STRUCTURE OF GLASSES CONTAINING TRANSITION METAL IONS

Progress Report

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1. Introduction

This research concerns the structure and properties of insulator glasses that contain transition metal ions. Investigation of host glass structures in silicate, borate, and other glasses is made with tools such as infrared and Raman spectroscopy. The environment of the dissolved transition metal ions is probed with optical absorption, Raman, and luminescence spectroscopy. Glass composition and valence states of transition metals are also used as variables. These physical properties of the glasses are used to characterize the thermodynamic behavior of the glasses with respect to nucleation, crystallization, phase separation and stability of the glasses.

The progress report spans about a one year period and describes work carried out up to about two thirds of the way through the second contract year. Completed studies on the structure of nitrate and lead silicate glasses, on a theoretical model for relaxation in glass, and on the behavior of chromium in glasses are included in preprint form in a series of appendices. Preliminary results are given on titanium and iron-containing glasses and on the luminescence of "ultrapure" glasses.

2. Results

2.1 THEORETICAL ADVANCES

2.1.1 Crystal Field Calculations

We have written a computer program to compute the crystal field levels of any transition metal ion in any type of environment. No symmetry is assumed. Spin-orbit coupling has also been included. Thus we can calculate by crystal field theory the electronic energy levels of any transition metal ion in any type of site. It is essential to have the flexibility of including any type of environment when trying to interpret the spectra of transition metal ions

in glass since glasses are disordered solids. Even if the immediate ligands are symmetrically placed, the next-nearest neighbors of the transition metal ion are expected to be randomly distributed to some extent.

The information from this calculation is necessary for interpreting the luminescence and absorption spectra of transition metal ions in glass. Another use to which such a calculation can be put is the interpretation of magnetic data, such as susceptibility and EPR. There is a great deal of data in the literature but not too many interpretations. Finally we note that crystal field calculations are common for cases in which the transition metal environment has a high degree of symmetry, usually O_h or T_d . Calculations in which the environment is randomly distorted and for which spin-orbit coupling are included are rare.

A further discussion of the program and its application to d^3 ions can be found in the article on the optical properties of Cr^{3+} in silicate glasses (Appendix 5).

2.1.2 Optical Absorption with Vibrational Coupling

A theoretical calculation has been made of the optical absorption of the vibronic states of two electronic levels, the levels interacting with each other and also with a vibrational mode. The model accurately represents a portion of the electronic spectrum of a transition metal ion in which two electronic levels are close enough to interact strongly by spin-orbit coupling and also for which the Jahn-Teller distortion of at least one level is large. The theory has been applied specifically to Cr^{3+} , but it is straightforward to apply it to any situation. The calculation shows that for such interacting electronic levels the electron-phonon interaction is important in the interpretation of the optical absorption. A detailed discussion of the calculation may be found in the article on the optical properties of Cr^{3+} in silicate glass (Appendix 5).

2.1.3 Optical Absorption Coupled to a Band of Phonon States

A theory of the vibronic levels of a two-level electronic system interacting with a band of phonons has been developed. This work was a natural outgrowth of the calculation with a single phonon state. The description that follows is an extended abstract of a paper to be presented at the Spring meeting of the Electrochemical Society:

It is our purpose to consider the relation between the vibronic levels of a two-level system coupled to either (1) a single harmonic oscillator or (2) a band of vibrational modes. The hamiltonian is

$$H = \sum_{j=1}^2 E_j A_j^+ A_j + \sum_{\{k\}} \omega_k a_k^+ a_k + \frac{\lambda}{\sqrt{N}} \sum_{\{k\}} (a_k^+ + a_k) (A_1^+ A_2 + A_2^+ A_1) \quad (1)$$

