STRUCTURE OF GLASSES CONTAINING TRANSITION METAL IONS

Progress Report

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TABLE OF CONTENTS

	Page
Abstract	iv
1.0 Introduction	1
2.0 Results	2
2.1 THEORETICAL APPROACHES	2
2.1.1 Calculations of IR and Raman Spectra of Disordered Systems	2
2.2 STRUCTURE OF BASE GLASSES	4
2.2.1 IR of Alkali-Silicate Glasses	4
2.2.2 Alkali-Alumina-Silica Glasses	7
2.2.3 Raman Spectra of $\text{SiO}_2\text{-B}_2\text{O}_3$ Glasses	9
2.3 TRANSITION METAL IONS IN GLASSES AND MELTS	13
2.3.1 Spectra of Iron-Containing Glasses	13
2.3.2 Transition Metals in Glass Solution	14
2.3.3 Reduction of Transition Metals from Melts	17
2.4 DISSOLUTION MECHANISMS OF GLASSES	17
2.4.1 Hydrogen Diffusion in Alkali Silicate Glasses	17
2.4.2 Dissolution Kinetics in Ternary Glasses	18
2.4.3 Infrared Reflectance Spectra of Leached Glasses	19
3.0 Management	20
3.1 COMPLIANCE WITH PROJECT OBJECTIVES	20
3.2 EQUIPMENT PURCHASE AND CONSTRUCTION	20
3.2.1 Spectroscopic Equipment	20
3.2.2 Sputter-Induced Photon Spectroscopy (SIPS)	21
3.3 PERSONNEL	21
3.4 PUBLICATIONS AND PRESENTATIONS	22
3.4.1 Continuing Bibliography	22
3.4.2 Papers Published in 1979-1980	23
3.4.3 Papers in Press from Previous Year	23
3.4.4 Papers Submitted for Publication during 1979-1980	24
3.4.5 Papers Presented at Professional Meetings	24
4.0 Appendices	
4.1 Vibrational Spectra and Glass Structure	
4.2 Raman Spectroscopic Investigation of Sodium Borosilicate Glass Structure	

Table of Contents (Continued)

Page

- 4.3 Transition Metal Ions in Glasses:
Network Modifiers or Quasi-Molecular Complexes?
- 4.4 Sodium-Hydrogen Interdiffusion in
Sodium Silicate Glasses
- 4.5 Glass Leaching Studies by Sputter-Induced
Photon Spectrometry (SIPS)

Abstract

New normal coordinate calculations have been used to relate the vibrational frequencies of silicate glasses to Si-O force constants. These appear to account for the observed frequency shifts with degree of silica polymerization. Raman spectroscopy has been used to elucidate the structure of sodium borosilicate glasses and of sodium aluminosilicate glasses. Structures of compositionally complex glasses can be understood if spectra are measured on many glasses spaced at small compositional intervals. Optical absorption spectra have been used to investigate the structural setting of iron in alkali silicate glasses. Research on the alkali-hydrogen exchange in alkali silicate glasses was completed and additional work on ternary glasses is under way. A series of appendices present completed work on the structural investigations of alkali borosilicate glasses, on the structural setting of transition metal ions in glasses, and on the diffusion of hydrogen in alkali silicate glasses.

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 fifth 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 and alkali aluminosilicate glasses. The use of Raman spectroscopy to characterize phase separation in the high alkali borosilicates is reported in an appendix. Further work remains to be done with the alkali-deficient borosilicates.

The optical absorption spectra of nickel and iron in a variety of glasses have been examined. This, along with the study of manganese-containing glasses completed last year has lead to a new concept of quasi-molecular complexes of transition metal ions in glass in addition to transition metals in the usual network-modifying sites.

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 THEORETICAL APPROACHES

2.1.1 Calculations of IR and Raman Spectra of Disordered Systems

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

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

where $u_i^{(k)}$ is the displacement of the i -th atom in the k direction, $u_j^{(l)}$ is the displacement of the j -th atom in the l direction, m_i is the mass of the i -th atom, and K_{ikjl} 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,

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

The dynamical matrix is defined as,

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

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

$$D(p,q) = D(i,k,j,l)$$

by

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

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

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,

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

The eigen value equations are written in matrix form as,

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

where ω 's are eigen values, $[E]$ 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. If the system has any symmetry, the dynamical matrix can be factorized into smaller matrices by use of group theory.

