.
- T. Furukawa and W.B. White: Raman scattering intensities and structural units in alkali silicate glasses. Glass Div., Amer. Ceram. Soc., Bedford Springs, PA.

APPENDIX 4.1

RAMAN SPECTROSCOPIC INVESTIGATION OF STRUCTURAL CHANGES DUE TO HEAT TREATMENT OF B_2O_3 - SiO_2 GLASSES

RAMAN SPECTROSCOPIC INVESTIGATION OF STRUCTURAL CHANGES DUE TO
HEAT TREATMENT OF B_2O_3 - SiO_2 GLASSES

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Raman spectra were measured on B_2O_3 - SiO_2 glasses heat-treated at different temperatures and for different periods of time. It was found that the intensity ratio of the 810 cm^{-1} and 475 cm^{-1} bands was dependent on the thermal history and composition of glass. The intensity versus heat treatment temperature curve exhibited a maximum in the glass transition temperature range. High temperature Raman spectra were measured on $0.5B_2O_3 \cdot 0.5SiO_2$ glass both with increasing and decreasing temperature between room temperature and 600°C . Above 300°C with increasing temperature, the intensity of the 810 cm^{-1} band decreased, while the intensity of the 475 cm^{-1} band increased. The changes reversed with decreasing temperature. The reversible change of the intensity of the two bands was interpreted as a reversible formation and decomposition of boroxo rings with temperature. The reaction becomes very sluggish below the glass transition so that the intensity ratio stayed constant below 300°C .

I. Introduction

The structural similarity between glass and the corresponding melt has been generally accepted^(1,2) and high temperature spectroscopic studies on

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sodium silicate^(3,4) and ZnCl_2 ⁽⁵⁾ support this hypothesis. On the other hand, recent high temperature Raman spectroscopic studies on boric oxide⁽⁶⁾ and alkali borate⁽⁷⁾ glasses indicate some rearrangement of borate groups at temperatures above the glass transition.

Walrafen, et al.⁽⁶⁾ measured Raman spectra of molten B_2O_3 between 475°C and 1594°C and observed a decrease in the intensity ratio of the boroxo-ring breathing-band at 810 cm^{-1} compared to the bands between 800 cm^{-1} and 300 cm^{-1} with increasing temperature. They interpreted this result to be due to the breakdown of boroxo rings. In the present study reversible decomposition and formation of boroxo rings in binary $\text{B}_2\text{O}_3\text{-SiO}_2$ glass and melt due to heat-treatment was observed.

Many properties of glass depend on thermal history, particularly thermal history in the glass transition range. Such thermally-dependent behavior is generally explained by small variations of melt structure frozen into glass at different temperatures around the glass transition range. However, such structural variations of glass due to different thermal histories have not been demonstrated by any direct experimental technique. Metastable phase separation induced thermally also influences properties of glass. In the $\text{B}_2\text{O}_3\text{-SiO}_2$ system phase separation was reported⁽⁸⁾, but the structural changes observed in this study occurred at much lower temperatures and over shorter periods of time.

The purpose of the present study is to investigate changes of glass structure due to thermal history and variations of glass and melt structure as a function of temperature. This is accomplished by measuring Raman spectra of selected $\text{B}_2\text{O}_3\text{-SiO}_2$ glasses both as quench products of various heat treatments and directly at the experimental temperatures.

II. Experimental Techniques

(1) Preparation of Glass

About 50 grams of finely-mixed powder was prepared by dissolving reagent grade H_3BO_3 in a diluted colloidal silica solution*, evaporating excess water, and grinding by a pestle and mortar. The batch was melted in a Pt-crucible in a SiC furnace at temperatures between 1050°C and 1400°C for 2 to 5 hours depending on the composition. Glass rods of 1-2 mm diameter were drawn from the melt. Boron tended to evaporate during melting, which could be detected by the small decrease of the relative intensity of the Raman 810 cm^{-1} band. The compositions cited are nominal ones based on weights of original starting materials.

(2) Raman Spectroscopic Measurements

Raman spectra were measured on a double-grating spectrometer[†] at a scattering angle of 90°, the excitation source was the 514.5 nm ($19435,6\text{ cm}^{-1}$) green line of an Ar-ion laser** at a power level between 150 and 600 milliwatts. Spectra were recorded with spectral slit width 5 cm^{-1} .

Glass rods of different composition were heated in an electric furnace to provide the desired thermal history. The temperature was controlled and measured within $\pm 5^\circ\text{C}$. Glass samples were quenched and unpolarized Raman spectra were recorded at room temperature.

The furnace for high temperature Raman spectroscopic measurements is shown schematically in Figure 1. It is similar to the set-up described in previous work⁽⁷⁾.

*DuPont Ludox AS40

†Spex Industries (Metuchen, NJ) Model 1401

**Spectra-Physics Model 164

A glass rod was re-melted in the platinum heating coil of the furnace and a thermocouple was inserted into the melt inside the coil. Temperature was controlled by two variable transformers within $\pm 5^\circ\text{C}$ below 300°C and $\pm 10^\circ\text{C}$ above 400°C , but the accuracy of the temperature measurements was probably much lower due to the thermal gradient in the sample.

Raman spectra of the $0.5\text{B}_2\text{O}_3 \cdot 0.5\text{SiO}_2$ glass were measured consecutively on two heating-cooling cycles at 100°C intervals. The initial sample was heated at 475°C for 1/2 hour and quenched to 40°C . Unpolarized spectra were measured during the first heating-cooling cycle. In the second cycle parallel-polarized spectra and crossed polarized spectra were measured between 200 cm^{-1} and 900 cm^{-1} and between 750 cm^{-1} and 900 cm^{-1} respectively with a lower scanning speed to determine accurate integrated intensities, band widths, and depolarization ratios of the 810 cm^{-1} band. Measurement at each temperature took approximately 30 minutes including the time required for heating or cooling.

III. Results

(1) Raman Spectra of As-Drawn Glasses

Unpolarized spectra of $\text{B}_2\text{O}_3\text{-SiO}_2$ glasses between pure B_2O_3 and 60 mole% SiO_2 are shown in Figure 2. A very sharp band at 810 cm^{-1} , which has been assigned to a breathing vibration of boroxo rings^(9,10), was observed to occur in all glass spectra at the same frequency and with the same band width. With increasing SiO_2 concentration the intensity of the band at about 475 cm^{-1} increases relative to the 810 cm^{-1} band. The 475 cm^{-1} band is probably due to a bending or rocking of B-O-B, B-O-Si, and Si-O-Si bridging bonds. The scattering due to the vibrations of the B-O-B bridging bonds is weaker than the scattering due to the vibrations of the B-O-Si and Si-O-Si bonds. As the

SiO_2 concentration increases a group of weak bands in the B-O stretching region, 1250-1500 cm^{-1} change contour and two weak bands appear in the Si-O stretching region, 1000-1200 cm^{-1} . Also a band was observed at 935 cm^{-1} , which may be associated with the mixed B-O-Si bridging bonds^(10,11). The lowest frequency band (often called the "boson peak") shifts to higher frequencies as the SiO_2 concentration increases. The shift is parallel to the increase of the glass transition temperature with increasing SiO_2 content (Table 1).

(2) Variation of Relative Peak Height of the 810 cm^{-1} Band to the 475 cm^{-1} Band

In Figure 3, the peak height ratio of the 810 cm^{-1} to the 475 cm^{-1} band is plotted as a function of annealing time for the $0.5\text{B}_2\text{O}_3 \cdot 0.5\text{SiO}_2$ glass. The glass rod, as drawn, was annealed at 300°C for different periods of time, quenched to room temperature, and the peak height ratio was determined from the average of four measurements. Since the band widths of the 810 cm^{-1} band (16 cm^{-1}) and of the 475 cm^{-1} band (160 cm^{-1}) did not change with heat-treatment, the peak height ratio is proportional to the intensity ratio of the two bands. By multiplying by 0.1, the peak height ratio can be converted approximately to the integrated intensity ratio. The relative intensity of the 810 cm^{-1} band to the 475 cm^{-1} band increased with longer heat-treatment and after 24 hours the ratio reached a steady value. On the other hand, when the glass previously annealed at 300°C for 72 hours was heated at 450°C, the peak height ratio dropped back to a value close to the value for the original glass within 5 hours.

(3) Variation of the Relative Peak Height of the 810 cm^{-1} Band to the 475 cm^{-1} Band with Heat-Treatment Temperature

In Figure 4 the peak height ratio of the 810 cm^{-1} band to the 475 cm^{-1} band is plotted as a function of heat-treatment temperature for three compositions:

40, 50, and 60 mole% SiO_2 . The as-drawn glasses were heated at temperatures between 250°C and 550°C for 24 hours, quenched to room temperature, and the peak height ratio of the unpolarized Raman scattering bands was determined from an average of three measurements. The band width again did not change with different heat-treatment temperatures. There is a maximum in the intensity ratio at about 300°C, 320°C, and 350°C for the glasses of 40, 50, and 60 mole% SiO_2 , respectively. The temperatures of the maxima correlate with the glass transition temperature but are slightly lower than the values obtained from an extrapolation of the glass transition temperatures of $\text{Na}_2\text{O-SiO}_2\text{-B}_2\text{O}_3$ glasses reported by Mazurin, et al.⁽¹³⁾ (Table 1). It was also noted that the relative intensity of the 810 cm^{-1} band increased even below the temperature of the maximum peak height ratio. A longer heat-treatment may possibly shift the position of the maxima to lower temperatures.

(4) Raman Spectra of $0.5\text{B}_2\text{O}_3\cdot 0.5\text{SiO}_2$ Glass at Elevated Temperatures

Raman spectra of the $0.5\text{B}_2\text{O}_3\cdot 0.5\text{SiO}_2$ glass were measured over two heating-cooling cycles at 100°C intervals. Figure 5-a and 5-b shows unpolarized Raman spectra measured over the first heating-cooling cycle. There is a decrease of the 810 cm^{-1} band intensity and increase of the 475 cm^{-1} band intensity with increasing temperature. The bands broaden and shift slightly to lower frequencies. These spectral changes are nearly reversible on cooling.

The peak height ratio of the 810 cm^{-1} band to 475 cm^{-1} band is plotted as a function of temperature for the first and the second cycle of heating in Figures 6-a and 6-b. For the first cycle (Figure 6-a), where the initial sample had been quenched from 475°C, the peak height ratio decreased with increasing temperature with a pronounced break in slope near 300°C. With decreasing temperature the intensity ratio follows back along the heating curve to 350°C and then

diverges from it at lower temperatures. As a result, the peak height ratio vs. temperature curve in Figure 6-a exhibits a hysteresis below about 350°C. For the second cycle (Figure 6-b), where the initial sample had been cooled down slowly, no hysteresis was observed and the same break in slope on the peak height ratio vs. temperature curve was observed around 300°C both on heating and on cooling.

In Figure 7-a and 7-b, the integrated intensities of the 810 cm^{-1} band and the 475 cm^{-1} band as measured during the second heating/cooling cycle are plotted as a function of temperature. The intensities of both bands were almost constant below 300°C during heating or cooling. Above 300°C the intensity of the 810 cm^{-1} band decreased on heating and recovered on cooling, while the intensity of the 475 cm^{-1} band increased on heating and dropped back on cooling. The systematic displacement observed between heating and cooling curves is mainly due to some loss of intensity caused by a small mis-alignment introduced before starting the cooling cycle. Any disturbances in the optical alignment during experiment time are a major source of error in the intensity measurements. When the relative intensity of the two bands is plotted instead, the error can be minimized (Figure 8). The intensity ratio stayed almost constant below 300°C and decreased above 300°C on heating. The variation of the intensity ratio was nearly reversible on cooling, but on cooling below 300°C the ratios were slightly larger than those on heating.