A_j^+ and A_j are creation and destruction operators for the electronic states 1 and 2 and a_k and a_k^+ are those for the phonons of wavevector k and frequency ω_k . The notation $\{k\}$ means that the sum is restricted to only those vibrational modes which are effective in coupling the electronic states. The coupling constant λ is independent of k and so an average over the most important modes has been made. The distribution of these effective phonon modes is assumed to be a square distribution about a central frequency ω_0 and with a width 2Δ . (The frequency spectrum of the whole solid will in general be much broader than this.) The constant λ is assumed smaller than the Jahn-Teller limit so the equilibrium positions of the nuclei are not altered. This means

$$\lambda < [(E_2 - E_1)(\omega_0 - \Delta)]^{1/2} \quad (2)$$

We are interested in the ground state and those first two excited vibronic states of H with considerable character of electronic state 2. There are two

limits in which the behavior of a system described by this hamiltonian is well understood. One is when $\lambda \ll \Delta$. Then a usual master equation approach is valid. The other limit is $\Delta=0$, finite λ , which describes a single harmonic oscillator coupled to the two level system. This case can be solved exactly. By varying λ and Δ we can interpolate between the two limits.

Let $E_1 = 0$ and $E_2 = \omega_0$ so that the separation of electronic states is in the middle of the effective phonon band. The energy of the ground state is approximately

$$E_{gs} = -\lambda^2 \frac{1}{N} \sum_{\{k\}} \frac{1}{E_2 + \omega_k} \quad (3)$$

The absorption coefficient $\alpha(\nu)$ for radiation of frequency ν from the ground state is

$$\alpha(\nu) = \text{const} \times \text{Im} \lim_{\epsilon \rightarrow 0^+} R(\nu)$$

To examine the behavior of the system, it is sufficient to use the approximate expression

$$R(\nu) = \left[s - E_2 + \lambda^2 [(E_2 - s)d + 1] \frac{1}{N} \sum_{\{k\}} \frac{1}{\omega_k - s - \lambda^2 d} \right]^{-1} \quad (4)$$

where

$$s = \nu + E_{gs} + i\epsilon \quad d = \frac{1}{E_2 + 2\omega_0 - s}$$

R always has one simple pole for $\nu < \omega_0 - \Delta$ and one for $\nu > \omega_0 + \Delta$. R is finite and complex for ν within the phonon band ($\omega_0 - \Delta < \nu < \omega_0 + \Delta$).

In the case $\lambda \gg \Delta$ (with restriction (2)) each simple pole has a residue of order unity. These are the primary absorbing levels and they are not homo-

homogeneously broadened. For λ within the phonon band, however, $\text{Im } R$ goes as $\Delta/\pi\lambda^2$. Hence the simple poles dominate the absorption.

On the other hand, for small λ ($\lambda \ll \Delta$) the residue at each simple pole goes as

$$\frac{2\Delta}{\lambda^2} e^{-(2\Delta/\lambda^2)}$$

The absorption thus occurs primarily at the frequency E_2 in the phonon band. The absorbing level is homogeneously broadened, the broadening being given by the golden rule.

In intermediate regions, the absorption (or excitation) consists of two sharp lines and a homogeneously broadened line, the three absorptions being of comparable intensities. For more precise intensities, (3) must be revised somewhat, but the qualitative conclusions remain unaltered.

2.1.4 Environmental Perturbations on Molecular Vibrations States

A theoretical study of the effects of amorphous environments on the vibrational spectra of nitrate ions has been made and applied to the Raman spectra of nitrate glasses. Two exact theorems have been proved about the effects of perturbations on the vibrations of the nitrate ion. These theorems explain the general form of the Raman spectra of nitrate ions in a variety of solutions and glasses. These theories are trivially extendable to any isolated molecule interacting relatively weakly with its environment. Some exact calculations on the frequency distributions of a valence force model of a nitrate ion subject to random perturbations have been made and interpreted using the theorems. These results may be found in the article on the vibrational spectra of nitrate glasses (Appendix 2).

2.1.5 Model for Glass Relaxation

An exactly soluble model was constructed to illustrate memory effects in the relaxation of glass. It was shown that the various atomic correlation functions required to characterize the non-equilibrium glass all relax at different rates and that this is responsible for the memory effects. The complete calculation is given in preprint form in Appendix 1.

