THE CRYSTALLIZATION BEHAVIOR OF THE WEST VALLEY REFERENCE BOROSILICATE GLASS

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Topical Report

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ABSTRACT

The crystallization behavior of a fully simulated reference borosilicate glass with potential application to the West Valley Demonstration Project has been studied. This work was required by the Waste Acceptance Preliminary Specifications. It included preparing and characterizing the base glass in various redox states, and assessing the influence of redox state on crystallization behavior. Characterization tools included optical and electron microscopy, wet chemical analysis, X-ray diffraction, dilatometry, and differential scanning calorimetry. The effect of cooling a melt at a rate and history which simulates in-canister cooling used for full-scale vitrification at West Valley also was determined.

From the data obtained, it was evident that the fully oxidized glass composition selected for this study contains residual crystalline phases (spinel and cerium-thorium oxide) at a volume percentage of approximately 0.4 - 1.6. Moreover, upon isothermal heat treatment above a measured glass transition temperature of 478°C, but below the estimated liquidus of 1000°C, crystallization would increase to 4 - 5 volume percent for heat treatment times up to 384 hours. The crystallization products included spinel, acmite, cerium-thorium oxide, and alumino silicates. The temperature range in which crystallization rate was a maximum was estimated as 700 - 800°C. After 12 hours at 800°C the glass crystallized to a volume percent of 3.0.

This same glass, when reduced to a redox state where the ratio of Fe^{++} / total iron was 10 percent, showed a lower crystallization maximum, i.e., 600 - 700°C. The glass transition temperature of this partially reduced glass also was lowered from 478°C (fully oxidized) to 474°C. All of these observations are in accord with the general theories of glass science. A critical cooling rate of 1.48°C / min would be sufficient to limit crystallization to less than 2.0 volume percent. This predicted value was ostensibly confirmed by cooling a melt at this temperature and then estimating the volume percent crystallization.

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1.0 INTRODUCTION/OVERVIEW

This report summarizes testing and characterization carried out at the New York State College of Ceramics for West Valley Nuclear Services Co., Inc. (WVNS) during the period Oct. 1, 1986 - Sept. 30, 1987. The major portion of this work was concerned with the determination of quantitative Time-Temperature-Transformation (T-T-T) diagrams on a fully simulated West Valley Demonstration Project (WVDP) borosilicate glass. A T-T-T diagram is required by the Waste Acceptance Preliminary Specifications for the WVDP High-Level Waste Form. This work involved the development of methods for both qualitative and quantitative determination of crystalline phases present in these glasses. These methods encompassed optical microscopy, x-ray diffraction analysis, and both scanning and transmission electron microscopy. Another important part of this work involved determination of the glass transition temperatures of the fully simulated glasses (both oxidized and partially reduced) by use of dilatometry (thermal expansion) and differential scanning calorimetry.

The other major part of this work was concerned with the development of a quantitative method for the determination of $\text{Fe}^{++}/\text{Fe}^{+++}$ ratios in the fully simulated glass samples by use of Mossbauer spectroscopy. This involved the preparation of a series of glasses with controlled redox state, i.e., various ratios of Fe^{++} / total Fe over the range of 0.0 - 0.65, and comparison of the results obtained from Mossbauer spectroscopy to those from wet chemical analysis. The procedures involving Mossbauer spectroscopy will be useful in those instances where wet chemical methods cannot be used for a determination of Fe^{++} / total Fe ratios, i.e., when several polyvalent species are present in addition to iron.

The results obtained in this work were used to construct a quantitative T-T-T diagram for both a fully oxidized and partially reduced glass. Additional crystallization studies involved determination of the effect of various cooling rates on residual crystallinity. Some of these controlled cooling studies closely approximated canister cooling curves observed during full-scale melting at West Valley, N.Y.

2.0 COMPOSITIONS STUDIED

2.1 Introduction

The major portion of the work done at Alfred University (AU) during 86-87 involved crystallization studies on the fully simulated reference glass. Glass samples used in crystallization studies were prepared at the Vitreous State Laboratory of the Catholic University of America using a slurry-fed electric melting furnace. These glasses were remelted at AU under controlled furnace atmospheres to obtain homogeneous glass samples with controlled oxidation state and known thermal history. Crystallization studies were done on a fully oxidized glass and also on a glass with 10.0 percent of Fe in the Fe^{++} state. A convenient summary of the properties of the glasses studied in this work is presented in Table 2-1.

Table 2-1. Characterization of Glasses Used in Crystallization Studies

	<u>WVCUO</u>	<u>WVCUO-18</u>	<u>WVCU10</u>	<u>WVCU48</u>
Remelting Temperature ($^{\circ}\text{C}$)	1100	1100	1100	1100
Remelting Time (h)	1.75	18	18	18
Furnace Atmosphere	Air	Air	Air followed by CO/CO_2	CO/CO_2
Fe^{++} /total iron ratio	0.0	0.0	0.10	0.48
Glass Transition Temperature ($^{\circ}\text{C}$)	478	--	474	464
Residual Crystallization (Volume %)	0.4	1.6	1.0	--

2.2 Preparation and Characterization of Oxidized Glass WVCUO

2.2.1 Chemical Composition

The glass composition used in these studies was a fully simulated borosilicate glass designated WVCM50 by Catholic University. The target glass composition as supplied by Catholic University along with the results of chemical analysis obtained in this work are given in Table 2-2.

2.2.2 Preparation of Glass WVCUO

Pieces of glass received from Catholic University were taken and remelted in a covered 95 percent platinum - 5 percent gold crucible for 30 minutes at approximately 1100°C . A Thermolyne Type 2000 furnace was used for melting. Four batches of 120 g each were made. The glasses were taken out of the furnace and cooled in the crucible. The glasses were extracted from the crucible and broken into fragments using a porcelain mortar and pestle. Glass samples from all four meltings were mixed using the mortar and pestle. The glass samples were recharged into the crucible and remelted for 1 hour at 1100°C in the Thermolyne furnace. The samples were taken out of the furnace, cooled, and subsequently taken out of the crucible and again broken into little pieces using a mortar and pestle. Four batches of the glass were prepared in this manner and mixed in order to get a master batch of glass for crystallization studies. This glass was designated as WVCUO.

Table 2-2. Composition of Glass WVCUO

<u>Oxide</u>	<u>Target Composition *</u> <u>Weight %</u>	<u>Analyzed Composition **</u> <u>Weight %</u>
Al ₂ O ₃	9.8	9.97
B ₂ O ₃	12.27	11.89
BaO	0.19	-
CaO	0.82	1.03
CeO ₂	0.7	0.64
CoO	0.02	-
Cr ₂ O ₃	0.14	0.21
Cs ₂ O	0.07	-
CuO	0.04	-
Fe ₂ O ₃	11.93	12.43
K ₂ O	1.6	2.27
La ₂ O ₃	0.04	-
Li ₂ O	2.22	2.29
MgO	0.79	1.07
MnO ₂	1.21	1.22
MoO ₃	0.04	-
Na ₂ O	9.79	10.11
Nd ₂ O ₃	0.14	-
NiO	0.3	0.21
P ₂ O ₅	2.47	2.57
PdO	0.02	-
Pr ₆ O ₁₁	0.04	-
RhO ₂	0.02	0.02
RuO ₂	0.03	0.04
SO ₃	0.22	-
SiO ₂	39.6	39.64
Sm ₂ O ₃	0.02	-
SrO	0.02	-
ThO ₂	3.52	3.57
TiO ₂	0.82	0.83
UO ₂	0.61	0.47 (as UO ₃)
Y ₂ O ₃	0.02	-
ZnO	0.03	-
ZrO ₂	0.39	0.34

* Supplied by Catholic University

** Analysis done at Corning Glass Works, Corning, NY

2.2.3 Characterization of Glass WVCUO

2.2.3.1 Chemical Analysis of WVCUO

A partial chemical analysis of glass WVCUO was performed at Corning Glass Works, Corning N.Y. Approximately 20 g of the glass was used for this analysis. The techniques used in the analysis of different oxides are given in Table 2-3. The results of these analyses are given in Table 2-2. The analyzed composition of the glass is very close to the target composition.