In Figure 9 the band width at half height of the 810 cm^{-1} band is plotted against temperature. The width increases linearly with increasing temperature and decreases reversibly with decreasing temperature. The depolarization ratio of the 810 cm^{-1} band measured on heating steps was constant at 0.6 ± 0.21 within experimental uncertainty.

IV. Discussion

The high temperature Raman spectroscopic observations of the intensity decrease of the 810 cm^{-1} band and the simultaneous intensity increase of the 475 cm^{-1} band with increasing temperature are strong evidence for the reversible formation and decomposition of boroxo rings in $\text{B}_2\text{O}_3\text{-SiO}_2$ glasses and melts.

The reaction may be expressed as:

where $\ominus$ is bridging oxygen. Boroxo rings, polyhedra built from BO_3 triangles and SiO_4 tetrahedra are the glass forming units, which are probably randomly connected.

The 810 cm^{-1} band arises from the symmetric breathing vibration of the boroxo ring^(9,10) and either loss of symmetry of the ring (D_{3h}) or decomposition of the ring would result in a decrease of the Raman scattering intensity. However, if the former was the main cause, the band would also become broader and the depolarization ratio would increase. Observations show that the depolarization ratio remains constant and no break in the band width vs. temperature curve (Figure 9) was observed at 300°C where the intensity of the 810 cm^{-1} band starts to decrease. The linear increase of the band width with increasing temperature is mainly due to an increasing damping factor of the vibrational mode induced by temperature. A similar line-broadening also observed for crystals^(7,15). Therefore, we attribute the decrease of the 810 cm^{-1} band intensity to a decrease in the number of boroxo rings. The increase of the 475 cm^{-1}

band intensity may be interpreted as a corresponding increase in the number of B-O-Si and B-O-B bridging bonds, due to decomposition of boroxo rings.

At low temperatures boroxo rings are energetically favored but at high temperatures they become unstable. The rate of the reaction seems to be determined by the viscosity of glass or melt. Above the glass transition temperature range the reaction reaches an equilibrium state within a short period of time but below the glass transition the reaction becomes very sluggish. A fairly large portion of boroxo rings decomposes into isolated BO_3 units above the glass transition temperature range but only small part of the isolated BO_3 units can be quenched to room temperature. Thus, the structure of the glass is close to the structure of melt only near the glass transition range and the exact structure depends on the quenching rate.

The residual high temperature structure frozen into the glass can be eliminated by annealing (Figure 3 and 4). However, annealing at temperatures below the glass transition does not eliminate all the residual high temperature structure for a short period of time because of the sluggishness of the reaction. As a result, the peak height ratio H_{810}/H_{475} vs. temperature curves in Figure 4 exhibit a maximum at around the glass transition range. Also the residual high temperature structure in the initial sample is responsible for the hysteresis observed in Figure 6-a. Flattenings of the curves (below 300°C) in Figure 7-a, 7-b, and 8 more likely arise from slow kinetics than from the exhaustion of isolated BO_3 units.

The ratio of the number of the isolated BO_3 units to boroxo rings in $\text{B}_2\text{O}_3\text{-SiO}_2$ glasses cannot be determined from presently available information. However it may be expected that the ratio increases with the increasing SiO_2 concentration, because the glass transition temperature increases with increasing

SiO_2 content. As the melt freezes to glass at higher and higher temperatures, isolated BO_3 units separated by more SiO_4 tetrahedra and must diffuse longer distance to form boroxo rings.

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Table 1. Glass Transition Temperatures of B_2O_3 - SiO_2 Glasses.

Mole% SiO_2	Glass Transition Temperature, °C
0	257 ^(a)
20	292 ^(b)
30	305 ^(b)
40	328 ^(b)
50	360 ^(b)
58	351 ^(c)
60	360 ^(b)

(a) from Mader and Loretz⁽¹²⁾.

(b) extrapolated from the glass transition temperatures of the Na_2O - B_2O_3 - SiO_2 system reported by Mozurin, Streltsina, and Tostesh⁽¹³⁾.

(c) from Maynell, Saunders, and Scholes⁽¹⁴⁾.

Legends for Figures

- Figure 1. Schematic of the high temperature Raman spectroscopy furnace and associated scattering geometry.
- Figure 2. Unpolarized spectra of as-drawn B_2O_3 - SiO_2 glasses.
- Figure 3. Peak height ratio of the 810 cm^{-1} band to the 475 cm^{-1} band of $0.5B_2O_3$ - $0.5SiO_2$ glass as a function of heat treatment time.
 (⊙): Glass heated at 300°C for the times as plotted.
 (x): Glass which had been previously annealed at 300°C for 72 hr. now heated at 450°C for the times as plotted. The peak height ratio is proportional to the intensity ratio.
- Figure 4. Peak height ratio of the 810 cm^{-1} band to the 475 cm^{-1} band of the glasses of 60, 50, and 40 mole% B_2O_3 as a function of temperature. The peak height ratio is proportional to the intensity ratio.
- Figure 5-a. High temperature Raman spectra of $0.5B_2O_3$ $0.5SiO_2$ glass measured on the first heating cycle.
- Figure 5-b. High temperature Raman spectra of $0.5B_2O_3$ $0.5SiO_2$ glass measured on the first cooling cycle.
- Figure 6-a. Peak height ratio of the 810 cm^{-1} band to the 475 cm^{-1} band measured on the first heating and cooling cycle as a function of temperature.
- Figure 6-b. Peak height ratio of the 810 cm^{-1} band to the 475 cm^{-1} band measured on the second heating and cooling cycle as a function of temperature.
- Figure 7-a. Integrated intensity of the 810 cm^{-1} band measured during the second heating and cooling cycle.
- Figure 7-b. Integrated intensity of the 475 cm^{-1} band measured during the second heating and cooling cycle.

Figure 8. Intensity ratio of the 810 cm^{-1} band to the 475 cm^{-1} band measured on the second heating and cooling cycle.

Figure 9. Full width at half-height of the 810 cm^{-1} band measured on the second heating and cooling cycle.

APPENDIX 4.2

RAMAN SPECTROSCOPIC INVESTIGATION OF THE STRUCTURE OF SILICATE GLASSES

III. RAMAN INTENSITIES AND STRUCTURAL UNITS IN SODIUM SILICATE GLASSES

[Submitted for publication to the Journal of Chemical Physics]

Raman Spectroscopic investigation of the structure of silicate glasses.

III. Raman intensities and structural units in sodium silicate glasses*

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The Raman scattering intensity of the 1100 cm^{-1} polarized band, which appears on the addition of Na_2O to SiO_2 glass, reaches a maximum at the disilicate composition. The intensity of the polarized band at 950 cm^{-1} increases sharply as the Na_2O concentration increases above 30 mole percent. These data were interpreted by normal mode calculations and by IR and Raman intensity calculations for the silicate anion structural units: SiO_4 isolated tetrahedra, Si_2O_7 dimers, Si_2O_6 chain links, Si_2O_5 sheet units, and Si_2O_4 framework units. According to these simplified models, the polarized high frequency band is due to symmetric stretching of Si-O^- non-bridging bonds and the frequency increases with degree of polymerization of the tetrahedra. The previous assignments of the 1100 cm^{-1} band to the symmetric stretch of tetrahedra containing one non-bridging oxygen and of the 950 cm^{-1} band to the symmetric stretch of tetrahedra containing two non-bridging oxygens was confirmed. The other main feature of the alkali silicate glasses, an intense polarized band in the range of $400\text{-}600\text{ cm}^{-1}$ was shown to be a mixed stretching bending mode of the Si-O-Si bridging bond. The model also accounts for the loss of intensity of the high frequency band with increasing degree of silica polymerization.

INTRODUCTION

The silica and alkali silicate glasses are useful prototypes for structural studies of glass, and an enormous amount of work has been done on the silicate glass-forming system. It is generally accepted that silica glass consists of a three dimensional framework of SiO_4 tetrahedra, and that introduction of alkali oxides to SiO_2 glass breaks the Si-O-Si bridging bonds, creating NBOs (nonbridging oxygens). The number of NBOs increases with increasing alkali oxide content and at the disilicate composition, SiO_4 tetrahedra have an average of one NBO. Further addition of alkali oxide creates SiO_4 tetrahedra of two NBOs, and at the metasilicate composition, SiO_4 tetrahedra have, on the average, two NBOs.

The earlier papers of this series^(1,2) and other Raman spectroscopic studies⁽³⁻⁶⁾ have supported the above structural model. Raman spectra of alkali silicate glasses and crystals are similar, and both exhibit a very characteristic intense band at about 1100 cm^{-1} in the disilicate glasses, and at about 980 cm^{-1} in the metasilicate glasses⁽¹⁾. At intermediate compositions the relative intensities of the bands vary according to the alkali oxide concentrations⁽³⁾. On the other hand, for silica glass^(7,8) and crystalline silica polymorphs⁽⁹⁻¹¹⁾ no intense bands (relative to a strong band around 400 cm^{-1}) are observed in the high frequency region. The 1100 cm^{-1} band was thus assigned to a vibration of the disilicate structural unit, and the 980 cm^{-1} band to a vibration of the metasilicate structural unit^(3,4,5).

It is the purpose of the present study to re-examine the interpretation of alkali silicate glasses structure using new Raman spectroscopic data in which the intensities of different glasses can be compared, and by the calculation of Raman spectra of different silicate anions.

Absolute Raman intensity measurements are considered difficult and very few attempts have been made to compare Raman intensities of different glasses⁽¹²⁾.

However when only the relative variation of intensity from sample to sample is needed, it is possible to measure Raman intensities of different glasses with reference to a standard glass sample. In this study, such Raman intensity measurements were made with good reproducibility.

The characteristics of silicate glass vibrations were calculated by Brawer⁽³⁾ using a basic structural unit which is then connected in random fashion to form the glass structures. He concluded that the vibrational displacements of the disordered silicate units in the frequency region above 500 cm^{-1} were qualitatively similar to those of the idealized silicate crystal structural units. Thus normal mode calculations on different types of silicate structural units should provide a guide to the interpretation of silicate glass spectra.

Normal mode calculations on various silicate anions have been performed by Gaskell⁽¹³⁻¹⁵⁾, Etchepare⁽¹⁶⁾, Saksena⁽¹⁷⁾, Stepanov and Prima^(18,19), and several other⁽²⁰⁻²⁴⁾, and the results compared with experimental data, mainly IR absorption spectra. However, with the exception of Stepanov and Prima's work, only calculations of normal frequencies were made and neither IR nor Raman band intensities were calculated.

EXPERIMENTAL

Glasses were prepared from silica floated powder and reagent grade Na_2CO_3 , both from Fisher Scientific Company. About 60 gram batches were thoroughly mixed with a mortar and pestle and melted in platinum crucibles in a SiC global furnace at temperatures between 1375°C and 1400°C. The melt was poured onto a heated (about 350°C) graphite disc mold, covered with a heated steel block and cooled to room temperature. The silica glass was Corning 7940. Glass discs of 3 to 5 mm thickness were polished to optical smoothness with parallel surfaces and one perpendicular surface. Glass rods of approximately 1 mm diameter were drawn from the melts for phase separation experiments.

Raman spectra were measured on a Spex Model 1401 double-grating spectrometer at a scattering angle of 90°. The excitation source was the 514.5 nm (19435.6 cm^{-1}) green line of a Spectra-Physics model 164 Ar-ion laser. The Raman scattering geometry is shown in Figure 1. The laser beam, which was polarized along the x-direction of the laboratory frame, propagated in the y-direction, while Raman scattered light was collected along the z-direction. In order to collect Raman scattered light from the same area for each measurement, a slit of 3 mm height and 5 mm width was used to mask the front perpendicular surface of the glass samples. In order to compare measurements for different samples, the optical alignment and other experimental conditions were kept constant. Parallel (xx) polarized spectra were recorded with a count rate of 2×10^4 counts/sec and crossed (xy) polarized spectra with a count rate of 5×10^3 counts/sec. All the spectra were measured with a spectral slit width of 3 cm^{-1} . A set of measurements was repeated four times to determine the reproducibility of the intensity measurements.