2.2 STRUCTURE OF BASE GLASSES

2.2.1 Nitrate Glasses

The structure of nitrate glasses was investigated by Raman spectroscopy. The complete results are given in preprint form in Appendix 2, where the experimental measurements have been combined with the theoretical calculations mentioned above.

2.2.2 Lead Silicate Glass

The study of lead silicate glasses has been subdivided into two parts: One is an investigation by Raman spectroscopy of the structure of lead silicate glasses themselves. This investigation is complete and appears in preprint form in Appendix 3. The most interesting conclusion is that the structures in the lead silicate glasses seem to most closely resemble the metastable crystalline phases rather than the thermodynamically stable phases. Thus the crystallization of a lead silicate glass proceeds along the sequence glass $\rightarrow$ metastable crystal $\rightarrow$ stable crystal with the major structural rearrangements taking place in the crystalline state. The second part was an investigation of the phase equilibria and crystal structures in the PbO-SiO_2 system. The investigation proved necessary because of the somewhat confused state of knowledge of the PbO-SiO_2 system in the literature and because of the necessity of distinguishing stable and metastable phases.

Several studies (1-5) on the phase relations in the PbO-SiO_2 system have been reported, but the results had many discrepancies. Therefore, the subsolidus phase relations were reexamined with x-ray diffraction, IR and Raman spectroscopies, and DTA.

Crystalline phases were obtained either by devitrification of glass rods, or by hydrothermal treatments, or crystallization from undercooled melts. The results of the isothermal crystallization of glass rods are summarized in Fig. 1.

2PbO-SiO_2 : At this composition, $\text{L-Pb}_2\text{SiO}_4$ crystallized below $\sim 400^\circ\text{C}$, and above $\sim 400^\circ\text{C}$ $\text{M-Pb}_2\text{SiO}_4$ crystallized from glass rods. $\text{H-Pb}_2\text{SiO}_4$ can be crystallized by cooling down slowly from above $\sim 700^\circ\text{C}$. Thus, the crystalline phase, $\text{M-Pb}_2\text{SiO}_4$, had been considered as a medium temperature metastable phase and $\text{H-Pb}_2\text{SiO}_4$ as a high temperature stable phase. In this study, however, it was found that $\text{M-Pb}_2\text{SiO}_4$ is actually a high temperature stable phase and $\text{H-Pb}_2\text{SiO}_4$ is a medium temperature stable phase. The phase transition is sluggish but reversible. DTA measurements showed that $\text{H-Pb}_2\text{SiO}_4$ transformed into $\text{M-Pb}_2\text{SiO}_4$ at 615°C by heating and $\text{M-Pb}_2\text{SiO}_4$ transformed sluggishly into $\text{H-Pb}_2\text{SiO}_4$ at about 530°C by cooling. By hydrothermal crystallization at 685°C , $\text{M-Pb}_2\text{SiO}_4$ was crystallized and $\text{H-Pb}_2\text{SiO}_4$ was crystallized at 480°C , 400°C , and 325°C .

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 - (3) R.M. Smart and F.P. Glasser, J. Amer. Ceram. Soc. 57 (9) 378-82 (1974).
 - (4) H. Hasegawa, Ph.D. Thesis, Osaka University, Japan (1974).
 - (5) J. Götz, D. Hoebbel and W. Wieker, J. Non-Cryst. Solids, 20, 413-25 (1976).

Fig. 1 Phase diagram for the system PbO-SiO₂ showing compositions investigated.

The crystallization of glass at this composition can be represented schematically in Fig. 2. Glass crystallizes first (a) into metastable $\text{L-Pb}_2\text{SiO}_4$, then (b) $\text{M-Pb}_2\text{SiO}_4$ as a metastable phase, which can be annealed into stable Pb_2SiO_4 (c) below 600°C .