Table 2-3. Procedures for Chemical Analysis

<u>Oxide</u>	<u>Analysis Techniques *</u>
Al ₂ O ₃ , CaO, Cr ₂ O ₃ , MgO, MnO ₂ , NiO	Atomic Absorption
B ₂ O ₃ , CeO ₂ , P ₂ O ₅ , RhO ₂ , RuO ₂ , TiO ₂ , ZrO ₂	Plasma Spectrophotometry
Na ₂ , K ₂ O, Li ₂ O	Flame emission
Fe ₂ O ₃ , SiO ₂ , ThO ₂ , UO ₂	Classical Wet Chemistry

* Analysis done at Corning glass Works, Corning, N.Y.

2.2.3.2 Determination of Glass Transition Temperature

The experimental procedure for the determination of glass transition temperature is given in section 3.1. The glass transition temperatures as determined by DSC and dilatometry are given in Table 2-4. The average glass transition temperature for sample WVCUO was 478°C.

Table 2-4. Glass Transition Temperatures for Glasses WVCUO, WVCU10 and WVCU48

<u>Analysis Technique</u>	<u>Sample Designation</u>	<u>WVCUO</u>	<u>WVCU10</u>	<u>WVCU48</u>
DSC	Sample # 1	479.5	472.0	464.0
	Sample # 2	474.5	474.0	466.0
Dilatometry	Run No. 1	479.0	473.0	464.0
	Run No. 2*	479.0	475.0	463.5
Average		478	474	464

* The sample was reannealed prior to the second run.

2.2.3.3 Scanning Transmission Electron Microscopy (STEM)

The experimental procedure for analysis by STEM is given in section 3.3.3. An electron micrograph of a sample of WVCUO is given in Figure 2-1. The sample appeared non-crystalline and homogeneous with the exception of one dark phase. Energy dispersive spectroscopy was used to identify the elemental composition of this phase. The major elements present in this phase are Fe, Cr and Ni. This is probably an Fe₃O₄ type spinel phase with part

of the iron substituted by Cr and Ni. The EDS spectrum of this phase is given in Figure 2-2. An EDS spectrum of the glass matrix is given in Figure 2-3.

2.2.3.4 Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy(EDS)

A few large crystals were observed in the untreated sample of WVCUO used in this study. The elemental composition of the crystalline phases were determined by EDS. Though all the crystals appeared similar on visual examination, EDS spectra indicated the presence of two different crystal phases. One of the phases contained Fe and smaller amounts of Cr and Ni. This is a spinel phase with part of the Fe substituted by Cr and Ni. EDS spectra of this phase is given in Figure 2-4. The other phase contains large amounts of Th and Ce and is probably a cerium-thorium oxide crystal. EDS spectrum of this phase is given in Figure 2-5.

2.2.3.5 Optical Microscopy and Image Analysis

An optical micrograph of untreated sample of WVCUO is given in Figure 2-6. The micrograph was taken at a magnification of 400X using reflected light optics. As can be seen from this figure, a small amount of residual crystallization was detected. Volume percent of crystal phase was determined by image analysis and was found to be 0.4. A few crystals with a size of approximately 2 micrometers was found in the sample. Crystals in the untreated sample of WVCUO occurred in clusters.

2.3 Preparation and Characterization of Reduced Glass WVCU10

2.3.1 Description of the Controlled Atmosphere Furnace

A furnace was designed and built in order to prepare glass samples with controlled oxidation state of iron. A schematic of the furnace is given in Figure 2-7. A Lindberg tube furnace was modified so that the furnace atmosphere could be controlled accurately. A closed mullite tube with water cooled jackets on both ends was placed in the tube furnace. The melting atmosphere was controlled by controlling the atmosphere inside this mullite tube. A second mullite tube was used as the sample holder and was designed so that the sample could be introduced into the furnace making an air tight seal with the cooling jacket on the first mullite tube. The sample holder was connected to a motor and gear assembly so that the sample could be rotated at a known rate. The melting atmosphere was controlled by regulating the flow of CO and CO₂ gases into the closed mullite tube. Sample temperature was monitored using a K type thermocouple placed close to the sample. Inclination of the furnace could be adjusted as to maximize the surface area of glass exposed to the atmosphere. Rotation of the sample during melting promoted mixing and hence a more homogeneous glass was obtained. Also, since the inclination of the furnace resulted in the exposure of a large surface of the sample to the furnace atmosphere, the reduction of the sample to the required state was accomplished in a relatively short period of time.

Figure 2-1. Electron Micrograph of WVCUO - Untreated

Figure 2-2. EDS Spectrum (0-10 Kev) of Spinel Phase in WVCUO - Untreated

Figure 2-3. EDS Spectrum (0-10 Kev) of WVCUO - Untreated Glass Matrix

WVCUO ROUND PARTICLE

Figure 2-4. EDS Spectrum of Spinel Phase in WVCUO - Untreated

WVCUO DARK PARTICLE

Figure 2-5. EDS Spectrum of a Particle in WVCUO - Untreated

Figure 2-6. Optical Micrograph of WVCUO - Untreated

DIMENSIONS IN INCHES

Furnace 20 X 19 X 25

Mullite tube OD3-1/4 ID L33

Rotating tube OD2-3/8 ID2-1/8 L24

Crucible OD2 ID1-31/32 L8

INCLINED-ROTATING FURNACE FOR REDOX STUDIES

Figure 2-7. Schematic of the Redox Furnace

2.3.2 Preparation of Glass WVCU10

Pieces of glass received from Catholic University were remelted in the controlled atmosphere furnace in order to partially reduce iron in the glass. The target Fe^{2+} to total iron ratio in the glass was 0.1. About 275 g of the glass was placed in a 95 percent platinum - 5 percent gold crucible. The glass was remelted in the controlled atmosphere furnace for a total of 18 hours at 1100°C. The crucible was rotated at 2 rpm. The glass was first remelted for 4 hours in an atmosphere of dry air and was then reduced for 14 hours using a mixture of CO and CO_2 . At the end of melting, the crucible was taken out of the furnace and the glass was poured into platinum-gold crucibles. The Fe^{2+} to total iron ratio was determined using Mossbauer spectroscopy and was found to be 0.1. Details of the Mossbauer analysis are given in section 3.2.3. The glass was designated as WVCU10.

2.3.3 Characterization of Glass WVCU10

2.3.3.1 Chemical Analysis of Glass WVCU10

The glass sample designated as WVCU10 had the same composition as sample WVCU0. The target and analyzed chemical compositions of these glasses are given in Table 2-2.

