COO-2754-3

STRUCTURE OF GLASSES CONTAINING TRANSITION METAL IONS

Progress Report

for Period Feb. 1, 1977-Jan. 31, 1978

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February, 1978

Prepared for

THE U.S. DEPARTMENT OF ENERGY

Under Contract No. EY-76-S-02-2754.000

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Contents

Abstract

1.0 INTRODUCTION -----	1
2.0 RESULTS -----	2
2.1 Theoretical Advances -----	2
2.1.1 Optical Absorption with Vibrational Coupling -----	2
2.2 Structure of Base Glasses -----	2
2.2.1 Lead-Silicate Glasses -----	2
2.2.2 Structure of Borate Glasses -----	3
2.2.3 Alkali Germanate Glasses -----	4
2.2.4 IR of Alkali Silicate Glasses -----	9
2.3 Transition Metal Ions in Glasses -----	11
2.3.1 Iron-Containing Glasses -----	11
2.3.2 Titanium-Containing Glasses -----	11
2.3.3 Manganese-Containing Glasses -----	16
2.4 Transition Metal Ions in Silicate Melts -----	16
2.4.1 Reduction of Transition Metals from Melts -----	16
2.5 Hydrogen Exchange in Glass -----	17
2.5.1 Leaching of Natural Glasses -----	17
2.5.2 Hydrogen Exchange in Alkali Silicate Glasses -----	23
3.0 MANAGEMENT -----	24
3.1 Compliance with Project Objectives -----	24
3.2 Equipment Purchase and Construction -----	24
3.2.1 Luminescence Lifetime Measurements -----	24
3.3 Personnel -----	26
3.4 Publications and Presentations -----	26
3.4.1 Continuing Bibliography -----	26
3.4.2 Publications Submitted During Current Year -----	28
3.4.3 Papers Presented at Professional Meetings -----	28
4.0 APPENDICES	
4.1 Dynamical Effects on Nearly Degenerate Levels in Solids	
4.2 Structure of Borate Glasses by Raman Spectroscopy	
4.3 Structure and Crystallization Behavior of $\text{Li}_2\text{O}-\text{Fe}_2\text{O}_3-\text{SiO}_2$ Glasses	
4.4 Raman and IR Spectroscopic Studies of the Crystalline Phases in the System $\text{Pb}_2\text{SiO}_4-\text{PbSiO}_3$	
4.5 Structure and Crystallization of Glasses in the $\text{Li}_2\text{Si}_2\text{O}_5-\text{TiO}_2$ System Determined by Raman Spectroscopy	
4.6 Obsidian Hydration Profiles Measured by Sputter-Induced Optical Emission	

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Abstract

The structures of insulator silicate, borate, and germanate glasses are inferred from Raman and infrared spectra. Optical absorption, luminescence, and Raman spectroscopy are used to determine the structural behavior of titanium, iron, and manganese in these glasses. A new method is demonstrated for determining the rate of hydrogen/alkali exchange in glasses leached in aqueous media. Six appendices present completed research on a model for electronic-vibrational coupling in glasses, on the structure of borate glasses, on the structure of lead silicate glass crystallization products, on titanium in lithium disilicate glass, on iron in lithium disilicate glass, and on the leaching of natural obsidian glasses.

1.0 Introduction

This research concerns the structure and properties of insulator glasses that contain transition metal ions. Investigation of host glass structures in silicate, germanate, borate and other glasses is made with infrared and Raman spectroscopy. The environments of the dissolved transition metal ions are probed with optical absorption, luminescence, and Raman spectroscopy. The glass composition and the oxygen fugacity of co-existing vapor phase (which in turn controls the valence state of the transition metal ions) are also used as variables. These physical properties of the glasses are then used in conjunction with thermodynamic models to determine the structural state of the transition metal ions in the glasses and to obtain some insight into the processes of nucleation, crystallization, and phase separation of these glasses.

The stabilities of transition ion-containing insulator glasses, especially with respect to attack by aqueous solutions, are probed by ion beam analytical techniques. Hydrogen/alkali diffusion profiles can be obtained and these in turn used as input for diffusion calculations.