The intensity of IR absorption is proportional to the change in the dipole moment of the system. If the effective charge of the atoms is assigned, the change of the dipole moment is calculated from the displacement vectors of the atoms. The Raman scattering intensity, on the other hand, is proportional to the change in the polarizability of the system. The change of the polarizability in a rough approximation proportional to the change of bond length from the equilibrium value. By assuming the reasonable proportionalities for different types of bond, the crude Raman intensities for each normal mode can be calculated from the displacement vectors of the atoms.

By the method described above, the frequencies and displacement vectors as well as the crude IR and Raman intensities were calculated for the silicate monomer $(\text{SiO}_4)^{4-}$, dimer $(\text{Si}_2\text{O}_7)^{6-}$, chain $(\text{Si}_2\text{O}_6)_n^{4-}$, and sheet $(\text{Si}_2\text{O}_5)_n^{2-}$ complex anions. The force constants for the Si-O stretching, Si-O-Si bending, and O-Si-O bending were used to construct the dynamical matrix. The eigenvalues and eigenvectors were solved by the subroutine program of the IBM 370 system at The Pennsylvania State University Computation Center. The subroutine can handle a matrix of dimension up to 50 by 50.

Our main objective is to extend the method to disordered systems, such as mixed crystals and glasses. The disordered system can be considered as a spectroscopic unit cell (primitive cell) of infinite size or a molecule of infinite size. It is practically impossible to solve the eigenvalue problem for a matrix of infinite dimension, and therefore some assumptions on the size of the system must be introduced. The assumed size of the model should be large enough to represent general features of disordered system. Bell and Dean calculated the density of state spectra for SiO_2 , GeO_2 , and BeF_2 model glasses with a model containing about 500 atoms. Even for the model of 500 atoms a 1500 by 1500 matrix must be solved. The computational techniques to calculate the eigenvalues and eigenvectors for a matrix of large dimension must be developed.

Although, the calculation of IR and Raman spectra of disordered systems is our long term objective, the method described above can be applied also to many other interesting vibrational spectroscopic problems of silicate crystals such as the influence of other cations (particularly Al^{3+}) by additional forces between the cation and nonbridging oxygens, LO-TO splitting by long-range Coulombic force and the influence of various types of tetrahedron polymerization.

2.2 STRUCTURE OF BASE GLASSES

2.2.1 Infrared Spectra of Alkali-Silicate Glasses

The investigation of the alkali silicate glasses made several years ago left several questions unanswered. First, the composition range extended from the metasilicate only to the trisilicate and this left a substantial compositional gap between the trisilicate and pure silica. Secondly, the interpretation was entirely in terms of the unpolarized Raman spectra. We did not measure the polarized and depolarized spectra separately and we did not correlate the Raman spectra with the infrared spectra.

Glasses in the $\text{Na}_2\text{O} - \text{SiO}_2$ system were prepared to span the composition range between SiO_2 and $\text{Na}_2\text{O} \cdot \text{SiO}_2$, the limit of the glass-forming region. Infrared spectra were measured by specular reflectance techniques from polished discs of glass. Raman spectra were measured (or remeasured) in both parallel and cross polarized orientations. The infrared reflectance spectra were converted to absorption spectra by Kramers-Kronig analysis and this permits an exact comparison between infrared and Raman line shapes.

As was reported last year, it was found that the weak cross-polarized (or depolarized) Raman spectra were identical down to quite small details of line shape, to the infrared absorption spectra, thus confirming that the same vibrational modes were responsible for each. The intense polarized Raman bands, on which most of our structural interpretation have been made, were distinct and independent from the infrared spectrum.

The band frequencies for the infrared active modes change continuously as the glass composition is varied. Figure 1 shows that the separation of the infrared-active asymmetric Si-O stretching frequency into two distinct bands takes place quite abruptly when there are (on the average) 0.5 non-bridging oxygens per silicon. The spectra of the high silica glasses show quite clearly that there is a continuous evolution of the glass structure from the framework units of silica glass to the convoluted sheets of the disilicate glasses.