RESULTS

Parallel polarized (xx) and crossed polarized (xy) spectra of SiO_2 and $\text{Na}_2\text{O} \cdot x\text{SiO}_2$ glasses are shown in Figures 2 and 3, where Raman intensities of different glasses can be compared. All the intense Raman bands except the lowest frequency band (the boson peak) were strongly polarized, with a depolarization ratio of practically zero, while the depolarized bands appeared weak in the parallel polarized spectra. In this paper parallel polarized spectra are referred to most of the time and if no polarization is given, parallel polarization should be assumed. The spectra vary systematically as the glass composition changes. With the increase of Na_2O concentration, (1) the broad polarized band at 435 cm^{-1} , dominant in the silica glass spectrum, diminishes rapidly; (2) a narrow polarized band appears near 520 cm^{-1} in the spectrum of the 15 mole percent of Na_2O glass and shifts to higher frequencies with increasing Na_2O concentration. It seems to merge with a small shoulder at about 600 cm^{-1} ; (3) a weak depolarized band at 800 cm^{-1} in the silica glass spectrum shifts to lower frequencies and its intensity decreases; (4) intensities of the bands in the high frequency region ($800 \text{ cm}^{-1} - 1250 \text{ cm}^{-1}$) change systematically. The systematic variations of the high frequency bands are of greatest interest and are analysed in detail below.

In the silica glass spectrum, two weak bands are observed at 1075 cm^{-1} and 1212 cm^{-1} . Both are depolarized with a depolarization ratio of about 3/4. The introduction of 15 mole percent Na_2O to silica glass causes a polarized band to appear at 1100 cm^{-1} . Its intensity increases as the Na_2O content increased, up to the disilicate composition, after which it decreased with further increase of Na_2O concentration. At compositions between 15 mole percent Na_2O and the disilicate composition, a weak band appears as a shoulder at about 1170 cm^{-1} . This band has been deconvoluted for the trisilicate glass, and is shown in Figure 4.

Mysen et al.⁽⁵⁾ have deconvoluted another weak band at about 1050 cm^{-1} . At Na_2O concentrations higher than the disilicate composition a weak band at about 1050 cm^{-1} becomes more evident, as shown in Figure 5. These weak bands are probably depolarized, but precise deconvolution is difficult.

Another polarized band appears at 950 cm^{-1} in the spectrum of the 15 mole Na_2O glass, and its intensity increases as the Na_2O content increases. The 950 cm^{-1} band is probably of different origin than the band appearing in (xy) polarization spectra at frequencies between 980 cm^{-1} and 940 cm^{-1} . The former shifts to higher frequencies while the latter shifts to lower frequencies with increasing Na_2O concentration. Also, a polarized band is observed at 860 cm^{-1} at 40 mole % Na_2O and its intensity, although weak, is greater at 45 mole % Na_2O .

In Figure 6, peak heights of the 1100 cm^{-1} and the 950 cm^{-1} are plotted as a function of the average number of NBOs per SiO_4 tetrahedron, $2/x$ which is calculated from the chemical formula of the glass, $\text{Na}_2\text{O} \cdot x\text{SiO}_2$. The curve pertaining to the 1100 cm^{-1} band exhibits a maximum at the disilicate composition. It cannot, however, be extrapolated to zero at the silica composition. The offset may be attributed to the intensity contribution from the depolarized components which are superimposed on the more intense polarized 1100 cm^{-1} band. The 950 cm^{-1} band, which first appears at 15 mole % increases sharply in peak height after about 30 mole % Na_2O concentration, rather than at the disilicate composition.

In Figure 7, (xx) polarized Raman spectra of glasses heat-treated at 575°C for 10 hours for phase separation are compared with those of the glasses as-drawn from the melts. The spectrum of the 20 mole % Na_2O glass did not change after the heat treatment. This is probably because the glass composition is very close to the phase separation boundary curve at 575°C ^(25,26). On the other hand, the Raman spectrum of the heat-treated 15 mole % Na_2O glass is different from that

of the untreated glass. The band at 520 cm^{-1} in the spectrum of the untreated glass splits into two bands at 530 cm^{-1} and 495 cm^{-1} . However, the high frequency bands remains unchanged. The resultant spectrum is due to superimposed scattering from the Na_2O rich region (close to 20 mole % Na_2O) and from the SiO_2 rich region (close to fused silica). Thus one of the split bands at 530 cm^{-1} corresponds closely to the 530 cm^{-1} band of the 20 mole % Na_2O glass spectrum, while the other band at 495 cm^{-1} corresponds closely to the 492 cm^{-1} band of the silica glass spectrum. The 1100 cm^{-1} band is not affected by the phase separation, as the mode is due mainly to the Si-O^- nonbridging bond stretching and the number of nonbridging bonds is determined by the concentration of Na_2O , which will be discussed later.

NORMAL COORDINATE ANALYSIS FOR SILICATE ANIONS

The vibrations of atoms about their equilibrium positions are described by the equations of motion in cartesian coordinates in the harmonic approximation as

$$m_i \cdot \ddot{u}_i^{(k)}(t) = - \sum_{j,\ell} K_{ikj\ell} \cdot u_j^{(\ell)}(t)$$

where $u_i^{(k)}$ is the displacement of the i -th atom in the k direction, $u_j^{(\ell)}$ is the displacement of the j -th atom in the ℓ direction, m_i is the mass of the i -th atom, and $K_{ikj\ell}$ is the force constant between the i -th and the j -th atoms in the particular displacement directions, k and ℓ . When the system is transformed to the mass weighted coordinate system,

$$q_i^{(k)}(t) = m_i \cdot u_i^{(k)}(t)$$

the equations of motion become,

$$\ddot{q}_i^{(k)}(t) = - \sum_{j,\ell} K_{ikj\ell} / (m_i \cdot m_j)^{1/2} \cdot q_j^{(\ell)}(t)$$

The dynamical matrix is defined as,

$$D(i,k,j,\ell) = -K_{ikj\ell} / (m_i \cdot m_j)^{1/2}$$

The four-index dynamical matrix is transformed to the $3n \times 3n$ two-index matrix, where n is the number of atoms,

$$D(p,q) = D(i,k,j,\ell)$$

by

$$p = 3(i-1) + k \text{ and}$$

$$q = 3(j-1) + \ell, \quad k, \ell = 1, 2, 3 \text{ and } i, j = 1, 2, \dots, n.$$

The dynamical matrix can be constructed by assigning best-estimate force fields such as stretching, bending, torsional, and long-range Coulomb force fields. The dynamical matrix is then the total contribution from each field,

$$(D) = (D)_{\text{stretching}} + (D)_{\text{bending}} + (D)_{\text{torsional}} + \dots$$

In this study, only stretching and bending forces between the nearest neighbor atoms were taken into account because they are the dominant forces influencing vibrations in the high frequency region. Details of the formulations of the dynamical matrix elements for stretching and bending force fields are summarized in an Appendix. Cyclic conditions were employed for a structural unit of polymeric silicate anions.

The eigenvalue equations were written in matrix form as,

$$\omega^2[E][e] = [D][e]$$

where ω 's are eigenvalues $[E]$ and $[e]$ are the $3n$ by $3n$ unit matrix and the $3n$ eigenvector column matrix, respectively. To solve the equations for the ω 's and $[e]$ is equivalent to finding the eigenvalues and the eigenvectors of the dynamical matrix $[D]$ which is now solely a computational problem. Solutions were obtained by the Jacobi method using a computer subroutine provided by the Computation Center at The Pennsylvania State University.

The normal modes and eigenfrequencies were calculated by Brawer's⁽³⁾ methods. The silicate anions are shown in Figure 8. Effects of the alkali cations on high frequency modes were considered to be small and ignored^(2,14-20,27). The SiO_4 polyhedron was assumed a perfect tetrahedron. Equilibrium positions of the atoms were expressed as a function of the $\text{Si}(1)\text{-O}(5)\text{-Si}(6)$ angle (γ) and the angle (ϕ) of rotation of the left side SiO_4 tetrahedron relative to the right side SiO_4 tetrahedron around the $\text{Si}(6)\text{-O}(5)$ bond. In this study ϕ was set zero so that the plane formed by $\text{Si}(6)\text{-O}(5)\text{-Si}(1)$ became a mirror plane. The atomic configurations of the Si_2O_6 chain and the Si_2O_5 sheet with $\gamma = 135^\circ$ are similar to those found in alkali silicate crystals⁽²⁸⁻³²⁾. The four force constants were assigned the following values:

Si-O nonbridging bond stretching	5×10^5 dyne/cm
Si-O bridging bond stretching	4×10^5 dyne/cm

O-Si-O bond bending	5×10^4 dyne/cm
Si-O-Si bond bending	5×10^3 dyne/cm

These force constants are of similar magnitude to those used in previous studies^(1,2,14-16,17). No attempt was made to adjust the force constants to fit the calculated frequencies. The same force constants were used for all silicate anions so that the variations of calculated spectra were due to change of degree of polymerization and change of geometry of silicate anions. The Si-O-Si bond bending force was constrained in the Si-O-Si plane and the bending force perpendicular to the plane was ignored. The calculations on the silicate anions of the linear Si-O-Si bond were made by the extrapolation of the Si-O-Si bond angle to 180°.

Raman scattering intensity is proportional to the change of polarizability during execution of a normal vibration. The polarizability derivative was roughly approximated to the change of all the Si-O bond lengths (for the nearest neighbor Si-O pairs) along the equilibrium Si-O bond^(1,2):

$$\frac{d\alpha}{dQ_i} \propto \sum_{\text{structure unit}} \frac{(\vec{r}_O - \vec{r}_{Si}) \cdot (\vec{x}_O - \vec{x}_{Si})}{|\vec{r}_O - \vec{r}_{Si}|}$$

where $\frac{d\alpha}{dQ_i}$ is the change of polarizability of a silicate structure unit for a normal mode i , $\vec{r}$ is the equilibrium atomic position vector and $\vec{x}$ is the displacement vector of the atom. In this approximation a small effect of atomic displacement perpendicular to the Si-O bond is ignored. IR absorption is proportional to the dipole derivative which was approximated to the change of the $\text{Si}^{4+}\text{-O}^-$ bond lengths in a structure unit:

$$\left| \frac{dp}{dQ_i} \right| \propto \left| \sum_{\text{structure unit}} (\vec{x}_O - \vec{x}_{Si}) \right|$$

where $\left| \frac{dp}{dQ_i} \right|$ is the change of dipole moment of a structure unit for a normal mode i .

The advantage of the present calculation method is that the vibrational spectra of silicate anions of different symmetries can be calculated by changing only γ and ϕ , because the symmetry properties of the anions were not used.

Computed normal frequencies, Raman scattering intensities, and IR absorption intensities of the optical active modes of the SiO_4 tetrahedron, Si_2O_7 dimer, Si_2O_6 chain, Si_2O_5 sheet, and Si_2O_4 3-dimensional framework for a 135° Si-O-Si angle are shown in Tables 1 to 5. Several zero frequencies appear for the dimer and the chain because of neglecting the bending forces perpendicular to the Si-O-Si plane. Calculated Raman spectra are shown in Figure 9. The normal mode displacements of the intense Raman modes are shown in Figures 10-12.