This progress report spans a one year period and describes the status of the work up through about two-thirds of the way through the third contract year. The theoretical analysis of the electronic and vibrational properties of glasses are now largely complete. Experimental studies of titanium, iron, and manganese in glass are reported. The first results on the alkali exchange and glass hydration work, initiated only this year, are also given.

2. Results

2.1 THEORETICAL ADVANCES

2.1.1 Optical Absorption with Vibrational Coupling

Vibronic coupling which is responsible for the large, nearly temperature independent, bandwidths of many d-d type electronic transitions is usually treated by perturbation calculations of the mixing of the electronic states with discrete vibrational levels. While such a procedure is appropriate to molecular complexes, it is less so in systems such as crystals and glasses where the vibrational modes are themselves delocalized. We have considered the optical absorption of a model system consisting of a two-electronic-level ion interacting with a continuum of vibrational states. The two-level system represents localized electronic energy levels such as are found in the transition elements. The separation of the electronic energies was taken to lie within the phonon band and the interaction with the lattice vibrations was assumed to be linear. For a single band of phonons the absorption is shown to consist of three peaks - a homogeneously broadened central peak flanked by two sharp lines. The existence of three absorption peaks is in contrast to the predictions of either a static crystal field or the two-level system interacting with a single harmonic oscillator. These results reduce to the latter case when the phonon band width becomes very narrow and to the former when the phonon band width becomes very large. The complete calculation is given in Appendix 4.1.

2.2 STRUCTURE OF BASE GLASSES

2.2.1 Lead-Silicate Glasses

The first part of our investigation of the structure of lead silicate glasses dealt with Raman spectra of the glasses, was described in last year's

report, and has been published (see list of publications at end of this report). The second portion of the work was an investigation of the crystalline phases that occur in the complex PbO-SiO_2 system.

Crystalline stable and metastable phases were synthesized in the composition range between Pb_2SiO_4 and PbSiO_3 both from recrystallization of glasses by slow heat treatment and by hydrothermal recrystallization. Two polymorphs of Pb_2SiO_4 have temperature ranges of thermodynamic stability; the remaining $\text{L-Pb}_2\text{SiO}_4$ is metastable. As expected from the glass crystallization experiments, Pb_2SiO_4 is a complex structure. The high temperature form consists of silicate rings with the excess oxygen appearing as the oxygen ion coordinating Pb^{2+} . There is some evidence for a chain structure in the intermediate temperature form and for a pyrosilicate structure in the low temperature form. The intermediate phases $5\text{PbO} \cdot 3\text{SiO}_2$ and $3\text{PbO} \cdot 2\text{SiO}_2$ are shown to be metastable and structurally similar. Both polymorphs of PbSiO_3 are chain structures but only the high temperature alamosite form is stable.

The second part of the lead silicate study has been prepared for publication and appears in Appendix 4.4.

2.2.2 Structure of Borate Glasses

A small investigation was made of the Raman spectra of alkali-borate glasses which, when supplemented with some previous unpublished spectroscopic work on these glasses, resulted in the paper given in Appendix 4.2. The borate glasses are interesting because they provide examples of structurally complex glasses of relatively simple chemical composition.

There is the possibility of at least four hierarchies of structural organization in the borate glasses: (i) the triangles and tetrahedra that act as the basic structural units; (ii) possible closed ring molecular-like structures such as the boroxal ring; (iii) organizations on a larger scale that might be described as clusters, thermal fluctuations in composition, or

incipient nuclei for phase separation, and (iv) distinct phase-separated regions. Experiments on quenched and heat-treated lithium borate glasses suggest that these glasses are already clustered, although not necessarily phase separated, in the liquid state. The clusters are of sufficient size to behave as distinct entities with respect to Raman scattering, perhaps on the order of 2 to 10 nm. The Raman spectra of alkali borate glasses at low alkali concentrations consist of one or two intense and narrow bands at 808 and 776 cm^{-1} but the other regions of the spectrum exhibit only broad and very weak scattering. As the alkali concentration increases the sharp bands broaden and the broad bands sharpen so that at alkali concentrations in excess of 40 mole percent, the Raman spectra of alkali borate glasses are similar in their general form to Raman spectra of silicate glasses. These results were interpreted as evidence for a clustered structure with highly ordered ring structures connected in a highly disordered fashion at low alkali concentrations and of a loss of clustering and the formation of a more homogeneous glass at high alkali concentrations. The complete results appear in Appendix 4.2.