2.3.3.2 Determination of Glass Transition Temperature

The experimental procedure for determination of glass transition temperature is given in section 3.1. The glass transition temperatures as determined by DSC and dilatometry are given in Table 2-4. The average glass transition temperature for sample WVCU10 was 474°C.

2.3.3.3 Scanning Transmission Electron Microscopy

Refer to section 3.3.3 for the experimental procedure used in STEM analysis. The electron micrograph of the untreated sample of WVCU10 is given in Figure 2-8. The sample appeared homogeneous with the exception of few scattered crystals. EDS analysis of the elemental composition of this phase showed the presence of Fe, Cr and Ni. It was concluded that this phase, which appeared dark in STEM micrographs, is a spinel phase with part of Fe substituted by Cr and Ni. The EDS spectrum of this phase is given in Figure 2-9.

2.3.3.4 Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS)

A few isolated large crystals were observed in the untreated sample of WVCU10. Elemental composition of the crystals were determined by EDS. EDS spectra were collected from two crystal phases. One of the phases contained Fe and small amounts of Cr and Ni. This is an Fe_3O_4 type spinel phase with part of the Fe substituted by Cr and Ni. An EDS spectrum of this phase is given in Figure 2-10. The other phase contains large amounts of Th and Ce and is probably a cerium-thorium oxide crystal. An EDS spectrum of this phase is given in Figure 2-11.

Figure 2-8. Electron Micrograph of WVCU10 - Untreated

Figure 2-9. EDS Spectrum of Spinel Phase in WVCU10 - Untreated

WVCU10 UNTREATED SMALL CRYSTAL

Figure 2-10. EDS Spectrum of Spinel in WVCU10 - Untreated

WVCU10 UNTREATED PARTICLE

Figure 2-11. EDS Spectrum of a Particle in WVCU10 - Untreated

2.3.3.5 Optical Microscopy and Image Analysis

An optical micrograph of untreated sample of WVCU10, in reflected light at a magnification of 400X, is given in Figure 2-12. Volume percent of crystals in the sample was determined by image analysis to be 1.0. Isolated single crystals, which were fairly large in size, were observed in the sample. Since glass sample WVCU10 was remelted for 18 hours at 1100°C it was concluded that a small amount of residual crystallization at 1100°C is a property of this glass composition.

2.4 Preparation and Characterization of WVCU48 AND WVCUO-18

In addition to samples WVCUO and WVCU10, which were used in crystallization studies, two other glass samples were prepared. The glass transition temperature of sample WVCU48 (glass with Fe²⁺/total Iron ratio of 0.48) was determined to study the effect of oxidation state of iron on the glass transition temperature. Sample WVCUO-18 was prepared to study the possible effect of melting time on the crystallization behavior of reference glass WVCUO.

2.4.1 Preparation of Glass WVCU48

Approximately 275 g of pieces of glass WVCU50 received from Catholic University were placed in a 95 percent platinum-5 percent gold crucible. The sample was remelted for 18 hours at 1100°C in the controlled atmosphere furnace. The furnace atmosphere was kept reducing by circulating a mixture of CO and CO₂ gases. The crucible was rotated at two rpm. At the end of melting, the melt was poured into platinum-gold crucibles. The ratio of Fe²⁺ to total iron in the glass was determined by Mossbauer spectroscopy and was found to be 0.48. The sample was designated as WVCU48.

2.4.2 Characterization of Glass WVCU48

2.4.2.1 Chemical Analysis of Glass WVCU48

Glass sample WVCU48 had the same base composition as sample WVCUO. Refer to section 2.2.3.1 for details of the chemical analysis.

2.4.2.2 Determination of Glass Transition Temperature

The glass transition temperature was determined by both DSC and dilatometry. (Refer to section 3.1 for the experimental procedure). The average glass transition temperature for glass sample WVCU48 was determined to be 464°C. The glass transition temperatures as determined by DSC and dilatometry are given in Table 2-4.

Figure 2-12. Optical Micrograph of WVCU10 - As Melted

2.4.3 Preparation of Glass Sample WVCUO-18

Approximately 275 g of pieces of glass WVCM50 received from Catholic University were placed in a 95 percent platinum-5 percent gold crucible. The sample was remelted for 18 hours at 1100°C in a controlled atmosphere furnace. The furnace atmosphere was kept oxidizing by circulating dry air. The crucible was rotated at two rpm. At the end of melting, the melt was poured into platinum-gold crucibles. The sample was called WVCUO-18.

2.4.4 Characterization of Glass WVCUO-18

2.4.4.1 Chemical Analysis of Glass WVCUO-18

Glass sample WVCUO-18 had the same base composition as sample WVCUO. Refer to section 2.2.3.1 for details of the chemical analysis.

2.4.4.2 Optical Microscopy and Image Analysis

An optical micrograph of untreated sample of WVCUO-18 is given in Figure 2-13. The micrograph was taken at a magnification of 400X using reflected light optics. This sample contained a few isolated crystals which were approximately 2 micrometers in size. The residual crystallization was measured by image analysis to be 1.6 volume percent. This glass sample was prepared by remelting WVCM50 for 18 hours in air and hence it can be concluded that a small amount of residual crystallization is a property of this glass composition.

Figure 2-13. Optical Micrograph of WVCUO-18 - Untreated

3.0 EXPERIMENTAL PROCEDURES

3.1 Determination of Glass Transition Temperature (T_g)

Glass transition temperatures reported for each glass sample are the average of the transition temperatures determined by dilatometry and also by differential scanning calorimetry (DSC). A small piece of the sample (10 mg) was taken and an approximate T_g was determined using DSC as described in Section 3.1.1. A few pieces of the sample were annealed at a temperature 5 to 15°C above the approximate glass transition temperature for a minimum of 30 minutes. T_g was determined using DSC on two different samples of the annealed glass. Data were considered acceptable if the two measured T_g values were within 5°C of the average.

The second method used in the determination of glass transition temperature was dilatometry. A glass rod, about 30 - 50 mm long was used in the analysis. The sample glass rod was annealed as described above. Thermal expansion data were collected using this sample from approximately 50°C to the dilatometric softening point. The procedure for data collection and analysis is given in Section 3.1.2. The glass transition temperature was determined from the thermal expansion curve. The sample was reannealed and data were collected again from the same sample and T_g was determined. The data were accepted only if both the T_g values were within 5°C of the average.

3.1.1 Differential Scanning Calorimetry (DSC)

3.1.1.1 Calibration of the DSC

Calibration of the DSC unit was assessed by comparing the measured onset of melting of a metal standard (indium or lead) of 99.9+ purity to the reported melting point of the metal. The DSC unit used in these studies was a Perkin Elmer DSC-4 with controller, computer and thermal analysis software. 5 to 10 mg of the standard metal was placed in an aluminum sample holder. The unit was purged using air or nitrogen and data were collected at a heating rate of 10°C per minute. The temperature of onset of melting was determined by peak analysis and the measured melting temperature was compared to the reported value. Calibration was considered acceptable if the difference between the measured and reported melting temperatures was less than 2°C. Verification of the calibration was performed in a similar manner using a second standard metal. A typical calibration curve with the analysis results is given in Figure 3-1.