Although the calculated frequencies of the intense high frequency bands are lower than the experimental values, the calculated spectra nicely show characteristic trends seen in the experimental spectra. The symmetric stretching mode of the SiO_4 tetrahedron, calculated at 728 cm^{-1} separates into two components when the tetrahedra are polymerized, a roughly symmetric stretching mode of the Si-O⁻ nonbridging bonds in the 850 cm^{-1} to 1000 cm^{-1} region and a symmetric stretching plus bending of the Si-O-Si bridging bond in the 500 cm^{-1} to 650 cm^{-1} region. The high frequency component shifts to higher frequencies while the lower frequency component shifts to lower frequencies as the degree of polymerization increases. The spectrum of the 3-dimensional Si_2O_4 framework has no intense bands in the high frequency region.

The effects of polymerization on the calculated frequencies generally agree with the results of Gaskell's calculations⁽¹³⁾, in which the silicate anions were assumed to contain linear Si-O-Si bridging bonds. In his calculations (see Figure 10 of Reference 13) the Raman active A_1 mode of the SiO_4 orthosilicate appears at 652 cm^{-1} . The Raman active A_{1g} or A_g mode in the 800 cm^{-1} to 900 cm^{-1} region of the Si_2O_7 pyrosilicate, Si_2O_6 metasilicate, and Si_2O_5

disilicate increases with an increase in degree of polymerization. On the other hand, Gaskell's calculated frequency of the A_{1g} or A_g mode in the 300 cm^{-1} to 500 cm^{-1} region decreased from pyrosilicate to disilicate. These modes are genetically related to the A_1 symmetric stretching mode of the SiO_4 tetrahedron.

Examination of the normal modes of the high frequency Raman bands (Figures 10 and 11) shows that they are due to motions in which symmetric stretching of Si-O^- nonbridging bonds is dominant. Likewise, the calculation indicated that the intensity of the high frequency Raman bands is due largely to stretchings of Si-O^- nonbridging bonds. The intensity contribution from Si-O^- nonbridging bond stretchings is shown by the solid line plus the broken line in Figure 9. The effect of the stretchings of the Si-O bridging bonds on the high frequency band intensity is opposite to that of Si-O^- nonbridging bond stretchings. It can be seen in the normal modes of the high frequency bands in Figure 10 and 11 that Si-O bridging bonds contract when Si-O^- nonbridging bonds stretch and vice versa. In Figure 9 the negative contribution of Si-O bridging bond stretchings are indicated by broken lines. The deduction from the Si-O^- intensity increases as the number of bridging bonds per SiO_4 tetrahedron increases. The solid part of the bar graph gives the calculated net intensity for the high frequency band.

Figures 13 and 14 give calculated spectra for chain and sheet units as a function of Si-O-Si bond angle. For both metasilicate and disilicate structures, the frequency of the intense high frequency band is almost independent of the Si-O-Si angle γ . The 654 cm^{-1} band ($\gamma = 105^\circ$) of the metasilicate and the 589 cm^{-1} band ($\gamma = 105^\circ$) of the disilicate, both of which are mainly due to the stretching plus bending of Si-O-Si bond, shift to lower frequencies and diminish their intensity with the increasing angle γ . The dependence of the Raman active bands on the Si-O-Si angle is in general agreement with Brawer's result^(1,3), even though he used only the centric (stretching) and the noncentric force constants of the Si-O bonds.

Computed IR absorption spectra are shown in Figure 15. In the 1000 cm^{-1} to 1100 cm^{-1} region three intense bands appear for the polymerized silicate anions, and a triply degenerate band for the SiO_4 tetrahedron. These bands are asymmetric stretchings of Si-O^- nonbridging bonds as well as asymmetric stretchings of Si-O bridging bonds, and their frequencies tend to increase as the SiO_4 tetrahedra are polymerized into a 3-dimensional framework. All three modes of the Si_2O_4 and of the Si_2O_5 structures, the two highest frequency modes of the Si_2O_6 structure, and the highest frequency mode of the Si_2O_7 structure are due to asymmetric stretches of the Si-O bridging bonds. The remaining intense IR modes and the triply degenerate mode of SiO_4 are due to asymmetric stretches of Si-O^- nonbridging bonds.

CONCLUSIONS

Comparison of the experimental Raman spectra (Figures 2,3) with the calculated spectra (Figure 9) shows that many of the essential and characteristic features of the spectra are accounted for by the relatively simple model employed. The frequency shifts and intensity changes that occur in alkali silicate glass spectra are shown to be a direct result of the degree of polymerization of silica tetrahedra. The dependence of Raman band intensity on number of non-bridging oxygens (Figure 6) then becomes a plot of the relative numbers of tetrahedra with one and two NBO's making up the glass structure. A band near 850 cm^{-1} that appears near the metasilicate composition (Figure 2) then indicates the appearance of a SiO_4 monomer in the structure. There has been much recent interest in using Raman spectra to determine speciation in silicate melts^(5,33). Although it remains to be established that the Raman intensities scale with the absolute concentrations of the silicate anion structural units, the results presented here indicate that, to some extent at least, Raman intensities do measure the relative populations of the various structural units.

A correlary to the assignment of specific bands to specific structural units, is the conclusion that the high frequency vibrational modes must be quite localized. Brawer's calculations on glass structure⁽³⁾ implied that the high frequency component was localized whereas the intermediate frequency band was more delocalized.

Vibrations of the discrete SiO_4 tetrahedron and the Si_2O_7 dimer are expected to be strongly isolated in a glass structure because of weak interactions between the modifier cations and the silicate anions. On the other hand, in a highly polymerized silicate glass structure, vibrations of silicate anions must be coupled through the bridging bonds strongly or weakly depending upon a particular mode. The appearance of the polarized high frequency bands of the chain structural

unit and the sheet structural unit at the discrete frequencies suggests a fairly strong isolation of these modes. The lack of effect of phase separation on the 1100 cm^{-1} band (Figure 7) may be also attributed to the isolation of the Si-O^- stretching mode. Bell et al.⁽³⁴⁾ showed in their calculation on the density of frequencies for SiO_2 glass that the stretching modes of Si-O^- nonbridging bonds, which are created under the 'free end condition' of the model, are very intensely localized. They also suggested the likelihood of intense localization of the Si-O^- nonbridging bond stretching modes in alkali silicate glasses.

The normal mode calculations showed that the increase in degree of polymerization of the silicate anions shift the high frequency Si-O^- nonbridging bond stretching modes to higher frequencies. There are also indications that the Si-O^- nonbridging bond becomes stronger as silicate anion polymerizes. It has been reported by Smith and Bailey⁽³⁵⁾ that in silicate crystals the average of all the Si-O bond lengths tends to decrease from silicates with isolated SiO_4 tetrahedra to framework silicates, suggesting that the Si-O bonds are strengthened as the polymerization increases. Accurate Si-O bond lengths in crystalline Na_2SiO_3 ⁽²⁹⁾, $\beta\text{-Na}_2\text{Si}_2\text{O}_5$ ⁽³¹⁾ and $\alpha\text{-Na}_2\text{Si}_2\text{O}_5$ ⁽³⁰⁾ were reported. According to the reported values, the average Si-O bond lengths are:

Si-O^- (nonbridging) = $1.592\text{ \AA}$, Si-O (bridging) = $1.672\text{ \AA}$ for Na_2SiO_3 ,

Si-O^- (nonbridging) = $1.580\text{ \AA}$, Si-O (bridging) = $1.639\text{ \AA}$ for $\beta\text{-Na}_2\text{Si}_2\text{O}_5$,

Si-O^- (nonbridging) = $1.578\text{ \AA}$, Si-O (bridging) = $1.630\text{ \AA}$ for $\alpha\text{-Na}_2\text{Si}_2\text{O}_5$.

It is noted that the Si-O nonbridging bond is shorter than the bridging bond at both compositions and both the nonbridging bond and the bridging bond shorten as the structure changes from the metasilicate to the disilicate. The strengthening of the Si-O bonds probably accounts for the larger frequency increase from the metasilicate to the disilicate of the observed spectra $1100\text{ cm}^{-1}/985\text{ cm}^{-1} = 1.12$ than the calculated ratio, $968\text{ cm}^{-1}/932\text{ cm}^{-1} = 1.04$. An ESCA study on alkali

silicate glasses by Brückner et al.⁽³⁶⁾ showed that the Si-O⁻ nonbridging bonds are stronger than the bridging bonds and the nonbridging bonds become stronger as the concentration of alkali oxide decreases.

APPENDIX: CALCULATION OF DYNAMICAL MATRIX ELEMENTS

The methods given here were originally formulated by S.A. Brawer (private communication).

Stretching Force Field

The elements of the dynamical matrix for the stretching force field are:

$$D(i,k,j,\ell) = - \frac{K_{ij}}{\sqrt{m_i \cdot m_j}} [\vec{v}_i^{(k)} \cdot \frac{(\vec{r}_i - \vec{r}_j)}{|\vec{r}_i - \vec{r}_j|}] \cdot [\vec{v}_j^{(\ell)} \cdot \frac{(\vec{r}_i - \vec{r}_j)}{|\vec{r}_i - \vec{r}_j|}] \text{ for } i \neq j, \quad (1)$$

and

$$D(i,k,j,\ell) = \sum_n \frac{k_{in}}{m_i} [\vec{v}_i^{(k)} \cdot \frac{(\vec{r}_i - \vec{r}_n)}{|\vec{r}_i - \vec{r}_n|}] \cdot [\vec{v}_n^{(\ell)} \cdot \frac{(\vec{r}_i - \vec{r}_n)}{|\vec{r}_i - \vec{r}_n|}] \text{ for } i = j \quad (2)$$

where k_{ij} is a stretching force constant between atom i and atom j . Vectors $\vec{v}_i^{(k)}$ ($k = 1, 2, 3$) are unit vectors of the displacement coordinate of atom i and they are set parallel to the axis of the laboratory Cartesian coordinates (x, y, z) for all atoms. The x, y and z directions are denoted by 1, 2 and 3, respectively. Vector $\vec{r}_i$ is the positional vector of atom i .

Bending Force Field

The bending force involves three atoms (Figure 16) and all possible ways of forming triplets must be taken into account. Figure 17 shows five possible triplet geometries. The elements of the dynamical matrix for the bending force field can be written as:

$$D(i,k,j,\ell) = \sum_{\substack{m \\ (m \neq i, j)}} \frac{\beta_{imj}}{\sqrt{m_i \cdot m_j}} (\vec{v}_i^{(k)} \cdot \vec{h}_{im}) \cdot (\vec{v}_j^{(\ell)} \cdot \vec{h}_{jm}) \\ - \sum_{\substack{n \\ (n \neq i, j)}} \frac{\beta_{ijn}}{\sqrt{m_i \cdot m_j}} (\vec{v}_i^{(k)} \cdot \vec{h}_{ij}) \cdot [\vec{v}_j^{(\ell)} \cdot (\vec{h}_{ij} + \vec{h}_{nj})]$$

$$- \sum_{\substack{h \\ (h \neq i, j)}} \frac{\beta_{hij}}{\sqrt{m_i \cdot m_j}} [\vec{v}_i^{(k)} \cdot (\vec{h}_{hi} + \vec{h}_{ji})] \cdot (\vec{v}_j^{(\ell)} \cdot \vec{h}_{ji}) \text{ for } i \neq j \quad (3)$$

and

$$D(i, k, i, \ell) = \sum_{\substack{h, p \\ (h, p \neq i, h \neq p)}} \frac{\beta_{ihp}}{m_i} (\vec{v}_i^{(k)} \cdot \vec{h}_{ih}) \cdot (\vec{v}_i^{(\ell)} \cdot \vec{h}_{ih}) \\ + \frac{1}{2} \sum_{\substack{m, n \\ (m, n \neq i, m \neq n)}} \frac{\beta_{min}}{m_i} [\vec{v}_i^{(k)} \cdot (\vec{h}_{mi} + \vec{h}_{ni})] \cdot [\vec{v}_i^{(\ell)} \cdot (\vec{h}_{mi} + \vec{h}_{ni})] \text{ for } i \neq j \quad (4)$$