2.2.3 Alkali Germanate Glasses

In certain aspects, the structures of the alkali germanate glasses should be analogous to the alkali silicate glasses studied previously. However, there is one essential difference. Germanium can take on both four and six coordination, whereas silicon appears only in four coordination except at extreme pressures. An investigation of the Raman spectra of the alkali germanate glasses was launched with the idea of providing additional tests for the correlation between Raman spectra and glass structure.

Alkali metal (K_2O , Na_2O , and Li_2O) germanate glasses and fused GeO_2 glass were prepared and their Raman spectra were measured in both parallel (xx) and crossed (xy) polarization. The glasses were crystallized at various subsolidus

temperatures, and the crystalline phases were characterized by x-ray powder diffraction and Raman spectroscopy.

The parallel (xx) polarized spectra of $K_2O \cdot xGeO_2$ and GeO_2 glasses are shown in Fig. 1. The spectra of $Na_2O \cdot xGeO_2$ glasses were very similar to the $K_2O \cdot xGeO_2$ glass spectra.

One of the most significant features of the glass spectra is the very weak high-frequency bands ($\nu > 700 \text{ cm}^{-1}$) compared with the middle-frequency bands ($700 \text{ cm}^{-1} > \nu > 400 \text{ cm}^{-1}$) when x is greater than 4.5. This is probably due to the small number of nonbridging oxygens in this composition range. The coordination number of increasing amount of Ge^{4+} ions possible changes from 4 to 6 with increasing K_2O content. The Raman spectra of the crystalline $K_2O \cdot 4.5GeO_2$ and $K_2O \cdot 4GeO_2$ (Fig. 2) exhibit very weak bands in the high-frequency range. These crystals consist of both 4 and 6 coordinated Ge^{4+} ions and no nonbridging oxygens.

Similar phenomena are observed for alkali metal borate glasses, where the coordination number of B^{3+} ions changes from 3 to 4 by addition of alkali metal oxide without forming nonbridging oxygens, and the high-frequency Raman bands of these glasses are very weak.

At x about 4.5, the high-frequency band at about 870 cm^{-1} appears and its intensity increases with the increasing K_2O content. This band is probably due to stretching mode of Si - one nonbridging oxygen. The increase of the band intensity suggests formation of more nonbridging oxygens by addition of K_2O . Only one nonbridging oxygen per one $[GeO_4]$ tetrahedron is formed at a time, and the digermanate glass ($x=2$) probably consists mainly of the $[GeO_4]$ tetrahedra which have one nonbridging oxygen and three bridging oxygens similar to crystalline digermanate. Crystalline $K_2Ge_2O_5$ is a stable phase and its Raman spectrum (Fig. 3) has characteristic strong bands at 860 cm^{-1}

Fig. 1. Raman spectra of potassium-germanate glasses.

Fig. 2. Raman spectra of recrystallized potassium germanate glasses. Composition and crystallization temperature shown on the spectra.

Fig. 3. Raman spectrum of potassium digermanate glass crystallized at 700°C.

and 530 cm^{-1} . Crystalline $\text{Na}_2\text{Ge}_2\text{O}_5$ phase, on the other hand, has not been reported in previous literature but in the present study $\text{Na}_2\text{Ge}_2\text{O}_5$ crystallized from the glasses of $x=2$ and 3 at low temperatures (Table 1). The crystalline $\text{Na}_2\text{Ge}_2\text{O}_5$ exhibits strong Raman bands at 850 cm^{-1} and 480 cm^{-1} .

Further addition of K_2O produces more nonbridging oxygens, and the number of the $[\text{GeO}_4]$ tetrahedra of two nonbridging oxygens increases. The band at about $750 - 800\text{ cm}^{-1}$, whose intensity increases with increase of the K_2O content, may be attributed to stretching mode of the Si-two nonbridging oxygens. Thus, metagermanate glass, $\text{K}_2\text{O} \cdot \text{GeO}_2$, consists of the tetrahedra of two nonbridging oxygens. Crystalline K_2GeO_3 exhibits a strong Raman band at 790 cm^{-1} . Therefore, between the meta and digermanate composition, the structures of the alkali metal germanate glasses are very similar to alkali metal silicate glasses.