3.1.1.2 Sample Preparation for DSC

A small piece of the unannealed glass sample (10 mg) was taken and sealed in an aluminum sample holder. This sample was used in the determination of approximate glass transition temperature. Few pieces of the glass were taken and annealed at a temperature 5 to 15°C above the approximate T_g . Two samples each were prepared from these annealed glass pieces. The samples were weighed (10 mg each) and sealed in aluminum DSC sample holders.

3.1.1.3 DSC Data Collection and Analysis

The glass sample was placed in the sample holder and data were collected at a heating rate of 10°C per minute. The unit was purged using air or nitrogen. After the data collection was completed a plot of the DSC curve was obtained. The glass transition temperature was determined from this curve by mechanical construction. Tangents

Figure 3-1. Typical DSC Calibration Curve

were drawn to the curve at the low and high temperature side of glass transition temperature. The temperature corresponding to the point of intersection of the tangents was estimated to be the glass transition temperature. A typical DSC curve along with the mechanical construction for the determination of glass transition temperature is given in Figure 3-2.

3.1.2 Dilatometry

3.1.2.1 Calibration of Thermal Expansion Unit

The equipment used in this part of the study consisted of a Theta Dilatronic II thermal expansion unit with temperature controller. Data were collected using a DEC RT1103 computer in conjunction with a Fluke 8502A multimeter and scanner. The thermocouple used in the thermal expansion unit to measure sample temperature was calibrated using a standard NBS calibrated thermocouple. The unit was calibrated for the expansion coefficient using an NBS standard, SRM731 borosilicate glass rod. The length of the glass rod was measured using a vernier caliper and the standard was placed in the unit. Temperature versus expansion data were collected in the temperature range of 50 to 300°C at a heating rate of approximately 200°C per hour. A plot of the thermal expansion curve was obtained and expansion coefficient was calculated. The difference between the measured and reported expansion coefficients was calculated and a correction factor equal to this difference was applied to subsequent measurements. Verification of the calibration was effected using a glass rod of known expansion supplied by Schott Optical Glass Company, Duryea, Pa. Data collection and analysis were performed as described above.

3.1.2.2 Sample Preparation for Dilatometry

Annealed glass rods (30 - 50 mm long) were used as samples for dilatometry. The ends of the glass rods were ground so that they were flat. Data were collected from the same sample twice. After the first data collection, the sample was reannealed prior to the second data collection.

3.1.2.3 Dilatometry Data Collection and Analysis

The length of the glass rod was measured using a vernier caliper and then the sample was placed in the thermal expansion unit. Data were collected in the temperature range of 50°C to just above the dilatometric softening point at a heating rate of approximately 200°C per hour. At the end of data collection, the furnace was turned off and the sample was allowed to cool in the furnace. A plot of the thermal expansion curve was obtained and the low temperature expansion coefficient and glass transition temperature were determined manually. The glass transition temperature was determined by drawing tangents to the thermal expansion curve at low and high temperatures and estimating the temperature corresponding to the point of intersection. The expansion coefficient was determined by calculating the slope of the thermal expansion curve in the low temperature range. In this calculation, only the linear part of the expansion curve was used.

3.2 Determination of Oxidation State of Iron In Glass

The classical technique for determination of Fe^{2+} to Fe^{3+} ratio in glasses is wet chemical analysis and is accurate when the only transition element present in the sample is iron. The West Valley reference borosilicate glass

Figure 3-2. Determination of T_g by DSC

contains almost all the transition elements and hence this analysis technique will not be accurate. In this work, ratio of Fe^{++} to total iron was determined by Mossbauer spectroscopy. In this technique the interaction of the radiation was tuned to a single species, i.e., iron. In order to use this technique to determine the oxidation state of iron in the glass, it was necessary to obtain a calibration curve that related Fe^{2+} to Fe^{3+} ratio measured by chemical analysis and Mossbauer spectroscopy. A series of glasses with different oxidation states of iron were prepared and analyzed by both chemical methods and Mossbauer spectroscopy and a calibration curve was made. A glass composition with only a single polyvalent species, iron, in a base borosilicate glass, was used in these studies. Details of the glass composition, preparation and analysis are discussed below.

3.2.1 Sample Preparation for Redox Studies

3.2.1.1 Glass Composition

The glass used in redox studies had a composition very similar to West Valley glass WV-205. All the polyvalent specie except iron were removed from the base composition so as to eliminate any error due to interaction of different ions during chemical analysis. The composition of the glass used in these studies is given in Table 3-1.

Table 3-1. Composition of Glass Used in Redox Studies

<u>Oxide</u>	<u>Weight %</u>
Al_2O_3	3.15
BaO	0.08
B_2O_3	10.94
CaO	0.58
Fe_2O_3	14.92
K_2O	3.91
Li_2O	3.33
MgO	1.45
Na_2O	12.11
P_2O_5	0.82
SO_3	0.39
SiO_2	48.25
SrO	0.04
ZrO_2	0.02
	100.01

3.2.1.2 Preparation of Base Glass

The raw materials were weighed and mixed using a mortar and pestle. The glass was initially melted in a 95 percent platinum - 5 percent gold crucible for 1 hour in a Lindberg furnace at 1150°C . The melt was poured on a

metal plate, crushed and remelted for 0.5 hour at the same temperature. At the end of melting, the glass melt was poured out, and was stored for further studies.

3.2.1.3 Reduction of Glass Samples

Different oxidation states (ferrous/ferric ratios) of iron in the base glass were achieved by heat treating the base glass under various partial pressures of oxygen. Heat treatments for reduction of the base glass were carried out in a controlled atmosphere furnace. The atmosphere inside the furnace was controlled by regulating the flow of CO and CO₂ gases. The partial pressure of oxygen in the furnace was varied by changing the CO/CO₂ ratio. Partial pressure of oxygen was measured using a zirconia probe. About 17 g of sample was heat treated at a time in a platinum-iridium crucible. The crucible was rotated at a rate of 2 rpm during heat treatment.

Samples used in the calibration of Mossbauer spectrometer were heat treated at a temperature of 1100°C for 24 hours. At the end of heat treatment, the crucible was taken out of the furnace and the melt was poured out. The sample was annealed and stored for further analysis.

A series of glass samples were prepared with different oxidation states of iron by changing the time and temperature of heat treatment while keeping the CO/CO₂ ratio constant. Four samples each were prepared at 1050, 1100 and 1150°C. Time of heat treatment were 3, 6, 12, and 24 hours. The glass melts were poured out at the end of heat treatment. The glass sample was annealed prior to further studies.

3.2.1.4 Sample Preparation for Chemical Analysis

A small piece of glass was cut from the annealed sample using a Buehler low speed diamond saw. Samples used in the calibration of Mossbauer spectrometer were broken into small pieces and were sent to Corning Glass Works, Corning, NY., for chemical analysis. Chemical analysis of the remaining samples were performed at the New York State College of Ceramics at AU. The analysis for Fe²⁺ and Fe³⁺ content of the glass samples was done at AU by wet chemical methods.

3.2.1.5 Sample Preparation for Mossbauer Analysis

Annealed pieces of the glass were cut using a Buehler low speed diamond saw to obtain samples approximately 1 mm thick. These samples were ground using a Buehler thin sectioning machine to a thickness of 0.5 mm.