where β_{ijk} is a bending force constant of the bond angle which is formed by atoms denoted by the subscripts. The atom indicated by the middle subscript is at the apex of a triplet. Vectors $\vec{h}_{nm}$ and $\vec{h}_{\ell m}$ are defined in the figure as:

$$\vec{h}_{nm} = \frac{1}{\sin \theta} \left\{ \left[\frac{\vec{d}_{\ell m} \cdot \vec{d}_{nm}}{(|\vec{d}_{\ell m}| \cdot |\vec{d}_{nm}|^5)^{1/2}} \right] \cdot \vec{d}_{nm} - \frac{\vec{d}_{\ell m}}{(|\vec{d}_{\ell m}| \cdot |\vec{d}_{nm}|)^{1/2}} \right\} \text{ and} \\ \vec{h}_{\ell m} = \frac{1}{\sin \theta} \left\{ \left[\frac{\vec{d}_{\ell m} \cdot \vec{d}_{nm}}{(|\vec{d}_{nm}| \cdot |\vec{d}_{\ell m}|^5)^{1/2}} \right] \cdot \vec{d}_{\ell m} - \frac{\vec{d}_{nm}}{(|\vec{d}_{\ell m}| \cdot |\vec{d}_{nm}|)^{1/2}} \right\}$$

where $\vec{d}_{nm} = \vec{r}_n - \vec{r}_m$ and $\vec{d}_{\ell m} = \vec{r}_\ell - \vec{r}_m$. The vector $\vec{h}_{nm}$ is normal to the n-m bond and $\vec{h}_{\ell m}$ is normal to the ℓ -m bond, and when $\vec{d}_{\ell m} = \vec{d}_{nm}$, $\vec{h}_{\ell m} = \vec{h}_{nm} = 1$. The first term of Equation 3 corresponds to case 1 in Figure 17 and the summation is over all possible apex atoms, m. The second and third terms of Equation 3 correspond to cases 2 and 3, and the summation is made over all possible atoms, n and atoms, h, respectively. Equation 4 is for the case of $i = j$ and the summation in the first term is over all possible combinations of h and p corresponding to case 4 in Figure 17. The second term of Equation 4 is for case 5 where atom i is at the apex of the triplet. Since $\beta_{nim} = \beta_{min}$, the term is multiplied by 1/2 after summation over all possible combinations of n and m.

Notes and References

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TABLE 1. Computed Vibrational Modes for the SiO_4 Tetrahedron,

Mode	Wavenumbers	Raman Intensity Arbitrary Units	IR Absorption Intensity Arbitrary Units
1	1009 (T_2)	0.000	9.86
2	728 (A_1)	2.000	0.00
3	425 (T_2)	0.000	3.25
4	399 (E)	0.000	0.00

TABLE 2. Computed Vibrational Modes for the Si_2O_7 Dimer

Mode	Wavenumbers	Raman Intensity Arbitrary Units	IR Absorption Intensity Arbitrary Units
1	1054	0.000	4.58
2	1014	0.035	4.36
3	1011	0.000	4.54
4	1007	0.000	0.00
5	1005	0.000	0.52
6	889	1.376	1.66
7	761	0.000	0.61
8	640	2.096	1.67
9	496	0.000	2.28
10	483	0.388	0.72
11	451	0.000	2.28
12	415	0.000	0.00
13	414	0.000	0.98
14	412	0.021	1.60
15	411	0.000	1.54
16	303	0.000	0.00
17	300	0.000	0.68
18	258	0.384	0.74
19	57	0.014	0.06
20	0	0	
21	0	0	

For Si-O-Si bond angle of 135° .

TABLE 3. Computed Vibrational Modes for the Si_2O_6 Chain

Mode	Wavenumbers	Raman Intensity Arbitrary Units	IR Absorption Intensity Arbitrary Units
1	1068	0.035	4.64
2	1044	0.000	4.58
3	1013	0.000	4.65
4	1005	0.000	0.00
5	932	1.212	1.13
6	802	0.000	1.80
7	790	0.000	1.32
8	562	1.700	2.23
9	527	0.000	1.01
10	501	0.000	2.94
11	488	0.000	0.00
12	477	0.686	1.24
13	418	0.000	1.70
14	352	0.574	0.82
15	330	0.000	0.00
16	282	0.000	0.00
17	213	0.000	0.56
18	156	0.103	0.44
19	0	0	0
20	0	0	0

For Si-O-Si bond angle of 135° .

TABLE 4. Computed Vibrational Modes for the Si_2O_5 Sheet

Mode	Wavenumbers	Raman Intensity Arbitrary Units	IR Absorption Intensity Arbitrary Units
1	1095	0.000	4.71
2	1077	0.049	4.65
3	1040	0.045	4.56
4	968	0.903	0.98
5	844	0.023	1.13
6	781	0.216	2.46
7	722	0.000	0.05
8	555	0.212	2.49
9	555	0.000	2.36
10	529	0.980	1.88
11	498	0.178	1.88
12	482	0.000	2.10
13	399	1.006	0.21
14	274	0.000	0.18
15	245	0.016	0.57
16	150	0.243	0.38
17	111	0.000	0.08
18	32	0.000	0.01

For Si-O-Si bond angle of 135° .

TABLE 5. Computed Vibrational Modes for the Si_2O_4 3-D Framework

Mode	Wavenumbers	Raman Intensity Arbitrary Units	IR Absorption Intensity Arbitrary Units
1	1096	0.000	4.79
2	1081	0.000	4.73
3	1071	0.019	4.80
4	874	0.000	0.72
5	790	0.000	2.18
6	764	0.178	2.48
7	715	0.000	0.00
8	553	0.000	1.63
9	552	0.000	3.36
10	549	0.000	0.00
11	536	0.055	2.21
12	527	0.000	1.97
13	339	1.236	0.33
14	138	0.000	0.00
15	110	0.000	0.08

Legends for Figures

- Figure 1. Experimental arrangement for Raman measurements.
- Figure 2. Parallel polarization Raman spectra.
- Figure 3. Crossed polarization Raman spectra.
- Figure 4. High frequency Raman bands of $\text{Na}_2\text{O} \cdot 3\text{SiO}_2$ glass.
- Figure 5. High frequency Raman bands of $\text{Na}_2\text{O} \cdot 1.5\text{SiO}_2$ glass.
- Figure 6. Peak heights of the 1100 cm^{-1} band and the 950 cm^{-1} band as a function of average number of NBO's per SiO_4 tetrahedron.
- Figure 7. Raman spectra of as-drawn (a) and heat-treated (b) glasses.
- Figure 8. Silicate anion structural units used in calculation of normal modes.
- Figure 9. Calculated Raman spectra of the silicate anions with $\gamma=135^\circ$. The dotted line near 1000 cm^{-1} gives the intensity lost due to cancelling effects of the bridging and non-bridging oxygen motions.
- Figure 10. Normal modes for the intense Raman bands of the Si_2O_6 chain.
- Figure 11. Normal modes for the intense Raman bands of the Si_2O_5 sheet.
- Figure 12. Normal mode for the most intense Raman band of the Si_2O_4 3-D framework.
- Figure 13. Calculated Raman spectra for Si_2O_6 chain units with different Si-O-Si bond angles.
- Figure 14. Calculated Raman spectra for Si_2O_5 sheet units with different Si-O-Si bond angles.
- Figure 15. Calculated IR absorption spectra for silicate anions with $\gamma=135^\circ$.
- Figure 16. Triplet formed by atoms n, m, and l.
- Figure 17. Five possible geometries for the formation of triplets of atoms.

Si_2O_7 dimer

Si_2O_6 chain

Si_2O_5 sheet

Si_2O_4 3D-framework

Si₂O₅ sheet
mode 4, 968 cm⁻¹

mode 10, 529 cm⁻¹

mode 13, 399 cm⁻¹

SiO₂ framework
mode 13, 339 cm⁻¹

1

2

3

4

5

APPENDIX 4.3

TRANSITION METAL IONS IN SILICATE MELTS: II. IRON IN SODIUM
SILICATE GLASSES

[Submitted for Publication to Physics and Chemistry of Glasses]

TRANSITION METAL IONS IN SILICATE MELTS. II.

IRON IN SODIUM SILICATE GLASSES*

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ABSTRACT

Optical absorption, luminescence and Raman spectra were measured for sodium silicate glasses melted in air, containing about 85% Fe(III) and 15% Fe(II). Luminescence intensities for individual samples were compared.

Three d-d bands in the optical absorption spectrum due to Fe(III) at about 26000, 24000 and 23000 cm^{-1} were assigned to the ${}^4\text{E}(\text{D})$, ${}^4\text{T}_2(\text{D})$ and ${}^4\text{A}_1\text{E}(\text{G})$ levels of the d^5 configuration. Another very weak band arose from the ${}^4\text{T}_2(\text{G})$ level. Luminescence spectra indicated an unobserved band at around 16200 cm^{-1} due to the ${}^4\text{T}_1(\text{G})$ level.

Raman and luminescence spectra both showed that the two distinct four-fold coordinated environments for Fe(III) existed in the glasses. In glasses of low sodium content, Fe(III) substitutes for Si with four bridging oxygens, producing Raman bands at 980 cm^{-1} and luminescence at 14600 cm^{-1} . In high sodium glasses, the Raman bands occurred at 890 cm^{-1} and luminescence appeared at 16200 cm^{-1} . It is argued that this may be a tetrahedral iron complex in the glass.

Ferrous iron appeared to occupy a 6-coordinated site the size of which decreased with increasing sodium concentration.

Alkali and alkaline earth silicate glasses can be prepared containing substantial quantities of transition metal ions which give the glasses special optical and magnetic properties. It is the object of this series of investigations to determine the detailed structural environment of transition metal ions in common silicate glasses. The first paper of the series⁽¹⁾ dealt with manganese. The present contribution is concerned with iron in alkali silicate glasses.

Ferrous and ferric iron in glass have been investigated by several methods. Most commonly used to determine local environment are optical absorption spectroscopy⁽²⁻⁷⁾ and the magnetic properties of iron^(2,3,7,8-12). In addition, there is extensive work on the thermodynamics of iron-containing melts⁽¹³⁻¹⁷⁾.

Ferrous iron has been dealt with fairly thoroughly^(3-5,18,19), and the work presented here reaffirms previous results.

On the other hand, the structural environment of ferric iron in glass is the subject of considerable controversy. Optical absorption spectra from Fe(III) tend to be very weak because the crystal field transitions are all spin-forbidden. In addition, the bands occur in a region of the spectrum where they overlap with the IR absorption bands due to Fe(II) and the exceptionally intense UV bands arising from ligand to metal charge transfer transitions. It is thus difficult to deconvolute the band shapes sufficiently accurately to draw conclusions about the Fe(III) coordination polyhedra.

Although Raman and luminescence spectroscopy are rarely used to study iron, they have been applied in this investigation in conjunction with optical absorption spectroscopy. The former two techniques independently revealed the presence of two distinct four-fold coordinated sites for Fe(III) in the glasses. Figure 1 summarizes the spectroscopic features observed.

Experimental

The glass compositions listed in Table 1 were prepared from 200 mesh silica floated powder (containing 0.0054 mole % impurity Fe_2O_3) and reagent grade Na_2CO_3 and Fe_2O_3 powders (Fischer Scientific).