2.2.4 IR of Alkali Silicate Glasses

The characteristic features of the Raman spectra of the alkali silicate glasses are that the strong high-frequency band shifts continuously to higher frequencies as the alkali content decreases, reaching a maximum at pure silica glass. At the same time the intensity of the band decreases. The trend is apparent at the trisilicate composition but the series has not been continued further because of the difficulty in pouring the glasses.

Work has been started toward filling in the gap between $\text{Alk}_2\text{O} \cdot 3\text{SiO}_2$ and SiO_2 glass compositions by using our Czochralski crystal growing furnace to prepare melts and then pulling the glass rods using the pulling attachment.

The infrared spectra of these glasses have been measured by others using alkali halide pellets of crushed glass, but this method does not give accurate intensities or line shapes. To get around this problem, we have been measuring the specular reflectance spectra of polished slabs of glass. Then by using a

Table 1. Crystallization of Alkali Metal Germanate Glass

	$K_2O \cdot 19GeO_2$	$K_2O \cdot 7GeO_2$	$K_2O \cdot 4.5GeO_2$	$K_2O \cdot 4GeO_2$	$K_2O \cdot 3GeO_2$	$K_2O \cdot 2GeO_2$	$K_2O \cdot 1.5GeO_2$
810°C	Quartz Rutile(s) 1:7 (s)	1:7 1:4(t)	1:4 1:7(t)	1:4	--	--	--
700°C	--	--	--	--	1:4 1:2	1:2	1:2 1:1
600°C	Quartz Crist(s) 1:7 (s)	1:7	2:9 1:4(s)	1:4	--	--	--
	$Na_2O \cdot 19GeO_2$	$Na_2O \cdot 7GeO_2$	$Na_2O \cdot 4.5GeO_2$	$Na_2O \cdot 4GeO_2$	$Na_2O \cdot 3GeO_2$	$Na_2O \cdot 2GeO_2$	
890°C	--	--	2:9	--	--	--	
730°C	--	--	--	2:9 1:1(t)	2:9 1:1(t)	1:1 2:9	
600°C	Quartz 2:9(s) 1:4(t)	Quartz 2:9 1:4(t)	--	1:4 2:9	2:9 1:4 1:1(t)	1:4 1:1	
490°C	Glass	Glass	Glass	2:9 Glass	2:9 1:4(t) 1:2	1:1 1:2 2:9	

t=trace

s=small amount

Kramers-Kronig transformation, it is possible to construct the dielectric loss function, $2nk$. Figure 4 shows the results for sodium disilicate glass and silica glass. It is seen that a doublet structure similar to that seen in the Raman spectrum occurs for the disilicate, whereas there is only a single band at higher frequencies in the silica glass. The line widths are much narrower in these spectra than were observed in the powder spectra, as expected. The infrared intensity, however, increases as the number of nonbridging oxygens decreases, a behavior exactly opposite to that observed in the Raman spectra.

2.3 TRANSITION METAL IONS IN GLASSES

2.3.1 Iron-Containing Glasses

The study of iron-containing glasses has been completed and the results appear in Appendix 4.3. In the as-quenched glasses the presence of iron leads to a strong Raman band at 950 cm^{-1} and to a broad Raman scattering continuum below 500 cm^{-1} . There is also an emission due to trivalent iron at about $14,000\text{ cm}^{-1}$. Lithium metasilicate has been identified in all crystallized glasses with more than 1% Fe_2O_3 . It was possible to crystallize some of the glasses by irradiating them with intense blue laser light, and Raman spectra of various stages of photocrystallization have been obtained. By comparing the Raman spectra of the crystallized glasses with those of the as-quenched glasses it is deduced that the trivalent iron has its own distinct local environment.

2.3.2 Titanium-Containing Glasses

The first part of this study utilized lithium disilicate glass as a host and the titanium concentration was varied. The completed study appears in Appendix 4.5 and is not repeated here. The second part of the study, now underway, concerns the influence of titanium on the Raman spectra of sodium silicate glasses.