3.2.2 Calibration of Mossbauer Spectrometer

A Ranger Scientific MS1200 Mossbauer spectrometer with a 60 millicurie ⁵⁷Co source, computer, and data collection and analysis software were used in the studies. The entire system was calibrated using a two step process. During the first step, the zero velocity channel and the velocity were determined using an NBS standard iron foil (SRM 1541). The second part of the calibration procedure involved the determination of a calibration curve that related the Fe²⁺ content of the glass to the area under the Fe²⁺ peak in the Mossbauer spectrum.

Five glass samples with known Fe²⁺ to total iron ratio were used in the determination of the calibration curve. The glasses were analyzed by chemical methods at Corning Glass Works to determine the oxidation state of iron. Mossbauer spectra were collected with 0.5 mm thick samples using a RAMP wave form and with the instrument in fly back mode. A typical Mossbauer spectrum with three peaks is given in Figure 3-3. The Fe²⁺ to total iron ratio in the glass was determined as the area under peak 1 divided by the sum of the areas under peak 1 and

peak 2. The results of chemical and Mossbauer analyses are listed in Table 3-2 and illustrated graphically in Figure 3-4. Within the limits of experimental error, the analysis results obtained by chemical methods and Mossbauer spectroscopy are identical.

Table 3-2. Fe^{2+} to Total Iron Ratio as Determined by Mossbauer Spectroscopy and Chemical Analysis

<u>Sample Identification</u>	<u>Mossbauer</u>	<u>Chemical Analysis</u>
W87ARED1D	0.07	0.09
W87ARED1E	0.11	0.12
W87ARED1C	0.22	0.23
W87ARED1L	0.36	0.33
W87ARED1K	0.63	0.64

* Analysis done at Corning Glass Works, Corning, N.Y.

3.2.3 Analysis by Mossbauer Spectroscopy

Annealed pieces of glass (0.5 mm thick) were placed in the sample location. A data collection program was started and a "RAMP" wave form was loaded to control movement of the source. Data were collected with the instrument in "fly back" mode. Initially, data were collected over the entire region, and Mossbauer region of the spectrum was identified. Limits were set so that only the Mossbauer region of the spectrum was collected. After the limits were set, memory of the Mossbauer spectrometer was cleared, and data collection was started. Data were collected until all peaks were clearly defined. Data collection time varied from 6 hours to 24 hours. A typical Mossbauer spectrum is given in Figure 3-5. The three peaks in the spectrum are labelled as peaks 1, 2, and 3. Data were analyzed using a curve fitting program. Curves were fitted to every peak and area under the peaks were determined. Fe^{2+} to total iron ratio was determined as the area under peak 1 divided by the sum of the areas under peak 1 and peak 2.

3.3 Phase Analysis

Qualitative and quantitative phase analysis of the heat treated, and as melted glass samples were performed by a variety of analysis techniques. Quantitative determination of the crystal content of glass samples was performed by reflected light optical microscopy in conjunction with image analysis. X-ray diffraction was used in the identification of crystalline phases in the glass samples. Quantitative X-ray diffraction was used in the determination of amount of spinel phase in a series of samples. Scanning transmission electron microscopy was used to study 1000 Å thick sections of the glass samples. Using this technique, the samples could be examined at very high magnifications and hence even very small crystals and other inhomogeneities could be observed and studied. Energy dispersive spectroscopy was used in the identification of the elemental composition of crystals and other discrete phases.

Figure 3-3. Mossbauer Spectrum of a Sample Used in Calibration

Figure 3-4. Fe⁺⁺⁺ to Total Iron Ratio as Determined by Mossbauer Spectroscopy and Chemical Analysis

Figure 3-5. Typical Mossbauer Spectrum of a Glass Sample

3.3.1 Optical Microscopy and Image Analysis

Reflected light optical microscopy along with image analysis was used in the determination of amount of crystals present in the glass samples. Analyses were done on polished sections of the samples.

3.3.1.1 Sample Preparation

Sections of heat treated and untreated samples of glasses used in the determination of T-T-T diagram were prepared for this study. Pieces of glass (10 x 10 x 1 mm) were cut from the bulk of the samples using a Buehler low speed diamond saw. The sections were mounted on glass slides and were ground and polished using Buehler Minimet grinding equipment. The polished sections were remounted on clean glass slides and were used in the analysis.

3.3.1.2 Calibration of Image Analysis System

The optical microscopy/image analysis system used in this study consisted of a Leitz Optical microscope with reflected light optics, video camera to transfer the image to a monitor, a device to digitize the image on the video monitor, and a computer with data collection and analysis software. A micrometer slide was used to determine the magnification factor to be used in the analysis. This magnification factor depended on the magnification of the objective used. The accuracy of area measurement, by the system at various magnifications, were checked using a test slide with figures of known area.

3.3.1.3 Data Collection and Analysis

A polished section of the glass sample was placed on the microscope stage and the image was brought into focus. The real image of the sample surface was transferred to the video screen. The contrast of the video image was adjusted using the program so that crystals appeared much brighter than the glass matrix. Areas of the crystals were measured and recorded using the image analysis software. The total area of the sample being analyzed was also stored. The procedure was repeated, by selecting at random different parts of the sample surface, until a statistically significant area of the sample surface was analyzed. The area percent of the crystals were calculated as the sum of the areas of the crystals divided by the sum of the areas of the sample surface analyzed during each step. Through this analysis, the total volume percent of crystals in the sample was determined.

3.3.2 X-ray Diffraction Analysis (XRD)

Crystal phases present in heat treated glass samples were identified by qualitative X-ray diffraction. The weight percent of an Fe_3O_4 type spinel phase present in WVCUO glass samples heat treated at 900°C was determined by quantitative X-ray diffraction.

3.3.2.1 Sample Preparation for X-ray analysis

A piece of the glass sample (13 x 13 x 2 mm) was cut using a Buehler low speed diamond saw. This section was used in XRD data collection. Care was taken to ensure that the analysis was not done on the surface of the heat treated glass sample.

3.3.2.2 Calibration of the X-ray Diffractometer

X-ray diffraction data were collected using a Philips Norelco or Siemens D500 X-ray diffractometer, with computer and data collection and analysis software. Calibration of the X-ray diffractometer for peak locations was checked using NBS standard silicon powder SRM 640a. The calibration was verified using Fe_3O_4 powder. The acceptance criterion was that the measured peak locations shall be within 0.05° of the reported values.

One of the main crystalline phases present in the heat treated samples of WVCUO glass was spinel. In order to determine the amount of spinel phase present in the samples, it was necessary to obtain a calibration curve that related integrated peak intensity to weight percent of Fe_3O_4 in the samples. Mechanical mixtures of Fe_3O_4 and powdered WV-205 glass were made with varying proportions of glass and Fe_3O_4 . The amount of Fe_3O_4 in the mixtures were varied from 1 to 10 percent at intervals of 1 percent. XRD spectra of the samples were collected and integrated intensity of 100 percent peak of Fe_3O_4 was computed for each sample. The intensities were plotted as a function of the weight percent of Fe_3O_4 and a linear relationship was obtained. This plot was used as the calibration curve for quantitative XRD analysis. The calibration curve is given in Figure 3-6

3.3.2.3 XRD Data Collection and Analysis

Quantitative XRD analysis was carried out on samples of WVCUO glass heat treated at 900° for 24 to 384 hours. Data were collected on solid pieces of glass using a count time of 10 s and step width of 0.02° . The area under the 100 percent peak of the spinel phase was computed and weight percent of this phase was determined from the calibration curve given in Figure 3-6. The weight percent values were converted to volume percent by using the density of spinel and glass to be 5.18 g/cc and 2.68 g/cc respectively.