It is also possible to determine the longitudinal optic-modes from the poles in the frequency dependence of the dielectric constant which can also be determined from the reflectance spectra. These are plotted in Figure 1. Curiously, there is no break in this curve at the 0.5 NBO/silicon composition.

The study as described thus far was largely completed in the spring of 1979 and many of the results were presented at the 1979 Meeting of the

Figure 1. Shifts in the infrared band frequencies of alkali silicate glasses with number of non-bridging oxygens. Closed circles are TO modes; open circles LO modes.

American Ceramic Society. However, the purchase of the new infrared spectrometer by the Mineral Constitution Laboratory made possible the determination of reflectance spectra down to 200 cm^{-1} . Accordingly, the glasses have been remeasured on the new instrument (which necessitated re-making some of the glasses since the high alkali glasses are hygroscopic and are not easy to preserve). This allows the comparison of the strong absorption features in the $450\text{ to }600\text{ cm}^{-1}$ range with the corresponding Raman bands and also to look for a predicted low frequency mode between $200\text{ and }300\text{ cm}^{-1}$ expected to be active in the infrared. The low frequency mode is said to be a motion of the sodium ion in the network-modifying site and its frequency would be a measure of the interaction of the alkali ion with its surroundings. This extension of the study is underway at the present time.

2.2.2 Alkali-Alumina-Silica Glasses

The structural role of aluminum in silicate glasses has proved an evasive and perplexing problem. Introduction of aluminum into alkali silicate glasses can proceed by substitution of aluminum into the network, in which case the ratio of bridging to non-bridging oxygens remains the same providing that charge compensation is provided, or it can proceed by substitution of the aluminum into "network modifying" sites which should be accompanied by the depolymerization of the network and the formation of non-bridging oxygens. It would seem an easy matter to resolve by Raman spectroscopy since the dominant controlling influence on the Raman spectrum is the number of non-bridging oxygens. In practice, the problem has proved exceedingly difficult.

The Raman spectra of a very large number of compositions in the system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ were examined and the first results and interpretations are being prepared for publication. The source of the difficulty is obvious in the spectra (Fig. 2). Most of the structural information is contained

Figure 2. Raman spectra of a sequence of sodium aluminosilicate glasses between sodium disilicate and alumina showing the band broadening as aluminum is added to the glass-forming network.

in the high frequency polarized Raman bands. When aluminum is added to the glasses these bands lose intensity and become broadened. This may arise because of the disorder created when aluminum is introduced into the framework or it may result from the small polarizability of the Al^{3+} ion. The problem is not solved and further work will follow two paths: (i) measuring the infrared spectra of some of this same series of glasses so that the compositional dependence of the intense asymmetric stretching bands can be determined and (ii) the synthesis of gallium-containing glasses so that advantage can be taken of the much higher polarizability of the Ga^{3+} ion.

2.2.3 Raman Spectra of SiO_2 - B_2O_3 Glasses

Structural changes due to different thermal histories have been detected by Raman spectroscopy for B_2O_3 - SiO_2 glasses. The effect is fairly large compared to those observed with Na_2O - SiO_2 glasses and with Na_2O - B_2O_3 - SiO_2 glasses both in the phase separation region.

Raman spectra of B_2O_3 - SiO_2 glasses shows two dominant bands at about 460 cm^{-1} (deformation of the Si-O-Si bond and Si-O-B bond) and at 810 cm^{-1} (symmetric stretching of boroxo ring) in (Fig. 3). The relative intensity of the two bands changes with different heating times and temperatures. In Figure 4, the intensity ratio I_{810}/I_{460} is plotted against heat-treatment time at 300°C .

The ratio increases rapidly for the first two hours and at a much slower rate for longer heating time, approaching some steady state value. Variation of the ratio with respect to the heating temperature is shown in Figure 5 for the three different compositions. The change of the relative intensity increases for the larger B_2O_3 content glass. It occurs within some temperature range, which is also dependent on the composition.

Figure 3. Raman spectrum of $0.5\text{SiO}_2 \cdot 0.5\text{B}_2\text{O}_3$ glass

Figure 4. Variation in the I_{810}/I_{460} intensity ratio as a function of heat treatment at 300°C.