Fig. 4. Upper Curve: Specular reflectance spectrum of polished glass surfaces. Lower curve: Dielectric loss function obtained by Kramers-Kronig transformation of the data in the upper curve.

In the Raman spectroscopic study of $\text{Li}_2\text{O} \cdot 2\text{SiO}_2 \cdot x\text{TiO}_2$ glass, a characteristic band was observed at 880 cm^{-1} in the parallel polarized spectra, and the band was attributed to the stretching mode of Ti-O of 4-fold coordinated Ti^{4+} ions. In the second part of the study, the TiO_2 content was fixed and the base glass composition, sodium silicate, was varied from the metasilicate to the trisilicate composition.

Figure 5 shows the parallel polarized (xx) spectra of $\text{Na}_2\text{O} \cdot x\text{SiO}_2 \cdot 0.1\text{TiO}_2$ and $\text{Na}_2\text{O} \cdot x\text{SiO}_2$ glasses. Addition of TiO_2 gives a characteristic band whose frequency changes systematically from 855 cm^{-1} to 905 cm^{-1} as the SiO_2 content of the base glass increases from the metasilicate to the trisilicate composition. The bands due to Si-O and Si-O-Si vibrations, particularly the high-frequency bands, do not alter much by addition of TiO_2 . The intensity of the band at $950 - 975 \text{ cm}^{-1}$, which is due to Si-two nonbridging oxygens stretching, also does not change by addition of TiO_2 relative to the band at about 1100 cm^{-1} of Si-one nonbridging oxygen stretching. It suggests that at any base glass composition most of Ti^{4+} ions do not act as modifiers which increase the number of nonbridging oxygens.

In Fig. 6 the frequencies of the high-frequency bands are plotted against the base glass composition. The frequency of the Si-one nonbridging oxygen stretching band increases rapidly with x between $x=1.2$ and 2.0 , while the frequency of the Si-two nonbridging oxygens stretching band decreases rapidly between $x=1$ and 1.6 . The frequencies of the high-frequency bands of the base glass with no TiO_2 change in the same manner. The frequency of the characteristic band due to Ti-O stretching changes in a similar manner to the Si-one nonbridging oxygen stretching band.

Thus, at any base glass composition, addition of 10 mole% TiO_2 does not change the arrangements of $[\text{SiO}_4]$ tetrahedra drastically, and most of Ti^{4+} ions are in 4-fold coordination sites, presumably as network formers, whose environment changes slightly with the base glass composition.

Fig. 5. Raman spectra of titanium-containing sodium silicate glasses.

Fig. 6. Frequency variation of principal Raman bands with alkali concentration in the glasses $\text{Na}_2\text{O} \cdot \text{xSiO}_2$.

2.3.3 Manganese-Containing Glasses

The optical absorption spectrum of Mn^{2+} in glass consists of broad bands at 16,000 and 19,000 cm^{-1} . The relative intensities of these bands depend on glass composition and have led to discussions as to whether Mn^{2+} is present on more than one site. Mn^{3+} is labeled with an intense band at 21,000 cm^{-1} whose intensity and resolvable fine structure depend on the host glass composition. The luminescence emission of Mn^{2+} likewise depends on host glass composition. It appears that in spite of a fairly extensive literature, that the structure role of manganese, particularly with respect to the relations between host glass composition, valence state, and local environment of the manganese ions, is not adequately understood.

New work, just underway as this report is written, will focus on the optical absorption, luminescence emission, and other optical properties of manganese in all its valence states in alkali-alumina-silica glasses. Some glasses have been synthesized but the spectral measurements have just been started.

2.4 TRANSITION METAL IONS IN SILICATE MELTS

2.4.1 Reduction of Transition Metals from Melts

The activity coefficient of a transition element in glass reflects the extent to which the glass behaves as an ideal solvent. If there is complexing, or if the transition metal tends to concentrate in clustered regions of composition different from that of the bulk glass, the glass will be seen as a non-ideal solvent and the activity coefficient will deviate from unity. If the activity coefficients can be determined for various transition metal ions, they can be used as a probe of the glass structure or at least of the transition metals' interaction with the host glass. Three transition metals have been selected: Ni^{++} which has a strong crystal field stabilization energy, Fe^{++} with an intermediate stabilizing effect, and Mn^{++} for which there is no contribution to the free energy from the d-electrons. The glass compositions

have been selected from two facing quaternary systems, $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{CaO}-\text{SiO}_2$ and $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{MgO}-\text{SiO}_2$ (Fig. 7). Initial compositions have been selected from the more restricted set on the bounding ternary system within the quadrilateral trisilicate-metasilicate-jadeite-albite.