$5\text{PbO}-3\text{SiO}_2-3\text{PbO}-2\text{SiO}_2$: In this composition range only single phase, phase X, crystallized below $\sim 600^\circ\text{C}$. At 650°C and above $\text{M-Pb}_2\text{SiO}_4$ and alamosite were crystallized. The d-values of phase X increase as PbO content increases. This suggests formation of a solid solution. Phase X decomposed into $\text{H-Pb}_2\text{SiO}_4$ and alamosite by hydrothermal treatment. Therefore, phase X must be metastable at all temperatures.

In this composition range glass crystallizes first into metastable Phase X which then decomposes into stable phases $\text{M-Pb}_2\text{SiO}_4$ and alamosite at high temperature.

PbO-SiO_2 : At this composition L-PbSiO_3 crystallized from glass rods below $\sim 500^\circ\text{C}$, and above $\sim 500^\circ\text{C}$ the alamosite polymorph crystallized. Hexagonal PbSiO_3 was crystallized from the undercooled melt at 650°C . It did not crystallize from glass rods at this composition, but it crystallized with phase X from 1.25PbO-SiO_2 glass rods at 550°C . By hydrothermal treatments at 685°C , 480°C , 400°C , and 325°C only alamosite was crystallized. L-PbSiO_3 and hexagonal PbSiO_3 , therefore, must be metastable phases.

2.3 TRANSITION METAL IONS IN GLASS

2.3.1 Chromium in Glass

Chromium in glasses fired in air exists in both trivalent and hexavalent states. It was established by Raman spectroscopy that the Cr^{6+} exists in glass as isolated molecular-like tetrahedra dissolved in the silicate or borate glass. These chromate tetrahedra are not polymerized into the glass structure. The only polymerization is the formation of dichromate entities in some host/chromium

Fig. 2 Schematic free energy diagram for the lead orthosilicate composition.

concentration combinations. This interesting result has been submitted for publication and appears in preprint form in Appendix 4.

Trivalent chromium dissolves in glasses as a network modifier. It modifies the local glass structure because of its high octahedral site preference energy in such a way that a regular octahedral complex is formed. The oxygens ligating the Cr^{3+} are non-bridging oxygens from the glass network, but their configuration is much more symmetrical than would be the case for such oxygens in parts of the network far from the influence of the Cr^{3+} ions.

Cr^{3+} in silicate glasses exhibits a rather complex broad band/narrow band superposition spectrum that has never been satisfactorily explained. A combination of new experimental measurements and a theoretical model for the energy level diagram which includes both spin-orbit mixing of quartet and doublet states plus the influence of phonon mixing, gives a reasonable explanation. Such absorption spectra appear when the host structure (glass, crystal or liquid) is such as to produce a crystal field in the crossing region of the crystal field energy level diagram. The complete results and calculations are given in preprint form in Appendix 5.

2.3.2 Iron-Containing Glasses

The Raman spectra of sodium trisilicate glass doped with Fe_2O_3 are shown in Fig. 3 and for a sodium borate glass in Fig. 4.

In the case of silicate glasses, the presence of Fe is associated with a well defined band at 975 cm^{-1} . This band is considerably more depolarized than the 1100 cm^{-1} Raman band of the undoped glass. Its intensity relative to the intensity of the 1100 cm^{-1} peak is independent of the excitation frequency used. In the case of borates the presence of Fe has a much smaller effect, bringing about a subtle change of the broad Raman band at around 1400 cm^{-1} . It is difficult to detect the results of less than 5% Fe_2O_3 in

Fig. 3 Raman spectra of iron-doped sodium trisilicate glasses.

Fig. 4 Raman spectra of iron-doped barium borate glasses

borate glasses, while the 975 cm^{-1} peak in the Raman spectra of silicate glasses is detectable for a glass doped with as little as 1 mole % Fe_2O_3 .