Batches of glass were melted in a covered platinum crucible in air at 1375-1400°C ($\text{PO}_2 = 0.21$ atm) in a globar furnace. The crucible was initially primed by melting several iron-containing glasses in order to establish some concentration of iron in the crucible walls. The effect of platinum is still controversial. Johnston⁽¹⁵⁾ reported no effect on the equilibrium of iron in silicate melts in air, while Paul and Douglas⁽¹⁴⁾ have suggested the dissolution of Pt^{4+} in the melt. Baak and Hornyak⁽¹³⁾ feel that the alloying of Fe with Pt greatly effects the equilibrium. The melts were stirred at least twice during heating to ensure homogeneity. They were then poured onto a heated (about 350°C) graphite disc mold, and cooled to room temperature over approximately two hours. These discs were polished to optical smoothness and a thickness of about three millimeters, with two parallel surfaces for optical absorption measurements, and a perpendicular surface for Raman and luminescence measurements (see Figure 2). Glass rods were also drawn.

Optical absorption spectra in the visible and infra-red range were measured on a Cary model 14 spectrophotometer.

Raman and luminescence spectra were measured on a SPEX Model 1401 spectrometer using the experimental geometry shown in Figure 2. The RCA model C 31034 photomultiplier had a cutoff frequency of about $11,800\text{ cm}^{-1}$. Coordinates in the laboratory frame are defined as in Figure 2 in which the laser beam was polarized in the x-direction. Parallel-polarized Raman spectra are denoted by xx, while xy refers to crossed-polarization. Although the measurement of Raman and luminescence intensities is not common, we have successfully compared Raman

scattering and luminescence intensities from sample to sample. This is achieved through the use of a standardized scattering geometry, and a sample holder which exposes a constant sample area to the light collecting system. Samples to be compared must all be measured using exactly the same optical alignment. Luminescence intensity measurements for the determination of heating time used the Raman 1100 cm^{-1} band as an internal standard to increase accuracy.

It was difficult to obtain luminescence and Raman spectra from samples with iron concentrations greater than about 5 mole % Fe_2O_3 , due to luminescence quenching and strong absorption of the incident laser beam and Raman scattered light.

The series of glasses containing nominally 0.50 mole percent Fe_2O_3 and varying sodium contents was analysed. Total iron and FeO were determined by redox titration, and ferric iron was given by difference. The sodium oxide concentrations were measured by zinc uranyl acetate gravimetric analysis. The results of the analysis are given in Figure 3, and show that approximately 85% of the iron exists as Fe(III), and the remaining 15% is present as Fe(II). The loss of sodium becomes significant as the sodium oxide concentration increases, and it reaches almost 10 percent in the nominal 45 mole percent Na_2O glasses (see Table 1).

Samples of sodium trisilicate glass formulated with 0.50 mole percent Fe_2O_3 were heated for time spans between five and 96 hours. Absorptivity at $10,000\text{ cm}^{-1}$ and intensity of luminescence at $14,600\text{ cm}^{-1}$ were measured. A plot of these results (Figure 4) shows that both the absorptivity and the luminescence intensities change rapidly during the first 24 hours, and equilibrium has practically been established after 48 hours. This is in agreement with the results of and Douglas⁽¹⁴⁾.

In accord with these results, samples with less than 25 mole % sodium content

were heated for 48 hours. To reduce the amount of sodium lost by vaporisation, samples of high sodium content were heated for only 24 hours.

Spectra and Local Environment of Ferrous Iron

The IR range absorption spectra for the $\text{Na}_2\text{O} \cdot x\text{SiO}_2 \cdot y\text{Fe}_2\text{O}_3$ (0.50 mole percent Fe_2O_3) glass series are given in Figure 5. Two bands are observed, one at about $10,000 \text{ cm}^{-1}$, the other at about 5000 cm^{-1} . Although these bands appear of similar shape when drawn by a linear wavelength spectrometer, the higher frequency band actually has a half-width of approximately three to four times that of the low frequency band when the bands are plotted on a linear wavenumber scale. The absorptivity of these bands is very high in the spectrum of a trisilicate sample prepared under reducing conditions (such that most of the Fe(III) has been reduced to Fe(II)), confirming that these bands are due to Fe(II) .

The ratio of the $10,000 \text{ cm}^{-1}$ to the 5000 cm^{-1} band absorbance remains constant with changing base glass composition (Figure 6). The band frequencies, however, shift as shown in Figure 7. As sodium content increases, the $10,000 \text{ cm}^{-1}$ band shifts to higher frequencies at a greater rate than the 5000 cm^{-1} band shifts to low frequencies.

The absorptivity of the $10,000 \text{ cm}^{-1}$ band as a function of the nominal concentration of Na_2O is plotted in Figure 8. It shows a maximum at about the disilicate composition.

Ligand field theory predicts only one spin-allowed absorption band, ${}^5\text{T}_2(\text{D}) \rightarrow {}^5\text{E}(\text{D})$, for divalent iron⁽¹⁹⁾. However, as has previously been observed^(3,4,18), there exist in these glasses two bands separated by 2000 to 5000 cm^{-1} . On the basis of peak height ratios and band widths, the suggestion by Bishay and Makar⁽³⁾ that these two peaks arise from Fe(II) in tetrahedral and octahedral sites may be discounted. It is unlikely that the relative number of ions in each coordination would remain fixed as the sodium concentration, and thus the silicate network structure, of the glass was varied. In addition, the slope of the first energy level of the d^6 configuration does not change between

octahedral and tetrahedral coordination. If the two bands were due to tetrahedral and octahedral sites, the band widths should be more or less equal, contradictory to the experimental findings.

Studies undertaken by several investigators^(3-5,9,10,18) are consistent with Fe(II) in six-fold coordination. The range in Dq observed is also in agreement with octahedral coordination. The small satellite band is similar to the band observed in Mn^{3+} -containing glasses⁽¹⁾. Whether it arises from site distortion or from a dynamic Jahn-Teller effect cannot be determined from the available data.

Figure 7 indicates that the $10,000\text{ cm}^{-1}$ band shifts to higher frequencies as sodium content is increased. Thus the crystal field experienced by Fe(II) in disilicate glass is less than that in metasilicate glass. Since the lengths of the Si-O⁻ bonds in disilicate and metasilicate glasses are different, the effective negative charge on the oxygen in the disilicate is smaller. In metasilicate glass the bond length is $1.592\text{ \AA}$, while in disilicate glasses the bond length averages $1.50\text{ \AA}$, as measured from sodium silicate crystals^(20,21). Goldman and Berg⁽¹⁸⁾ also conclude that Fe(II) exists in modifier sites. At low sodium concentrations, Fe^{2+} occupies somewhat larger sites dictated by the size requirements of the Na^{+} ion. As the glass becomes de-polymerized, increased flexibility of the non-bridging bonds permits Fe^{2+} to assume an octahedral coordination polyhedron appropriate to its ionic size. Thus Dq for Fe^{2+} in high soda glasses is very close to its value in crystalline Fe^{2+} compounds.

Spectra and Local Environment of Ferric Iron

The optical absorption spectra (Figure 9) show the d-d transitions due to Fe(III) in sodium silicate glasses formulated with 0.50 mole percent Fe_2O_3 . In the original spectra, these bands are superimposed upon a strong UV absorption tail, which has been subtracted out. These bands were not observed in a sample in which most of the Fe(III) has been reduced to Fe(II). The sharp peak at about $26,000\text{ cm}^{-1}$, and the two moderately well-resolved bands at around $24,000$ and $23,000\text{ cm}^{-1}$ are easily distinguished. However, at lower frequencies no distinct bands are observed in the long tail of the spectrum. Figure 10 shows that peak frequencies of the three main bands shift at different rates as a function of the sodium content of the glass. The absorptivity of the $26,000\text{ cm}^{-1}$ peak is minimum around the trisilicate composition (Figure 11).

The relative luminescence intensities arising from the samples mentioned above when excited by the $19,436\text{ cm}^{-1}$ (green) laser line are shown in Figure 12. The peak occurs at about $14,600\text{ cm}^{-1}$ in the red region of the spectrum, and is completely absent in a reduced sample containing primarily Fe(II). The emission band is symmetrical, and shows a smooth decrease in intensity as sodium content is increased (Figure 13). A break in the rate of change of intensity occurs between the disilicate and trisilicate compositions.

The luminescence excited by the higher energy $21,839\text{ cm}^{-1}$ violet line differs greatly from that excited by the green laser line (Figure 14). In addition to the red $14,600\text{ cm}^{-1}$ luminescence originally excited by the green line, another band appears around $16,200\text{ cm}^{-1}$. At low sodium concentrations the low frequency band is most intense. As sodium content is increased, the band decreases in intensity. At the disilicate composition, the second band at about $16,200\text{ cm}^{-1}$ makes its first appearance and becomes most intense for the high sodium glasses.

Figure 15 gives luminescence intensity as a function of the nominal mole percent Fe_2O_3 added to $\text{Na}_2\text{O} \cdot 3\text{SiO}_2$ glass. The most intense luminescence occurs between about 0.05 and 0.5 mole percent Fe_2O_3 . Concentration quenching occurs at higher iron concentrations.

In Figure 16 are shown the Raman spectra of $\text{Na}_2\text{O} \cdot 3\text{SiO}_2 \cdot 0.02\text{Fe}_2\text{O}_3$ glass and its reduced counterpart $\text{Na}_2\text{O} \cdot 3\text{SiO}_2 \cdot 0.04\text{FeO}$, as well as the spectrum of the trisilicate base glass. Bands which are not present in the base glass or reduced glass spectra are apparent in the 900 to 1000 cm^{-1} range of both parallel- and crossed-polarized spectra of the doped glass. When the concentration of iron in a sodium trisilicate sample is increased, the intensity of the 900 - 1000 cm^{-1} bands increase (Figure 17 and 18), as has also been reported by Brawer and White⁽²²⁾. The band at 980 cm^{-1} has a depolarization ratio of about $3/4$, which is the maximum theoretical value. This band must be distinguished from the strongly polarized band due to the base glass, which occurs in the same region.

The effect of iron on the Raman spectra were more closely examined by increasing the Fe_2O_3 content to 2.4 mole percent for several base compositions. The extra bands due to Fe(III) were deconvoluted, as shown in Figure 19, by subtracting the base glass spectra from the doped glass spectra. The results are summarized in Figure 20, which shows two bands present at about 980 cm^{-1} and 890 cm^{-1} . The band at higher vibrational frequency is present in glasses of low sodium content. As the sodium content is increased to the trisilicate composition, this band diminishes in intensity and a second band appears at about 890 cm^{-1} . This low frequency band becomes most prominent in the high sodium glasses. The behavior of these Raman bands is very similar to that observed in the luminescence spectra (Figure 14).

Figure 21 shows that as the level of iron-doping in $\text{Na}_2\text{O} \cdot 1.5\text{SiO}_2$ glass is increased, the height of the polarized Raman band near 950 cm^{-1} decreases with

respect to the height of the polarized band at about 1100 cm^{-1} . The band at 950 cm^{-1} is due to the stretching vibration of $\text{O}^- - \text{Si} - \text{O}^-$ non-bridging bonds, while the 1100 cm^{-1} band arises from the stretching of $\text{Si} - \text{O}^-$ nonbridging bonds in SiO_4 tetrahedra⁽²³⁾. The intensity ratio of the two bands, I_{950}/I_{1100} , is 0.88 for the base glass, and decreases to 0.81 and 0.63 for samples formulated with 0.50 and 2.4 mole percent Fe_2O_3 respectively.

Assignments for the Fe(III) d-d absorption bands in silicate glasses have previously been reported by Kurkjian and Sigety⁽²⁾. Although their assignments have been generally accepted^(5,7,24), they conflict with the luminescence results of this investigation, to be discussed below. An alternative assignment has been suggested by Manning⁽²⁵⁾, and by Linnehan et al.⁽²⁶⁾ for tetrahedrally coordinated Fe(III) in orthoclase (KAlSi_3O_8 - a framework structure). Absorption bands observed in the present iron-doped glasses have been assigned in accordance with the orthoclase spectra.