The activity of the transition metal in the melt can be determined by varying the oxygen fugacity of the furnace atmosphere in which the melt is held. There will be some minimum fugacity below which the transition metal will separate from the glass as a metallic phase. Since the concentration of the transition metal in the melt can be followed by the optical absorption spectrum of the quenched glass, the onset of phase separation can be determined with some precision. The phase-boundary relationship between the activity of the transition metal (expressed as the monoxide) and the fugacities is given by

$$a_{\text{mo}}(\text{glass}) = \left[\frac{f_{\text{O}_2}(\text{glass})}{f_{\text{O}_2}(\text{oxide})} \right]^{1/2}$$

The concentration of transition metal in the melt is controlled by the initial compositions so that the activity coefficient can then be calculated

$$\gamma = \frac{a(\text{glass})}{m(\text{glass})}$$

The fugacity at which the pure transition metal oxide begins to break down into metal plus oxygen was calculated for a range of temperatures from the free energies of formation of the oxides (Fig. 8).

2.5 HYDROGEN EXCHANGE IN GLASS

2.5.1 Leaching in Natural Glasses

The stability of glasses in the presence of an aqueous environment is usually measured by some kind of leaching experiment in which the alkali metals

Fig. 7. Composition ranges for glasses to be used in melt reduction experiments

Fig. 8. Univariant equilibrium curves for the reduction of transition metal monoxides to the metal.

in the glass are replaced by hydrogen. There is formed in this process an alkali-depleted layer in the outer surface layers that acts as a diffusion barrier to further atomic migration. We started this year a new aspect of the project, namely to investigate the nature of the ion exchange process with a depth-profiling ion beam technique. Because it was necessary to have some control on the sorts of hydration layers and their thickness, it proved expedient to begin the experiments on specimens of the natural glass, obsidian. Obsidians are relatively low in silica (45-55% weight percent) and are high in alumina, magnesium, and iron. Their general composition is not far from many of the glasses used in other parts of this study. The advantage is that obsidians have weathered for known periods of time and specimens were available from the Department of Anthropology at The Pennsylvania State University that had already been dated and the thickness of the hydrated layer measured.

The leaching process of natural glasses is studied by measuring the surface compositional profiles of H, Na, K, Li, Ca, Mg, Si and Al in obsidian using the technique of Ion Beam Spectrochemical Analysis (IBSCA), otherwise also known as sputter-induced optical emission.

When an ion beam is incident on the surface of a target surface, neutral and charged atomic species of the target material are ejected as a result of the sputtering process. In the IBSCA technique we detect the optical radiation emitted as a result of the de-excitation of the neutral target atoms leaving the surface in excited states. This radiation consists of spectral lines characteristic of the constituent elements in the solid. Since most elements have their prominent lines in the UV and visible region, a grating monochrometer or spectrometer can be used to detect and identify these spectral lines. Tsong (1) and White and Tolk (2) were first to suggest the use of this sputter-induced

1. I.S.T. Tsong (1971) Photon emission from sputtered particles during ion bombardment, *Phys. Stat. Sol.(a)* 7, 451-458.
2. C.W. White and N.H. Tolk (1971) Optical radiation from low-energy ion-surface collisions, *Phys. Rev. Lett.* 26, 486-489.

optical emission for the analysis of solid surfaces.

To measure the concentration-versus-depth profile of a particular element in a solid, we can simply monitor the intensity of the appropriate spectral line as a function of time. Characterization of solid surfaces using the IBSCA method has been recently reviewed by Tolk, Tsong and White (3).