In Fig. 5 it is seen that the presence of only 10^{-2} mole % of Fe_2O_3 is easily detectable in the luminescence spectrum of a soda lime silica glass and that the presence of iron in even the nominally pure glass can be detected by the slight peak in the red region of the spectrum. In Fig. 6 the emission spectra of iron-doped sodium trisilicate is seen to depend on the excitation frequency, showing the existence of a variety of iron sites in the glass.

The absorption spectra of iron-doped borate and silicate glasses were found to be the same as reported in the literature. One interesting result for the borate glasses is shown in Fig. 7. It is seen that the extinction coefficient increases with increasing iron concentration. This indicates considerable exchange coupling between adjacent Fe^{3+} in agreement with the conclusions of McCrone who performed magnetic measurements on the same composition glass.

Since all of these glasses were melted and poured in air, the ferrous/ferric iron ratio will be that of the $10^{-0.68}$ oxygen isobar. The emission band near $14,000\text{ cm}^{-1}$ is approximately at the correct frequency to be due to Fe^{3+} on a tetrahedral site within the glass structure. However, effects of Fe^{2+} which should act as a luminescence poison, and the exact glass environment have yet to be investigated.

2.3.3 Titanium-Containing Glasses

Glass rods of composition $\text{Li}_20.2\text{SiO}_2 \cdot x\text{TiO}_2$ ($x = 0.0$ to 1.0) were prepared from the melts in air. Only the glass with $x = 1.0$ was opaque due to phase separation. The glass rods were devitrified at various temperatures up to 950°C after heat treatment for nucleation at about 500°C .

Fig. 5 Emission spectra of a soda-lime-silica glass containing various concentrations of iron.
Glass melted and poured in air.

Fig. 6 Emission spectra of sodium trisilicate glass showing peak shift with excitation frequency.

Fig. 7 Absorption of $\text{BaO} \cdot 4\text{B}_2\text{O}_3$ glass doped with various amounts of iron. The quantity, t , is the thickness of the specimen and ΔI is the absorbance relative to the absorbance at 650 nm.

The Raman spectra of the glass rods had a band at 875 cm^{-1} , the intensity of which increased enormously as the TiO_2 content was increased. This behavior is very similar to that observed in the Fe_2O_3 -containing glasses. For glasses with $x = 0.5$, the broad diffuse Raman scattering below 900 cm^{-1} became a dominant feature of the spectra.

When glass rods with $x \leq 0.1$ were devitrified below 800°C , only lithium disilicate crystallized. The Raman spectra of the devitrified glasses exhibited characteristic sharp bands at 880 cm^{-1} and 915 cm^{-1} . The intensities of these bands increased as x increased. The lattice parameters of the orthorhombic lithium disilicate, formed by devitrification below 800°C , changed systematically with x . The a and c parameters increased while the b parameter decreased with increasing x . Above 850°C , the phase $\text{Li}_2\text{O} \cdot \text{SiO}_2 \cdot \text{TiO}_2$ (LST) started crystallizing and was recognized by a strong Raman band at 825 cm^{-1} . The relative intensity of the LST band increased at higher temperatures.

When glass rods with $x \leq 0.3$ were devitrified below 800°C , lithium disilicate, rutile (TiO_2) and an unknown phase crystallized. Above 850°C , LST began crystallizing. The relative intensities of the LST Raman bands increased as temperature was raised. When a glass with $x = 1.0$ was devitrified at 950°C , only the bands of LST were observed.

2.3.4 Trace Impurities in Very Pure Glasses

All silicate glasses luminesce under both visible laser and uv excitation. We have measured the luminescence spectra of a number of nominally pure glasses obtained from a variety of sources. All silicate glasses, and especially those made from reagent grade chemicals, appear to contain both impurities and intrinsic color centers which produce luminescence.

The emission typical of silicate glasses prepared from reagent grade chemicals and melted in Pt in air exhibit bands at 16,600, 15,400 and $17,900\text{ cm}^{-1}$

that have a strong dependence on the exciting line (an Ar laser is used for excitation). Two broad emissions observed in the yellow and red are only weakly dependent on the exciting line. It is probable that much of the red emission is associated with Fe contamination, as Fe is present in Reagent-grade glasses in at least tens of ppm (c.f. Fig. 5).