Figure 5. Variation in the I_{810}/I_{460} intensity ratio with heat treatment temperature for several $\text{SiO}_2\text{-B}_2\text{O}_3$ glasses.

The increase of the intensity of the 810 cm^{-1} band relative to the 460 cm^{-1} band by the heat-treatments below a certain temperature range indicates that some rearrangement of the structure has occurred, resulting in the increase of the number of boroxo rings.

At the present moment, the cause of this phenomenon is not clear. This structural change may possibly be related with the metastable phase separation. However, the temperature range where the change of the intensity ratio occurs is somewhat lower than the reported upper phase separation boundary temperature (about 500°C) and the boundary curve is flat over a wide composition range, in contrast to the compositional dependence of the transition temperature range observed here. Another possible explanation is the structural rearrangement associated with the glass transition.

To study further this interesting phenomenon, the experiments covering wider composition range including high temperature Raman spectroscopy and thermal analysis are in progress.

2.3 TRANSITION METALS IN GLASSES AND MELTS

2.3.1 Spectra of Iron-Containing Glasses

A study of the effects of iron in sodium silicate glasses by means of optical absorption, luminescence and Raman spectroscopy is being carried out to investigate the structural setting of iron and the nature of bonding between iron and the surrounding silicate network. Changes in band shapes and intensities and in the crystal field strength parameter Dq will be noted.

Iron, as Fe_2O_3 , was mixed with base glass ingredients Na_2CO_3 and SiO_2 and heated in air between 1350 and 1400°C in a platinum crucible. The melt must be stirred or cooled and crushed several times to ensure homogeneity of the glass. Inhomogeneity produces inconsistent spectroscopic data. Glass samples were made by pouring the melt into a heated graphite plate

(about 350°C) and allowing it to cool. Luminescence due to Fe^{3+} was excited by the 514.5 nm line of an Argon-ion laser at 400 mW, and was measured relative to the Raman Si-O stretching band at 1100 cm^{-1} . Thus luminescence intensities may be compared from sample to sample.

During heating, some of the ferric iron is reduced to ferrous iron, and heating should continue until this reaction has reached equilibrium, allowing reproducibility of experiments, and thermodynamic calculations. Glass of composition $\text{Na}_2\text{O} \cdot 3\text{SiO}_2 \cdot 0.02\text{Fe}_2\text{O}_3$ was chosen to study the attainment of equilibrium with heating time. Sodium trisilicate is not hygroscopic and has manageable viscosity. An iron concentration of $X = 0.02$ produces easily measured absorption, luminescence and Raman peaks. The molar absorptivity of the 1100 nm band, normally ascribed to the spin allowed transition ${}^5\text{T}_2(\text{D}) \rightarrow {}^5\text{E}(\text{D})$ for Fe^{2+} in an octahedral field, was calculated to be on the order of $17\text{ litre mol}^{-1}\text{ cm}^{-1}$. The equilibrium concentration was assumed to be 15% of the total iron, as reported in the literature, and the density of sodium trisilicate glass was estimated to be 2.43g/cc.

Electronic absorptivities due to Fe^{2+} , measured at 1100 nm and normalized for thickness, as well as the luminescence/Raman ratios, are plotted versus the heating times in Figure 6. Reduction of Fe^{3+} to Fe^{2+} is rapid during the first 24 hours, after which steady state conditions have almost been attained.

In this experiment the necessary melting time for the glasses has been established, and samples of varying base glass composition will now be examined.

2.3.2 Transition Metals in Glass Solution

Glasses colored by transition metal ions exhibit characteristic optical absorption spectra which can be interpreted by crystal field theory to yield information about the local environment of the ion. Many such studies have

Figure 6. Changes in absorbivity and luminescence as a function of heating time.

○ Absorbivity (1100 nm band)

○ Ratio of luminescence intensity at 14,500 cm⁻¹ to the Raman band at 1100 cm⁻¹.

been published and one of the more common conclusions is that the transition metal ions exist in the glass in regular octahedral sites. The optical spectra of many ions in many glasses is, in fact, similar to the spectra of the same ions in aqueous solutions where the crystal field is generated by a regular coordination octahedron of water molecules. It is our contention that this is a surprising result. If transition metal ions substitute for alkali or alkaline earth ions in pre-existing sites created by the topology of the network, it is not clear why the spectra should indicate regular octahedra. Geometrical considerations of the sorts of interstitial cavities in three-dimensional frameworks or convoluted sheets would be larger than required by the transition metal ions, and would be of irregular geometry.