The energy level diagram shown in Figure 22 for the d^5 electronic configuration was calculated for the $\text{Na}_2\text{O} \cdot 5.67\text{SiO}_2 \cdot 0.033\text{Fe}_2\text{O}_3$ glass. It shows that the ${}^4\text{E}(\text{D})$ and ${}^4\text{A}_1, {}^4\text{E}(\text{G})$ levels are field-independent, and the ${}^4\text{T}_2(\text{D})$ level is nearly field independent at crystal field strength (Dq) values below 2000 cm^{-1} . Transitions to these levels will thus produce three narrow bands. The lower two levels ${}^4\text{T}_2(\text{G})$ and ${}^4\text{T}_1(\text{G})$ have a considerable slope, and will give rise to very broad absorption bands.

The glass spectra have three fairly well-resolved bands near 26,000, 24,000 and $23,000\text{ cm}^{-1}$ which are assigned to the ${}^4\text{E}(\text{D})$, ${}^4\text{T}_2(\text{D})$ and ${}^4\text{A}_1, {}^4\text{E}(\text{G})$ levels, respectively. The two lowest frequency bands (${}^6\text{A}_1(\text{S}) \rightarrow {}^4\text{T}_2(\text{G})$ and ${}^6\text{A}_1(\text{S}) \rightarrow {}^4\text{T}_1(\text{G})$) were not observed. The first three bands in the absorption spectra of orthoclase⁽²⁶⁾ have intensities and frequencies similar to those observed in the $\text{Na}_2\text{O} \cdot 5.67\text{SiO}_2 \cdot 0.33\text{Fe}_2\text{O}_3$ glass spectra. There also appears in the orthoclase

spectrum two low frequency bands which have very low absorptivity. The low intensities are perhaps the reason that these bands do not appear in the glass spectra.

The luminescence band observed at $14,600 \text{ cm}^{-1}$ implies that the absorption band due to the lowest energy level, $^4T_1(G)$, should occur at a frequency in the vicinity of $16,000 \text{ cm}^{-1}$. In fact, the luminescence band for orthoclase (number 1392 in reference 26), which has a $^4T_1(G)$ absorption band at around $16,200 \text{ cm}^{-1}$, occurs at about $14,500 \text{ cm}^{-1}$. The corresponding Stokes shift is 1700 cm^{-1} . If the absorption band at $20,800 \text{ cm}^{-1}$ in the spectrum of $40\text{Na}_2\text{O} \cdot 60\text{SiO}_2 + 0.1\% \text{Fe}_2\text{O}_3$ glass⁽²⁾ is assigned to the first energy level, $^4T_1(G)$, the luminescence band would be expected in the region $19,000$ to $20,000 \text{ cm}^{-1}$, much higher than is observed.

The above assignment implies that Fe(III) in the iron-doped glass is present in tetrahedral coordination. Luminescence due to six-fold coordinated Fe(III), if present, would be expected to occur around $11,500 \text{ cm}^{-1}$ (27). There is no luminescent emission in this region and thus no evidence for octahedral Fe(III).

The shift in peak frequency of bands arising from the two field-independent levels of the d^5 configuration ($^4E(D)$ and $^4A_1, ^4E(G)$) shows that the changes in the B and C Racah parameters are taking place. Using the solutions to the Tanabe-Sugano matrices for the $^6A_1(S) \rightarrow ^4E(D)$ and the $^6A_1(S) \rightarrow ^4A_1, ^4E(G)$ transitions, B and C may be calculated as follows:

$$\nu(^4E(D)) = 17 B + 5 C$$

$$\nu(^4A_1, ^4E) = 10 B + 5 C$$

Thus, for 15 mole percent Na_2O , $B = 469$, $C = 3689 \text{ cm}^{-1}$
and for 45 mole percent Na_2O , $B = 417$, $C = 3722 \text{ cm}^{-1}$.

Using these B and C parameters, energy level diagrams for either end of the series of glasses formulated with 0.50 mole percent Fe_2O_3 were calculated. That for the 15 mole percent Na_2O glass is given in Figure 22. The differences in B and C values used for each composition result in only small differences in the upper energy levels, and practically no change in the first and second levels. The luminescence due to four-fold coordinated Fe(III) in high sodium glass occurs at $16,200\text{ cm}^{-1}$, while it is observed at $14,600\text{ cm}^{-1}$ in low sodium glass (Figure 14). The differences in B and C are not sufficient to explain the observed 1600 cm^{-1} shift in luminescence frequency. Thus a shift to lower Dq must simultaneously occur to produce the $16,200\text{ cm}^{-1}$ luminescence from the site present in high sodium glasses and the $14,600\text{ cm}^{-1}$ luminescence from the low sodium glasses.

The presence of two luminescence bands which vary in intensity as a function of sodium concentration (Figure 14) indicates the existence of two Fe(III)-containing structures, both tetrahedral, in the glass.

The intensity variation of the depolarized Raman bands at 890 cm^{-1} and 980 cm^{-1} (Figure 20) as a function of sodium concentration is very similar to the variation found in the luminescence spectra. These results also indicate the presence of two kinds of Fe(III), whose concentrations change as the sodium content of the glass is varied. The fact that these bands have the maximum allowed depolarisation ratio implies that they arise from asymmetric vibrations, probably stretching of Fe-O-Si bonds. In high sodium glasses, the bond vibration frequency of 890 cm^{-1} is lower than that of 980 cm^{-1} found in low sodium glasses, suggesting that Fe-O bonds in high sodium glasses are weaker than those in low sodium glasses.

In orthoclase, aluminum occurs as Al^{3+}O_4 tetrahedra, forming a three-dimensional network with Si^{4+}O_4 tetrahedra. The charge deficiency in the Al^{3+}O_4

tetrahedra is balanced by nearby K^+ cations. Ferric iron substitutes for Al^{3+} as FeO_4 tetrahedra in the framework. The similarity between the $Na_2O \cdot 5.67SiO_2 \cdot 0.033Fe_2O_3$ glass and the orthoclase d-d absorption spectra suggests that $Fe(III)$ is also present in network-former sites in the low sodium glasses.

An estimate for Dq can be obtained by adding the Stokes shift, 1700 cm^{-1} , to the observed $14,600\text{ cm}^{-1}$ luminescence band and then scaling Dq from the energy level diagram of Figure 22. A value of 1000 cm^{-1} is obtained. Using as a reference Fe^{3+} on a normal octahedral site with $Dq = 1400\text{ cm}^{-1}$ (28) and $Fe^{3+}-O = 2.031\text{ \AA}$ (29), calculation of the necessary $Fe-O$ distance to account for $Dq = 1000\text{ cm}^{-1}$ on a tetrahedral site yields $Fe^{3+}-O = 1.85\text{ \AA}$ in moderately good agreement with expectations for a network-forming FeO_4 tetrahedron.

There remains the problem of interpretation of the Fe^{3+} species responsible for the $16,200\text{ cm}^{-1}$ luminescence band. Converting the luminescence band to an absorbance band by adding the Stokes shift and scaling Dq from the Tanabe-Sugano diagram produces a value of Dq of 770 cm^{-1} , not too different from the $4/9$ proportion of the octahedral Dq predicted by crystal field theory. There are several possibilities for this species which cannot be unequivocally distinguished on the basis of the available evidence. One is that this species, which occurs at the higher sodium concentrations, represents a network-forming FeO_4 group containing one or two non-bridging oxygens. Leaving aside the questions of whether such structural units would be stable, the observation from many crystal structures is that non-bridging oxygens have shorter metal-ligand bonds than bridging oxygens. This would predict a higher value of Dq for this sort of structure than for an FeO_4 tetrahedron entirely incorporated in the network. The opposite is observed. An alternative hypothesis is that ferric iron occurs in the high sodium glasses as a tetrahedral complex, FeO_4^{-5} , coordinated either by non-bridging oxygens or else actually tying up oxygens from the network leaving

other parts of the network more highly polymerized. This would be the opposite to the usual effect of "network modifying" cations whose addition creates non-bridging oxygen. Complex formation would reduce the number of non-bridging oxygen.

Some evidence for this interpretation may be obtained from the behavior of the 950 cm^{-1} polarized Raman line as the concentration of iron in the glass is increased. The polarized Raman bands at 950 and 1100 cm^{-1} are due to symmetric stretchings of the Si-O^- bonds in SiO_4 tetrahedra with two non-bridging oxygens, and with one non-bridging oxygen, respectively. The relative intensity of the bands is indicative of the number of NBO's in the glass. As Fe(III) ions are added, the number of NBO's decreases, suggesting a more highly polymerized network to balance the oxygens consumed in the formation of the complex.

Conclusion

The combination of optical absorption, luminescence, and Raman spectroscopic data presented here provides strong evidence that iron in sodium silicate glasses occurs in at least three distinct environments.

Divalent iron exhibits an optical absorption spectrum consistent with six-fold coordination. As the alkali concentration is increased the effective Fe^{2+} -O bond length decreases. It is argued that in the highly polymerized structure, the Fe^{2+} ion occupies a coordination polyhedron with size dictated by the bonding requirements of the silica framework. Addition of soda increases the number of non-bridging oxygens and the coordination polyhedron adjusts itself to more nearly meet the size and bonding requirements of Fe^{2+} and as a result the optical spectrum of the high sodium glasses is much like the spectrum of Fe^{2+} in crystals.

Most of the iron in these glasses exists as Fe^{3+} which can be shown by luminescence and Raman data to occur in two distinct tetrahedral arrangements. One appears to be an FeO_4 tetrahedron linked into the glass-forming network by Fe-O-Si bridging bonds. The interpretation of the FeO_4 tetrahedron that occurs in high soda glasses is more ambiguous but crystal field parameters and the influence of this entity on the Raman spectrum provides evidence that it is a quasi-molecular complex dissolved in the glass.

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Table 1. Glass Compositions

Nominal Formula	Formulated Mole % Na ₂ O	Formulated Mole % Fe ₂ O ₃	Analysed Mole % FeO	Analysed Mole % Σ Fe ₂
Na ₂ O·5.67SiO ₂	14.99	0.03 [†]		
Na ₂ O·3SiO ₂	25.00	0.02 [†]		
Na ₂ O·2SiO ₂	33.33	0.01 [†]		
Na ₂ O·1.5SiO ₂	40.00	0.01 [†]	NOT ANALYSED	
Na ₂ O·SiO ₂	50.00	0.01 [†]		
Na ₂ O·3SiO ₂ ·0.005Fe ₂ O ₃	24.97	0.13		
Na ₂ O·3SiO ₂ ·0.04Fe ₂ O ₃	24.75	0.99		
Na ₂ O·5.67SiO ₂ ·0.033Fe ₂ O ₃	14.82*	0.49*	0.14	0.56
Na ₂ O·4SiO ₂ ·0.025Fe ₂ O ₃	19.75*	0.52*	0.17	0.61
Na ₂ O·3SiO ₂ ·0.02Fe ₂ O ₃	24.78*	0.51*	0.20	0.61
Na ₂ O·2SiO ₂ ·0.015Fe ₂ O ₃	32.43*	0.53*	0.17	0.62
Na ₂ O·1.75SiO ₂ ·0.014Fe ₂ O ₃	33.79*	0.49*	0.14	0.56
Na ₂ O·1.5SiO ₂ ·0.013Fe ₂ O ₃	37.85*	0.50*	0.18	0.59
Na ₂ O·1.22SiO ₂ ·0.044Fe ₂ O ₃	40.00*	0.50*	0.12	0.56
Na ₂ O·5.67SiO ₂ ·0.167Fe ₂ O ₃	14.63	2.44		
Na ₂ O·3SiO ₂ ·0.1Fe ₂ O ₃	24.39	2.44		
Na ₂ O·2.5SiO ₂ ·0.088Fe ₂ O ₃	27.87	2.45	NOT ANALYSED	
Na ₂ O·2SiO ₂ ·0.075Fe ₂ O ₃	32.52	2.44		
Na ₂ O·1.5SiO ₂ ·0.063Fe ₂ O ₃	39.02	2.44		

[†] impurity level.