Qualitative XRD analysis was carried out on a number of heat treated glass samples. A solid piece of glass was used as the sample. Data were collected on solid pieces of glass using a count time of 10 s and step width of 0.02° . The area under the 100 percent peak of the spinel phase was computed and weight percent of this phase was determined from the calibration curve given in Figure 3-6. The weight percent values were converted to volume percent by using the density of spinel and glass to be 5.18 g/cc and 2.68 g/cc respectively.

Qualitative XRD analysis was carried out on a number of heat treated glass samples. A solid piece of glass was used as the sample. Data were collected in the 2θ range of 10 to 90° with a count time of 8 s and step width of 0.02° . Phases were identified by comparison of the measured peak locations (d values) to the reported peak locations. The peak locations reported in the JCPDS cards are for pure crystal phases. In the heat treated glasses, most of the crystalline phases that formed were impure solid solutions and hence the measured peak locations did not always match the reported values. In these cases, a graphical pattern evaluation was done to identify the phases.

3.3.3 Scanning Transmission Electron Microscopy (STEM)

Analysis of heat treated and untreated glasses were done using scanning transmission electron microscopy. Part of the work was done at Corning Glass Works Sullivan Park Research Laboratory on a JEOL 100 CX STEM. Electron micrographs of a few samples were taken at Alfred University using a JEOL 2000 FX STEM. Three types of analyses, which are listed below, were performed using the STEM.

- a. Samples were inspected and photographed in transmission at different magnifications.

Calibration Curve For Quantitative X-Ray Diffraction Analysis

Figure 3-6. Calibration Curve for Quantitative X-ray

- b. Qualitative determination of the elemental composition of the glass matrix and crystalline phases in the glass was done by energy dispersive spectroscopy.
- c. Selected area electron diffraction was performed on crystalline phases in the glass samples to identify the crystal phases.

3.3.3.1 Sample Preparation for STEM

For analysis using STEM it is required that the portion of the sample being analyzed be transparent to the electron beam of the instrument. To accomplish this, glass samples, parts of which were about 1000 angstroms thick, were prepared according to the procedure described below.

A wafer 0.6 mm thick was cut from the bulk sample using a Buehler low speed diamond saw. The sample wafer was mounted on a glass support and was ground manually using a Buehler precision grinding attachment. Using a Gatan ultrasonic disc cutter, side one of the sample was cut to a depth of about 0.25 mm. The diameter of the disc was 3 mm. The sample was remounted and side two was ground and polished to a thickness of 100 microns or less. The discs were dimpled (ground) to a minimum center thickness of 30 microns using a Model 656 Gatan dimpler. The discs were ion milled at the thinnest part of the dimple till the sample was perforated. Ion milling was done in a Gatan Model 600 ion mill. The edges of the perforation were electron transparent and were studied using STEM. The samples were coated with carbon to thickness of 50 -100 Å to avoid charging during analysis.

3.3.3.2 Visual Survey and Photography

Transmitted image of the sample was viewed on the fluorescent screen of the instrument and features of interest were located. Areas of interest were photographed in transmission at magnifications of 10,000X to 50,000X. Subsequent photographic enlargement produced magnifications in the range of 40,000 to 200,000X.

3.3.3.3 Energy Dispersive Spectroscopy (EDS)

EDS spectra were collected from the glass matrix and also from different phases observed in the samples. The area of interest was selected and brought into focus at the center of the screen. The instrument was switched to STEM mode and spectra were collected.

Peak locations in the EDS spectra were determined, and the peaks were identified and labelled. Plots of the EDS spectra with the peak identifications were made.

3.3.3.4 Selected Area Electron Diffraction

Electron diffraction analysis was performed on selected features of interest. The part of the sample to be analyzed was brought into focus, a diffraction aperture was inserted and the resulting pattern was observed. The character of the pattern indicated whether the selected particle was single crystalline or amorphous. Calibration of the instrument was checked using aluminum and thallus chloride standards.

Patterns of interest were photographed. "d" values, which are distances between interatomic planes, were determined by measuring the distance between the center, undiffracted beam and the various locations of the diffracted beam. These "d" values were compared to the reported d values to identify crystal phases present in the samples.

3.3.4 Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS)

Analysis by energy dispersive spectroscopy was performed to determine the elemental composition of different phases observed in the glass samples. Scanning electron microscope was used to locate the features of interest.

3.3.4.1 Sample Preparation

Annealed samples of the glass were cut using a Buehler low speed diamond saw to obtain small pieces (10 x 10 x 2 mm). The samples were mounted on SEM sample holders and coated with gold-palladium to a thickness of 100 to 200 Å to prevent charging of the sample during analysis. Metal samples which were used in the calibration of the EDS unit were not coated with gold-palladium.

3.3.4.2 Calibration of the EDS unit

Energy dispersive spectroscopy was performed using a Princeton Gamma Tech Energy Dispersive Spectrometer along with an ETEC Autoscan Scanning Electron Microscope. Calibration of the EDS unit was checked using high purity (99.9+) silver and aluminum metal standards. The measured peak locations were compared to the reported values, the peaks were labelled and plots of the spectra were obtained.

3.3.4.3 Data Collection and Analysis

Image of the sample surface was obtained on the screen of the Scanning Electron Microscope. The sample was scanned for the presence of crystals and other distinct phases. After a particle of interest was located, the magnification was increased until the feature of interest filled the entire screen. In the case of very small crystals, the highest magnification available for the instrument was used. EDS spectra were collected, in the energy range of 0 to 10 keV, from the different phases observed in the samples.

Peaks were identified by comparing measured peak locations to the peak locations reported for different elements. The major peaks in the spectra were labelled and plots were made. In most cases, more than one measured peak was matched with reported peak locations for a particular element, before identification was made.

4.0 HEAT TREATMENT OF THE GLASSES

A T-T-T diagram for the WVDP borosilicate glass was determined and a comparison of crystallization kinetics of the glass samples during isothermal and non-isothermal heat treatments was made. Non-isothermal heat treatments involved simulation of canister cooling curves and also critical cooling. Ideally, the critical cooling rate is defined as the minimum cooling rate which is required to avoid crystallization when a glass melt is cooled from the melting temperature to room temperature. However, since the reference borosilicate glass composition showed some residual crystallization, even after melting at a temperature of 1100°C, the critical cooling rate chosen was the cooling rate required to have residual crystallization of less than two volume percent. In the simulation of canister cooling curves, selected cooling curves, which were supplied by WVNS, were used in the studies.

4.1 Isothermal Heat Treatments

T-T-T diagrams were determined for glass samples WVCUO and WVCU10. For determination of the T-T-T diagram glass, samples were heat treated in the temperature range of 500 to 1000°C over time periods of 1 to 384 hours. The heat treated samples were then analyzed for crystal content.