Consideration of this problem has lead us to review the available optical spectroscopic literature in some detail and to extend the available measurements. There appear to be at least four ways in which transition metals can be dissolved in glasses

- i. As distinct molecular units carrying excess oxygen as part of the unit. The chromate, CrO_4^{-2} ion identified in silicate and borate glasses by Raman spectroscopy in an earlier study is an example.
- ii. Quasi-Molecular complexes in which a regular octahedron is constructed around the transition metal using the non-bridging oxygens of the glass network. Many transition metals in high alkali glasses seem to have this arrangement. The transition metal modifies the local glass structure to satisfy its own bonding requirements.

- iii. As network-modifying cations. This is the classical picture in which the transition metal occupies a site whose size and geometry is determined by the bonding requirements of the glass network. Transition metal ions seem to occur in these sorts of sites in glasses with fewer non-bridging oxygens.
- iv. By substitution directly into the network. This requires replacement of Si by the transition metal and occurs only when the transition ion is small and highly charged. There is evidence for the substitution of Fe^{3+} and Ti^{4+} into the glass network.

These concepts have been expanded into a short paper which appears as Appendix 4.3.

2.3.3 Reduction of Transition Metals from Melts

The proposed experiments to determine the activity coefficients for transition metals in glass solution are under way. The host glasses chosen lie in the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ and $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ systems. The metals chosen were nickel, iron, and manganese. Glass compositions have been prepared and the times and temperatures necessary to establish an equilibrium reaction with a buffer gas atmosphere has been determined. The presence of metallic phases in the highly reduced glasses has been established by optical microscope. Quantitative determination of the oxygen fugacity at which the metallic phase appears awaits the measurement of the optical absorption spectra on the glasses.

2.4 DISSOLUTION MECHANISMS OF GLASSES

2.4.1 Hydrogen Diffusion in Alkali Silicate Glasses

The study of dissolution in sodium trisilicate glass has been completed (see Appendix 4.4). The diffusion coefficients for the Na^+ and H^+ (or H_3O^+)

ions were determined using the model developed in Landford et al. [1]. Glass samples were hydrated for various times in a constant pH and Na^+ concentration in the solution. Other samples were hydrated at constant time and at temperatures ranging from 25°C to 40°C. These samples were used in the determination of the activation energy for the interdiffusion process.

Composition versus depth profiles of sodium and hydrogen were obtained for all hydrated and several unhydrated samples using sputter-induced photon spectrometry (SIPS). These profiles were then corrected for "edge effects" using a new computer routine [2,3]. The "edge-effect" is due to contributions from signals originating from crater walls caused by the erosion by a spatially non-uniform ion beam. To obtain diffusion coefficients, curves solutions to the diffusion equation were generated by computer and the slope of these curves compared to the experimental data. The values obtained by this method were $D_{\text{H}} = 148 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ and $D_{\text{Na}} = 0.48 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$. The determination of the activation energy led to a value of $44.1 \pm 7 \text{ kcal/mole}^{-1}$.

2.4.2 Dissolution Kinetics in Ternary Glasses

Sodium-calcium-silicate glasses were chosen for the next stage in the dissolution studies since they form the basis for many commercial glasses. Glass compositions were prepared with 70 mole % SiO_2 and mole % Na_2O /mole % CaO ratio of 24:6, 22:8, 20:10, 18:12 and 16:14.

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- [1] W. A. Landford, K. David P. La Marche, T. Laursen, R. Golesu, and R. H. Doremus, *J. Non-Cryst. Solids* **33** (1979) 249.
 - [2] I.S.T. Tsong, G. L. Power, D. W. Hoffman, and C. W. Magee, *Nuc. Instrum. Meth.* (in press).
 - [3] D. W. Hoffman, I.S.T. Tsong, and G. L. Powers, *J. Vac. Sci. Technol.* (in press).