A schematic diagram of the IBSCA apparatus is shown in Fig. 9. It consists of a duoplasmatron ion source capable of delivering an intense, stable, and monoenergetic ion beam. Argon gas is chiefly used to provide the bombarding ions although other gases can also be used. The beam is extracted and focused by a gridded decelerating gap lens. A beam spot of 0.5 mm diameter at the target is generally used, although a smaller spot size can be achieved by inserting apertures. The ion current density is very high, typically around $20 \mu\text{A mm}^{-2}$, and it will sputter glass surfaces at a rate of over $10 \mu\text{m}$ per hour. The target holder can accommodate six samples at one time. The system is pumped to less than 10^{-7} torr and the partial pressure of argon is $\sim 1 \times 10^{-6}$ torr when the beam is in operation.

The IBSCA system shown in Fig. 9 is manufactured by General Ionex Corporation and is originally equipped with Echelle grating spectrometer. The advantage of using an Echelle spectrometer is the two-dimensional display of spectral information allowing rapid multi-element analysis to be performed either by computer-controlled image tubes or by an array of conventional photomultipliers. However, because of the need of scanning the emitted spectra in some cases and because of the greater ease in singling out particular spectral lines of interest. The Echelle spectrometer has been substituted by a Jarrell-Ash monochromator. A cooled photomultiplier and a single-photon counting system are used for the measurement of light intensities.

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3. N.H. Tolk, I.S.T. Tsong and C.W. White (1977) In situ spectrochemical analysis of solid surfaces by ion beam sputtering, *Anal. Chem.* **49**, 16A-30A.

Fig. 9. Schematic diagram of IBSCA apparatus.

ION LUMINESCENCE SURFACE ANALYZER

The ion beam is usually operated at energies between 15 and 25 KeV. Surface charge build-up on insulating targets is alleviated by flooding the target surface with electrons from a heated LaB₆ filament positioned near the target holder. A small degree of charging on an insulating surface (say to a few hundred volts) does not appear to affect the sputtering rate, nor does it affect the collection of optical emission, since the light originates from neutral excited atoms.

Apart from de-excitation by emitting radiation, an excited atom leaving the surface of a metallic target can de-excite by non-radiative processes such as resonance and Auger electronic transitions between the atom and the metal. Many workers have studied these processes in some detail (1,4,5). In insulating materials, however, these non-radiative electron-transfer processes are thought to be absent because of the large forbidden energy band gaps in the solid. As a result, the photon emission process is more efficient for insulating targets than metallic targets. IBSCA is therefore an extremely sensitive tool for studying surface composition of insulating materials. Light elements such as Li and Na have detection limits better than 1 part in 10⁸. Any element in the periodic table from H to U can be detected.

A report on the measurement of obsidian hydration profiles by the IBSCA technique has been submitted for publication (Appendix 4.6).

2.5.2 Hydrogen Exchange in Alkali Silicate Glasses

Having established that the IBSCA technique would produce good diffusion profiles for hydrated natural glasses, the next step was to begin work on synthetic glasses of bulk compositions similar to those used in the structural measurements. A series of sodium silicate glasses was prepared by melting

4. W.F. van der Weg and P.K. Rol (1965) On the excited state of sputtered particles, Nucl. Instrum. Meth. 38, 274-276 (1965).
5. N.H. Tolk, D.L. Simms, E.B. Foley and C.W. White (1973) Photon emission from low-energy ion and neutral bombardment of solids, Rad. Effects 18, 221-229.

the glass at 1400°C and then pouring into a graphite mold. The preparation of sodium trisilicate was difficult by this technique because of the high viscosity at the pouring temperature. However, blocks of sodium trisilicate glass, cut, polished, and then hydrated in distilled water at room temperature for five hours produced good diffusion profiles (Fig. 10).

The more alkali-rich glasses, $x < 2$ in $\text{Na}_2\text{O} \cdot x\text{SiO}_2$, hydrate too rapidly. It was found that these compositions tended to form a powdery layer on the surface when placed in the vacuum of the IBSCA apparatus and usually did not yield good profiles. However, it is the more resistant, rather than the water-glass composition glasses that are of interest so that this finding does not seem to be an important limitation to the method.