4.1.1 Sample Preparation

Refer to Sections 2.2.2 and 2.3.2 for preparation of glasses WVCUO and WVCU10, respectively. The glasses obtained after remelting were broken into small pieces. The small pieces of glass were used in sample preparation for heat treatment.

4.1.1.1 Preparation of WVCUO Samples for Heat Treatment

Approximately 4 g of pieces of WVCUO glass were placed in crucibles made of a platinum-gold alloy. The foil crucibles had dimensions of approximately 13 x 13 x 13 mm. The samples were melted in a Thermolyne furnace for 15 min at 1100°C. At the end of melting, the samples were removed from the furnace and allowed to cool.

4.1.1.2 Preparation of WVCU10 Samples

Approximately 4 g of pieces of the partially reduced glass WVCU10 were placed in platinum - gold foil crucibles. The samples were remelted in a Thermolyne furnace for 15 min at 1100°C. At the end of melting, the samples were removed from the furnace and allowed to cool. A small amount of carbon was placed in the furnace during remelting so that the furnace atmosphere was slightly reducing. After remelting, the samples were covered completely with platinum-gold foil to minimize reoxidation of the glass during subsequent heat treatment. Mossbauer analysis of the samples after heat treatment, to determine the redox state, was not successful.

4.1.2 Heat Treatment of Glass Samples

Heat treatment schedules were chosen so that more samples were heat treated at temperatures where the glass was expected to crystallize more extensively. Sufficient amounts of glass sample were heat treated so that enough glass was available from the same sample for analysis using different techniques.

4.1.2.1 Heat Treatment of WVCUO Samples

Glass samples were heat treated in calibrated Lindberg tube furnaces. The furnace was heated to the desired temperature prior to the introduction of the sample. The temperature of the sample was monitored using a calibrated type K thermocouple placed close to the sample. A maximum of three samples were placed in the furnace at a time so that all the samples were located in the hot zone of the furnace. The temperature of the furnace during heat treatment was recorded on a strip chart recorder. At the end of heat treatment the samples were taken out of the furnace. During heat treatment the temperature in the furnace was controlled to within 2°C of the target temperature. Heat treatment times and temperatures used in this study are listed in Table 4-1.

Table 4-1. Heat Treatment Times and Temperatures for WVCUO
Sample: WVXUO (Oxidized Glass)

Temperature (°C)	Time (hours)							
500	--	--	12	24	48	96	192	384
600	3	6	12	24	48	96	192	384
650	3	6	12	24	48	96	--	--
700	3	6	12	24	48	96	192	384
750	3	6	12	24	48	96	--	--
800	3	6	12	24	48	96	192	384
850	3	6	12	24	48	96	--	--
900	3	6	12	24	48	96	192	384
1000	--	--	--	24	48	--	--	--

Samples heat treated at 650, 750, and 850°C were not analyzed

4.1.2.2 Heat Treatment of WVCU10 Samples

WVCU10 samples were heat treated in the same way as WVCUO samples. Heat treatment times and temperatures used for WVCU10 samples are listed in Table 4-2.

4.2 Non-Isothermal Heat Treatments

Nonisothermal heat treatments consisted of two main types of heat treatment schedules. One of them was cooling of the glass from the melting temperature at a specified cooling rate. The second type of nonisothermal heat treatment was done to simulate the thermal history of glasses in the canister used at WVNS. For this part of the study, canister cooling curves supplied by WVNS were used as the target heat treatment schedule. Three different glass samples were used in the studies of critical cooling and simulation of canister cooling curves. The samples were the oxidized glass WVCUO, reduced glass WVCU10 and another oxidized glass WVCUO-18. Section 2 discusses the preparation and characterization of these glasses.

Table 4-2. Heat Treatment Times and Temperatures for WVCU10
Sample: WVXU10 (Partially Reduced Glass)

Temperature (°C)				Time (hours)				
500	--	--	--	--	--	48	96	--
600	1	3	6	12	24	48	96	192
700	1	3	6	12	24	48	96	192
800	1	3	6	12	24	48	96	192
900	1	3	6	12	24	48	96	192
100+	--	--	--	--	24	--	96	--

4.2.1 Simulation of Canister Cooling Curves

The procedure for vitrification of waste at WVNS involves intermittent discharge of molten glass into a steel canister. Thus, the glass in the canister is subjected to complicated thermal histories. A few canister cooling curves were selected for the studies. Glass samples WVCUO, WVCUO-18 and WVCU10 were used in these studies.

4.2.1.1 Determination of Canister Cooling Curves

Time versus temperature data for the canister cooling curves were obtained from the TC-4 melter run at West Valley. Data files of time in hours versus temperature in celsius were made for canister curves TC1804, TC1811 and TC2312.

The data sets were fitted using third degree polynomials and the coefficients of the polynomials were determined. In order to obtain a good fit, each canister cooling curve was split up into three sets of data and the coefficients were determined. A typical canister cooling curve is given in Figure 4-1. Data were split into three sets; A-B, B-C, C-D as shown in Figure 4-1. Third degree polynomial coefficients for the canister cooling curves applicable in specific ranges of time are given in Table 4-1. These coefficients were used to calculate the furnace controller set point during the heat treatment of samples.

4.2.1.2 Simulation of Canister Cooling Curves

The experimental configuration used in the simulation of canister cooling curves is given in Figure 4-2. Samples of glass WVCUO, WVCUO-18 and WVCU10 in platinum-gold foil crucibles were placed in another crucible. The crucible was then placed in the heat treatment furnace and a calibrated thermocouple was placed next to the crucible to measure the sample temperature. The furnace was heated with the controller set to 1100°C. The initial heating took approximately 1 hour. After the furnace reached temperature, the program to simulate canister cooling curve was started. During the first step of the program, the furnace set point was modified to the starting temperature of the canister cooling curve. The set point was held constant at this temperature for 15 minutes so that the furnace and samples reached equilibrium. The required set point was then calculated as a function of time and the set point of the controller was modified from the computer at 10 s intervals. The output of the sample thermocouple was measured as millivolt readings using the digital multimeter and computer, and was subsequently converted to corresponding temperature values. Temperatures indicated by sample thermocouple, furnace control thermocouple, calculated set point, and time were recorded at 120 s intervals.

Some of the data points used in the determination of coefficients given in Table 4-3, along with the measured sample temperatures are given in Figures 4-3, 4-4, and 4-5 for canister cooling curves TC1804, TC1811, and TC2312, respectively. At the end of heat treatment, the furnace was turned off and the samples were allowed to cool in the furnace.

Table 4-3. Coefficients Used in the Calculation of Canister Cooling Curves
Temperature ($^{\circ}\text{C}$) = $A + BX + CX^2 + DX^3$ (X is time in hours)

<u>T/C No.</u>	<u>Time Range (h)</u>	<u>Coefficients</u>			
		<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>
TC1804	0.00 - 1.33	1027.350	-369.805	348.305	-126.083
TC1804	1.33 - 12.50	904.787	-41.454	3.465	-0.140
TC1804	12.50 - 24.75	797.284	-2.844	-0.901	0.018
TC1811	0.00 - 1.78	931.099	-64.016	-18.570	5.411
TC1811	1.78 - 2.08	13008.100	-19757.600	10523.500	-1842.790
TC1811	2.08 - 26.42	935.230	-39.306	1.308	-0.019
TC2312	0.00 - 3.23	1022.160	-197.576	50.326	-6.422
TC2312	3.23 - 4.53	-2245.180	1997.140	-440.338	32.384
TC2312	4.53 - 36.55	857.935	-18.050	0.234	-0.002

4.2.2 Simulation of Critical Cooling

Critical cooling studies were performed using glass samples WVCUO and WVCUO-18. The cooling rate which was predicted to give a residual crystallization of two volume percent or less, from an initial melt temperature of 1100°C , was used in the study. A cooling rate to obtain a lower amount of crystallization was not chosen because the furnace used in these studies could not be cooled at very fast rates.