All silicate glasses, even very pure ones, have a yellow emission when excited by uv radiation. It has been suggested that this emission is due to Cu contamination of the glass. There is also a weak yellow emission excitable by the Ar laser. Figure 8 shows that that yellow emission which is excited by argon laser is definitely not due to Cu contamination. (The Raman spectra of these figures provide a normalization for the intensities.) We have also observed that the excitation spectrum of the yellow emission for undoped glass is different from that of Cu-doped glasses. These results indicate that in fact the yellow emission is not entirely due to Cu.

Figures 3, 6, and 8 show that some of the emission features of undoped glasses are quenched by the presence of Fe and Cu ions in quantities greater than 1 mole %.

The emission of very pure glass is quite different from the emission of glass made from reagent-grade material, indicating the importance of impurities in this emission. Figures 9 and 10 show the emission of some very pure glass obtained from W.B. French and coworkers at Bell Telephone Laboratories.

None of these emission data has been reported in the literature. The change of emission with glass composition and preparative methods is drastic and remarkable. While no interpretation has yet been made, still these observations indicate that laser-excited luminescence may be a useful analytical tool for glasses. To see whether this is the case, we have obtained some glasses from Professor Guy Rindone, who has made an extensive study of the

Fig. 8 Emission of a soda-lime-silica glass doped with CuO .

Fig. 9 Emission spectrum of very pure 0.74 SiO₂.0.20Na₂O.0.06CaO glass (courtesy of W.B. French, Bell Telephone Laboratories) showing effects of excitation frequency. The glass was melted by RF in a silica crucible.

Fig. 10 Emission spectra of a very pure $0.70 \text{ SiO}_2 \cdot 0.20 \text{ Na}_2\text{O} \cdot 0.10 \text{ CaO}$ Glass (courtesy of W.B. French, Bell Telephone Laboratories) showing the shifts in emission with excitation frequency. 55 db/km refers to the absorption at $1.06 \mu\text{m}$.

manner in which small amounts of impurities and preparative conditions affect the phase separation kinetics and morphology of silicate glasses. We intend to examine these glasses to see if this behavior can be correlated with the emission spectra.

3. Management

3.1 COMPLIANCE WITH PROJECT OBJECTIVES

The outline of work proposed included the following:

1. Structure of insulator glasses of the silicate, borate, borosilicate, and other compositions mainly by Raman and Ir spectroscopy.
2. Local structural environments of transition metal ions in insulator glass hosts. Transition metals were to include essentially all of the 3d series. This was to be accomplished by combinations of Raman, optical absorption, and luminescence spectroscopy.
3. Influence of glass composition and structure on the valence state and redox behavior of transition metal ions. Experiments were to be carried out at varying oxygen fugacities and the valence states present determined by optical spectroscopy.
4. Mechanisms of glass nucleation and crystallization and particularly the role of transition metal ions in formation of critical clusters and enhancing nucleation.

As documented in this progress report, substantial progress has been made on items 1, 2, and 4 above. 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 Liquid Helium Dewar System

With funds made available on this contract, an Air Products Company "Heli-Tran" dewar system was purchased. This device permits the measurement

of Raman, optical, and luminescence spectra to temperatures of 4 K. A built-in heater and control system allow the dialing of any temperature between the temperature of the refrigerant and room temperature. Repetitive scans of spectra at various temperatures can easily be done. Temperature for any scan is read out digitally.

3.2.2 Luminescence Lifetime Measurements

As documented elsewhere in this report, the luminescence from traces of transition metal ions in glasses produces quite complex spectra. Interpretation of the spectra would be greatly enhanced if lifetime and decay characteristics of the luminescent states were available in addition to the emission spectra. Unfortunately, most of the luminescence from the glasses is very weak, and without laser excitation much of it would not be measurable. It therefore requires some kind of repetitive, time-averaging, device to determine the decay of these weak signals. A considerable amount of time was invested in the design of an appropriate signal averager as described in the following paragraphs.