3. Management

3.1 COMPLIANCE WITH PROJECT OBJECTIVES

The proposed technical scope given in the 1977 renewal proposal was "Continuation is proposed for a study of transition metal ion-containing insulator glasses utilizing Raman, optical absorption, and luminescence spectroscopy. Emphases are (i) host glass structure; (ii) local environment and structural influence of Cr, Fe, Mn, Ni, Ti, and Cu. New work is proposed on determination of glass leaching by ion beam luminescence 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 Luminescence Lifetime Measurements

As described in some detail in last year's report, it has become necessary to have the capability for determining lifetimes of luminescent states

Fig. 10. Concentration profiles of hydrogen and sodium in a hydrated sodium trisilicate glass. The depth profiling is done by ion beam sputtering so that the time axis is effectively a depth axis. However, calibrations that would give the actual depth have not yet been made.

and of determining time-delayed spectra to separate energy levels with different decay rates. A conceptual design utilizing available chip circuitry was arrived at last year. The design concept was transformed into specific hardware by Locus Incorporated, a small electronics firm in State College, Pa. After review of the design, Locus was given the job of constructing the device. The final design, in block diagram form, is given in Fig. 11.

Delivery of the device occurred in January, 1978. The equipment has been tested, some small problems remedied, and is now in service. It appears to perform as designed and is an important advance in the luminescence measurement facility.

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 Senior Project Associate, Dr. Steven Brawer, left Penn State in July to join the Lawrence Livermore Laboratory. Dr. Brawer's place has been taken by Dr. Toshiharu Furukawa, who completed his Ph.D. in fall, 1977, under the sponsorship of this project.

The IBSCA work is carried out under the direct supervision of Dr. I.S.T. Tsong, Research Associate. Dr. Tsong devotes 10% of his time over the 12 month year to this project.

The graduate students on the project are Miss Carolynn Nelson and Miss Cheryl Houser. Also working on the project as a part-time technical assistant is Mrs. Carol Goett.

3.4 PUBLICATIONS AND PRESENTATIONS

3.4.1 Continuing Bibliography

The papers listed in last year's report as being submitted to journals have now mostly appeared in print. These are listed below.

Fig. 11. Block diagram of device for luminescence decay time measurements.

256 Channel Pulse Counter Block Diagram

- 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).
- S.A. Braver. Memory effects in the relaxation of glasses: An exactly soluble model. *Phys. Chem. Glasses* (accepted).
- S.A. Braver 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).
- T. Furukawa, S.A. Braver and W.B. White. Raman spectra and structure of nitrate glasses. *J. Chem. Phys.* (accepted).
- T. Furukawa, S.A. Braver and W.B. White. The structure of lead silicate glasses determined by vibrational spectroscopy. *J. Materials Sci.* 13, 268-282.

3.4.2 Publications Submitted During the Current Year

The portions of research that have been completed and submitted to journals during the period covered by this report are listed below. These are the same items that appear in full in the appendices to this report.

- S.A. Braver. Dynamical effects on nearly degenerate electronic levels in solids. *J. Chem. Phys.* (accepted).
- W.B. White, S.A. Braver, T. Furukawa and G.J. McCarthy. Structure of borate glasses by Raman spectroscopy. *Proc. Internatl. Conf. on Boron in Glass and Glass Ceramics* (Alfred University), Plenum Press (accepted).
- S.A. Braver 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. Materials Sci.* (accepted).
- T. Furukawa, S.A. Braver and W.B. White. Raman and IR spectroscopic studies of the crystalline phases in the system $\text{Pb}_2\text{SiO}_4-\text{PbSiO}_3$. *J. Amer. Ceram. Soc.* (submitted).
- T. Furukawa and W.B. White. Structure and crystallization of glasses in the $\text{Li}_2\text{SiO}_5-\text{TiO}_2$ system determined by Raman spectroscopy. *Phys. Chem. Glasses* (submitted).
- 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* (submitted).

3.4.3 Papers Presented at Professional Meetings

- S.A. Braver and W.B. White: Luminescence of trivalent chromium in some oxide glasses. *Electrochem. Soc.*, Philadelphia, Pa.
- S.A. Braver and W.B. White: Dynamic effects of localized nearly degenerate electronic states in a solid. *Electrochem. Soc.*, Philadelphia, Pa.

W.B. White and S.A. Brawer: Structure of borate glasses by Raman spectroscopy. Alfred Conference on Boron in Glass and Glass Ceramics, Alfred University, June, 1977.