* analysed.

FIGURE CAPTIONS

- Figure 1. Summary of spectroscopic features observed. Those in top spectrum were measured by absorbance; those in the lower spectrum by laser excitation.
- Figure 2. Experimental geometry for Raman and luminescence measurements.
- Figure 3. Analysed Fe(II) and total iron contents versus analysed Na_2O content.
- Figure 4. Intensity of Fe(III) luminescence at $14,600\text{ cm}^{-1}$ (●) and absorptivity of Fe(II) d-d band at $10,000\text{ cm}^{-1}$ (○) versus heating time for $\text{Na}_2\text{O} \cdot 3\text{SiO}_2 \cdot 0.02\text{Fe}_2\text{O}_3$ glass.
- Figure 5. Absorption bands due to Fe(II) d-d transitions in iron-doped sodium silicate glass (nominally 0.50 mole percent Fe_2O_3).
- Figure 6. Ratio of the Fe(II) absorption band at $10,000\text{ cm}^{-1}$ to that at 5000 cm^{-1} as a function of the nominal mole percent Na_2O .
- Figure 7. Peak frequencies of the Fe(II) d-d absorption bands as a function of the nominal mole percent Na_2O .
- Figure 8. Absorptivity of the Fe(II) d-d band at $10,000\text{ cm}^{-1}$ as a function of nominal mole percent Na_2O .
- Figure 9. Absorption bands due to Fe(III) d-d transitions in iron-doped sodium silicate glasses (nominally 0.50 mole percent Fe_2O_3).
- Figure 10. Peak frequencies of the Fe(III) d-d absorption bands as a function of analysed mole percent Na_2O .
- Figure 11. Absorptivity of the Fe(III) d-d band at $26,000\text{ cm}^{-1}$ as a function of analysed mole percent Na_2O .
- Figure 12. Luminescence of iron-doped sodium silicate glasses (nominally 0.50 mole percent Fe_2O_3) excited by the green laser line ($19,436\text{ cm}^{-1}$).
- Figure 13. Luminescence intensity of iron-doped sodium silicate glasses (nominally 0.50 mole percent Fe_2O_3) excited by the $19,436\text{ cm}^{-1}$ laser line as a function of the calculated number of NBO's.

- Figure 14. Luminescence of iron-doped sodium silicate glasses (nominally 0.50 mole percent Fe_2O_3) excited by the violet $21,839\text{ cm}^{-1}$ laser line.
- Figure 15. Luminescence intensity of iron-doped sodium trisilicate glass as a function of the total iron concentration.
- Figure 16. Raman spectra of sodium trisilicate glass containing: (top) Fe(III); (centre) Fe(II); (bottom) no iron.
- Figure 17. Parallel-polarized Raman spectra of sodium trisilicate glass showing the growth of the 980 cm^{-1} band as the iron content is increased.
- Figure 18. Crossed-polarized Raman spectra of sodium trisilicate glass showing the growth of the 980 cm^{-1} band as the iron content is increased.
- Figure 19. Base-glass Raman spectra are subtracted from doped-glass spectra to obtain bands due to the presence of Fe(III).
- Figure 20. Depolarized Raman bands due to the presence of Fe(III) in sodium silicate glasses.
- Figure 21. Parallel-polarized Raman spectra showing the drop in intensity of the polarized 950 cm^{-1} band as Fe(III) concentration is increased.
- Figure 22. Energy level diagram for $\text{Na}_2\text{O}\cdot 5.67\text{SiO}_2\cdot 0.033\text{Fe}_2\text{O}_3$ glasses.

Laboratory
Coordinate
System

Glass
Sample

Analyser

Spectrometer

Laser

RAMAN SPECTRA OF TRISILICATE GLASS WITH IRON

APPENDIX 4.4

LUMINESCENCE OF Fe^{3+} IN METAPHOSPHATE GLASSES: EVIDENCE FOR FOUR AND SIX-COORDINATED SITES

Luminescence of Fe³⁺ in Metaphosphate Glasses:

Evidence For Four and Six-Coordinated Sites

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Luminescence of Fe^{3+} in Metaphosphate Glasses:

Evidence for Four and Six Coordinated Sites

KAREN E. FOX, TOSHIHARU FURUKAWA and WILLIAM B. WHITE

Abstract

Ferric iron-substituted sodium metaphosphate and calcium metaphosphate glasses exhibit a very weak luminescence that can be observed under laser excitation. Broad emission bands at $16,000\text{ cm}^{-1}$ and at $12,000\text{ cm}^{-1}$ are assigned to the ${}^4\text{T}_1 \rightarrow {}^6\text{A}_1$ transitions of Fe^{3+} in four-coordinated and six-coordinated sites respectively. The interpretation is supported by crystal field theory calculations based on known absorption spectra of Fe^{3+} .

Various methods have been used to probe the local structural environment of Fe^{3+} in crystals and glasses. Among these are optical absorption spectroscopy¹⁻⁶, Mössbauer spectroscopy^{1,6-8} and electron spin resonance spectroscopy^{2,5,7,9}. Fe^{3+} has the d^5 electron configuration and, like the isoelectronic Mn^{2+} ion, can act as an activator for luminescence. The luminescence emission bands are indicative of the local structural environment of the Fe^{3+} ion. This note presents results on the luminescence emission of two metaphosphate glasses which indicate that Fe^{3+} in these glasses occupies both four- and six-coordinated sites.

Activation of glasses and crystals by Mn^{2+} produces efficient luminescence in a spectrum of colors from green to red, depending on details of coordination number, local site symmetry and Mn-O bond lengths¹⁰. The luminescence of Fe^{3+} occurs in the far red to near-infrared and is difficult to observe. Only a few efficient Fe^{3+} -activated phosphors are known, for example $\gamma\text{LiAlO}_2:\text{Fe}^{3+}$ ¹¹ and $\text{LiAl}_5\text{O}_8:\text{Fe}^{3+}$ ¹². In these materials, Fe^{3+} is in four-coordination and emits in the region between about 650 and 750 nm ($13,000\text{--}15,000\text{ cm}^{-1}$). The ferric ion substituting for Al^{3+} in the four-coordinated sites of the aluminosilicate framework, is responsible for the deep red luminescence of feldspars¹³. The same characteristic red luminescence of four-coordinated Fe^{3+} has been observed in lithium disilicate glasses¹⁴ and in sodium silicate glasses¹⁵.

Fe^{3+} luminescence in the phosphate glasses is extremely weak; the band intensities are comparable to Raman scattering intensities. The spectra of $\text{NaPO}_3 \cdot 0.002\text{Fe}_2\text{O}_3$ and $\text{Ca}(\text{PO}_3)_2 \cdot 0.002\text{Fe}_2\text{O}_3$ glasses were obtained by exciting as-pulled rods with the 458 nm (21839 cm^{-1}) line of an argon ion laser. The spectra were measured using the Raman spectrometer with a GaAs-cathode, IR-sensitive photomultiplier*. Two broad luminescence bands were observed for

*RCA model C 31034

each glass, one near $16,300\text{ cm}^{-1}$ which will be ascribed to four-coordinated Fe^{3+} , and one near $12,000\text{ cm}^{-1}$ which will be ascribed to six-coordinated Fe^{3+} . The $12,000\text{ cm}^{-1}$ band is truncated by the cut-off of the photomultiplier and the exact band maximum may be slightly offset from the value shown.

Both absorption and luminescence spectra of Fe^{3+} can be interpreted with the Tanabe-Sugano diagram of Figure 2. Spin-forbidden transitions from the ${}^6\text{A}_1$ ground state to the various quartet levels account for the characteristically weak absorption spectrum of Fe^{3+} . Emission takes place from the ${}^4\text{T}_1(\text{G})$ level and is Stokes shifted from the frequency at which absorption occurs. Since the ${}^4\text{T}_1(\text{G})$ level has a steep negative slope, the energy of both absorption and emission decreases with an increase in crystal field strength. This accounts for the differences between Mn^{2+} , for which the octahedral value of Dq is on the order of 750 cm^{-1} resulting in an emission band in the red region of the spectrum, and Fe^{3+} , for which the typical octahedral value of Dq is on the order of 1400 cm^{-1} ¹⁶. Allowing for a nominal Stokes shift, the emission band for octahedral Fe^{3+} is predicted to occur at about $12,000\text{ cm}^{-1}$ ($830\text{ }\mu\text{m}$) (Figure 2).

Studies by Kirkjian and Sigety¹ indicate that Fe^{3+} in phosphate glasses exists primarily in six-fold coordination. They observed an absorption from the ${}^4\text{T}_1(\text{G})$ level at $13,600\text{ cm}^{-1}$ in iron-doped NaPO_3 glass. Assuming that the $12,000\text{ cm}^{-1}$ luminescence band in Figure 1 is due to the same transition, the Stokes shift must be 1600 cm^{-1} , a reasonable value.

Several lines of evidence suggest that the $16,000\text{ cm}^{-1}$ bands arise from Fe^{3+} in four-fold coordination.

The optical absorption spectrum of Fe^{3+} in orthoclase¹³ contained a band at $16,200\text{ cm}^{-1}$ which was assigned to the ${}^4\text{T}_1(\text{G})$ level. The corresponding

luminescence band occurs at $14,500\text{ cm}^{-1}$ giving a Stokes shift of 1700 cm^{-1} , well within the expected range. The emission band frequency of Fe^{3+} in the feldspar, however, is somewhat smaller (i.e., Dq is larger) than the emission band of the phosphate glasses.

Consider the FeO_4^{-5} cluster itself. Crystal field theory predicts that

$$Dq(\text{tetrahedral}) = -4/9 Dq(\text{octahedral})$$

This relationship assumes that the cation-anion distances are the same for both tetrahedral and octahedral coordinations. On the contrary, the Shannon-Prewitt¹⁷ radius for high spin Fe^{3+} in four-coordination is 63 pm while in six-coordination it is 78.5 pm. Since the oxygen ligand most closely approaches two-fold coordination, the ionic radius of oxygen is taken to be 121 pm. Thus the ratio of crystal field strengths may be written

$$Dq(\text{tet})/Dq(\text{oct}) = -4/9 (r_{\text{Fe}}(\text{oct}) + r_{\text{O}})^5 / (r_{\text{Fe}}(\text{tet}) + r_{\text{O}})^5 = 0.67$$

Using the $12,000\text{ cm}^{-1}$ emission band as a measure of $Dq(\text{oct})$ (1250 cm^{-1}) and assuming that the $16,300\text{ cm}^{-1}$ band measures $Dq(\text{tet})$ (800 cm^{-1}) with the Stokes shift taken as 1700 cm^{-1} in both, the ratio $Dq(\text{tet})/Dq(\text{oct})$ is calculated to be 0.64 in quite good agreement with the theoretical value of 0.67.

These results suggest that Fe^{3+} occurs in metaphosphate glasses in two kinds of sites, one tetrahedral and one octahedral. However, the fact that $Dq(\text{tet})$ in the phosphate glass is smaller than $Dq(\text{tet})$ for Fe^{3+} substituting for Al^{3+} in feldspar indicates that the "tetrahedral" site in the glass structure has a larger cation-anion distance than would be expected for the PO_4 tetrahedra of the glass framework. The evidence is suggestive that the Fe^{3+} in metaphosphate glass occurs as a tetrahedral complex as has already been suggested for lithium disilicate glass¹⁴ and other transition metal ion-containing glasses¹⁸.

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Legends for Figures

1. Luminescence spectra of Fe^{3+} in two metaphosphate glasses.
2. Tanabe-Sugano energy level diagram for the d^5 electron configuration showing approximate positions for the luminescent emission transitions of Fe^{3+} .