The purpose of the device is to determine the time dependence of the luminescence. The device records the number of data pulses arriving within a preset time interval, the interval being delayed a variable amount from some initial trigger pulse. The trigger pulse occurs at the same time as the light flash which excites the luminescence centers.

The special feature of the design is that the device records digitally up to 64 successive time intervals following each trigger pulse. Thus it records the entire decay curve at each trigger. This feature makes the device particularly suited to the low intensity levels of luminescence from glass, and it is 64 times as fast as boxcar integrators. The shortest time interval is 1 microsecond and the longest is 10 ms. The data are retrievable on a teletype, on a panel LED display, on a strip-chart recorder or on a scope.

A block diagram of the device is given in Fig. 11. The device functions as follows: A time interval, call it Δt , is selected. The data are stored in a 64-channel very fast random-access memory. When the trigger pulse arrives, the memory address is set to 1. The data arrive between times 0 and Δt after the trigger are added to the contents of memory location 1 (the data in memory 1 being the sum of previous cycles). The address is then advanced so the data arriving between times Δt and $2\Delta t$ after the trigger are added to the contents of memory location 2, and so forth. The process is repeated either until the 64 channels are used up or until another trigger occurs, when the address is reset to 1 and the cycle starts over.

The heart of the device is the two counters A and B. The data are routed to one or the other of the counters, and at the end of a time interval Δt the data are routed to the other counter. Say the data are routed to counter A. Then stored in counter B is the number of counts which arrived during the previous time interval Δt . The counts in B are added to the contents of the appropriate memory by a small dedicated computer. At the end of the time interval the incoming data are switched to counter B. Counter A is then idle and its contents are added to the next memory location, and so forth.

Fig. 11 Block diagram for data storage and processing "mini computer" to be used for decay time and time delay spectroscopy measurements.

3.3 PERSONNEL

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

The postdoctoral person on this project is Dr. Steven A. Brawer, Senior Project Associate. Dr. Brawer devotes full time to this project.

The graduate assistant on the project is Mr. Toshiharu Furukawa. Mr. Furukawa holds a 50% time graduate assistantship. The work that he does on this project will form part of his doctoral dissertation.

3.4 PUBLICATIONS AND PRESENTATIONS

3.4.1 Publications in Journals

*Reprints + Preprints
Removed*

The following aspects of this project have been completed and have been submitted for publication. These are the same articles that appear in preprint form as appendices to this report.

S.A. Brawer and W.B. White. Raman Spectroscopic Study of Hexavalent Chromium in Some Silicate and Borate Glasses. Materials Res. Bull. (to appear in March, 1977 issue).

S.A. Brawer. Memory Effects in the Relaxation of Glasses: An Exactly Soluble Model. Phys. Chem. Glasses (submitted).

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. (submitted).

T. Furukawa, S.A. Brawer and W.B. White. Raman Spectra and Structure of Nitrate Glasses. J. Phys. Chem. (submitted).

T. Furukawa, S.A. Brawer and W.B. White. The Structure of Lead Silicate Glasses Determined by Vibrational Spectroscopy. J. Materials Sci. (submitted).

3.4.2 Papers Presented at Professional Meetings

The following papers were presented at the annual meeting of the American Ceramic Society, Cincinnati, Ohio, May, 1976.

S.A. Brawer and W.B. White. Spectroscopic Investigation of Silicate Glasses Doped with Cr, Ti and Fe.

T. Furukawa, S.A. Brawer and W.B. White. Raman Spectroscopic Investigation of Pb Silicate Glasses.

3.4.3 Other Meetings and Presentations

W.B. White participated in the workshop on "Ceramic and Glass Radio-active Waste Forms" held at ERDA in January, 1977.