Samples of these glasses were hydrated at 90°C in deionized water for times up to 3 days. It was found that the 24:6 composition crystallized at this temperature and will be done at a lower one. Composition-versus-depth profiles for the other four glasses were obtained on the SIPS unit. Presently, only the data for the 18:12 composition has been analyzed to obtain diffusion coefficients.

The diffusion coefficient found thus far have involved a theoretical fitting to the hydrogen profile using a model with two interdiffusing species. However, surface profiles show that calcium is also leached from these glasses, though to much less of an extent than sodium. Models with three diffusing species have not been developed, but in this case, it is believed that the process can be adequately described by the two-species model.

In order to observe to what extent the calcium leaching is affecting the hydrogen profile, work has now begun to develop a computer program to give theoretical curves to fit the sodium profiles as developed in a paper by Doremus [4]. The diffusion coefficients from the two methods will then be compared.

2.4.3 Infrared Reflectance Spectra of Leached Glasses

The objective of this portion of the work is to obtain information about the structure of cation-depleted surface layers of leached glasses. It has been well established by L. L. Hench and his coworkers that the infrared reflectance spectrum is very sensitive to the degree of hydration of surface layers and our intention was to see if we could extend the analysis by transforming the reflectance spectrum to an absorption spectrum and using the absorption spectrum to determine structure.

[4] R. H. Doremus, J. Non-Cryst. Solids 19 (1975) 137.

Samples of sodium trisilicate glass were prepared, polished and the infrared reflectance spectra measured. Then the glasses were leached in 30°C water and the spectra measured again. Transformations of the reflectance spectra are under way at the present time.

3.0 Management

3.1 COMPLIANCE WITH PROJECT OBJECTIVES

The proposed technical scope given in the 1979 renewal proposal was:

"Continuation is proposed for a study of transition metal ion-containing insulator glasses utilizing Raman, optical absorption, luminescence and sputter-induced optical emission spectroscopy. Thrusts are (i) structure and phase separation of alkali-alumina and borosilicate glasses; (ii) local environment and thermodynamics of Fe, Mn, Ni, and Ti, and (iii) dissolution and diffusion processes in glasses."

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

There have been few changes in the spectroscopy facility during the past year. The Spex Ramalog Raman spectrometer continues to be heavily used, much of the usage by this project. Instrument breakdown is becoming more common and downtime for several pieces of equipment have become significant factors. There is an ongoing search for capital equipment funds to bring the facility up to date. Unfortunately, all spectrometers are nearing obsolescence and complete replacement will be a large undertaking.

On the brighter side, the Mineral Constitution Laboratory of the College of Earth and Mineral Sciences this past year purchased a new Perkin-Elmer model 283 infrared spectrometer. This is the latest automated instrument of its kind. They have also purchased a specular reflectance attachment for this instrument so that we have a completely new capability for infrared analysis of glasses.

3.2.2 Sputter-Induced Photon Spectroscopy (SIPS)

The SIPS facility under the guidance of Professor Tsong continues to expand and improve. The present instrument was improved during the year with the addition of a new pumping system partly supported by this project.

The new SIPS apparatus, ordered nearly a year ago with NSF and University matching funds, is expected momentarily. When it arrives and is installed we will have doubled our sample handling capacity. The usage of the SIPS technique has grown greatly during the past year or two and the existing equipment is near saturation usage. The greatly improved facility will be of great value to this project which is a heavy user of the equipment.

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 continues to be Dr. Toshiharu Furukawa, Project Associate. Dr. Furukawa devotes 100% of his time to the project and is responsible for most of the Raman spectroscopic work.

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 assistantships and their research on the thermodynamics of melts and on dissolution mechanisms respectively will be the subject 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 been working 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. Braver and W.B. White. Raman spectroscopic study of hexavalent chromium in some silicate and borate glasses. *Mat. Res. Bull.* 12, 281-287 (1977).
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- C. Nelson and W.B. White. Transition metal ions in silicate melts.
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- I.S.T. Tsong, C.A. Houser, W.B. White, G.L. Power and S.S.C. Tong. Glass leaching studies by sputter-induced photon spectrometry (SIPS). Inter. Glass Congress (submitted).

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