4.2.2.1 Determination of Critical Cooling Rate

The method for determining the critical cooling rate is illustrated in Figure 4-6. From an initial temperature of 1100°C a line, tangential to the two volume percent curve of the T-T-T diagram, was drawn. From the intercept of this line on the x-axis, a critical cooling rate was estimated and was found to be 1.48°C per minute. For a given volume percent crystallization, the critical cooling rate depends on the initial melt temperature. 1100°C was chosen for these studies since it was derived from the routine overflow temperature of 1100°C now employed at the West Valley melter.

4.2.2.2 Simulation of Critical Cooling

Glass samples WVCUO and WVCUO-18 were used in critical cooling studies. Samples were placed in the furnace as described in Section 4.2.1.2. The furnace was heated to 1100°C and kept at that temperature until equilibrium was attained. The furnace was then cooled at a rate of 1.48°C per minute. Furnace set point was modified every 10 s and data were recorded at 120 s intervals. A few of the set point values calculated by the program and the measured sample temperatures are given in Figure 4-71.

Canister Cooling Curve - TC2312 (from TA No. 35)

Figure 4-1. Typical Canister Cooling Curve

Figure 4-2. Setup for Simulation of Canister Cooling Curve

Canister Cooling Simulation - TC1804

Figure 4-3. Canister Cooling Curve - TC1804

Canister Cooling Simulation - TC1811

Figure 4-4. Canister Cooling Curve - TC1811

Canister Cooling Simulation - TC2312

Figure 4-5. Canister Cooling Curve - TC2312

Figure 4-6. Determination of Critical Cooling Rate

Critical Cooling (1.48 C per min.)

Figure 4-7. Simulation of Critical Cooling

5.0 RESULTS

This section is divided into four sub-sections. The first part deals with redox studies on a glass composition in which iron was the only polyvalent species present. Results for the untreated glass samples used in T-T-T studies are given in the second part. The third part deals with analysis of heat treated glasses. Results of both isothermal and non-isothermal heat treatments are presented here. In the last part of this section, T-T-T diagrams are presented for the oxidized glass, WVCUO, and the reduced glass, WVCU10.

5.1 Redox Studies of the WV205 Base Glass

In addition to the development of glass standards for use in Mossbauer spectroscopy, other work was carried out to obtain a better understanding of the redox behavior of the base glass used to prepare these standards. Table 3-1 lists the composition of this glass. Results of the redox studies are tabulated in Table 5-1. From the data presented it is seen that the greatest reduction was obtained at 1050°C where the partial pressure of oxygen was the lowest. The smallest amount of reduction was obtained at 1150°C where the partial pressure of oxygen was the highest. The data indicate that equilibrium was attained in a shorter period of time at a higher temperature. These results are consistent with the fact that the lower viscosities of a melt at higher temperatures result in higher diffusion rates. We regard these data as preparatory to a full determination of the redox behavior of the system.

The glass transition temperature of some of these glasses were measured by DSC. The results are presented in Table 5-2. It is seen that as the degree of reduction increases, the glass transition temperatures decreases.

Table 5-1. Summary of Redox Studies

<u>Melting Temperature</u>	<u>PO₂ (atm)</u>	<u>Time (h)</u>	<u>Fe⁺⁺ / Total Fe</u>	
			<u>Wet Chem</u>	<u>Mossbauer</u>
1050	3.2x10 ⁻¹⁰	3	0.08	<0.07
		6	0.08	<0.07
		12	0.11	-0.07
		24	0.20	0.17
		48	0.59	0.55
1100	1.3x10 ⁻⁸	3	-	<0.07
		6	-	<0.07
		12	0.22	0.20
		24	0.22	0.19
1150	8.6x10 ⁻³	3	0.11	<0.07
		6	0.09	<0.07
		12	0.07	-0.07
		24	0.13	0.08

Oxygen partial pressure was measured using a zirconia probe

5.2 Analysis of Untreated Glasses

Results of the analysis of untreated samples of the different glasses are presented in Section 2. In this section a summary of the analysis results is presented.

5.2.1 Glass Transition Temperature

Glass transition temperatures for samples WVCUO, WVCU10 and WVCU48 along with Fe^{2+} to total iron ratio are listed in Table 2-1. Glass transition temperature decreases with an increase in the Fe^{2+} content of the glass. This is expected because in glasses Fe^{2+} acts as a network modifier whereas Fe^{3+} acts as a network former.

Table 5-2. Glass Transition Temperature versus Redox State for the Base Borosilicate Glass

<u>Fe^{++} / Total Iron Ratio</u>	<u>Glass Transition Temperature ($^{\circ}\text{C}$) *</u>
0.07	460
0.07	456
-0.07	453
0.08	455
0.17	451
0.20	449

* Glass Transition Temperatures reported here are the results of a single determination by DSC

5.2.2 Crystallization Behavior

Untreated samples of all the glasses used in this study showed the presence of some residual crystallization even after remelting for 18 hours at 1100°C . The crystals which were observed in these samples were 2.0 micrometers in size. The crystals in sample WVCUO occurred in clusters, whereas single crystals were observed in WVCU10 and WVCUO-18. Based on analysis by EDS two types of crystals were identified in the samples. One of them is an Fe_3O_4 type spinel phase and the other crystalline phase is cerium-thorium oxide. Residual crystallization as determined by image analysis varied from 0.4 to 1.6 volume percent.

5.3 Analysis of Heat Treated Glasses

Heat treated glass samples were analyzed by qualitative and quantitative X-ray diffraction, optical microscopy and image analysis, scanning electron microscopy, scanning transmission electron microscopy, and energy dispersive spectroscopy. The results are presented under three major classifications. The first part deals with oxidized glass, WVCUO. In the second part, results of the analysis of partially reduced glass, WVCU10 are presented. The third part deals with the analysis of glass samples heat treated using a schedule which simulated canister cooling curves.

5.3.1 Analysis of Oxidized Glass WVCUO

The volume percent of crystals in the heat treated glass samples was determined by image analysis. Elemental composition of the crystals was determined by energy dispersive spectroscopy. Identification of the crystal phases present in heat treated glass samples was done by x-ray diffraction.

5.3.1.1 Scanning Transmission Electron Microscopy

Identification of the samples analyzed by scanning transmission electron microscopy are listed in Table 5-3. Samples which were heat treated for short periods of time (1-3 hours) were analyzed using STEM.

Table 5-3. Identification of WVCUO Samples Used in Analysis by Scanning Transmission Electron Microscopy		
<u>Sample Designation</u>	<u>Heat Treatment Temperature (°C)</u>	<u>Heat Treatment Time (h)</u>
WVCUO		
WVCUO-600-3	600	3
WVCUO-700-1	700	1
WVCUO-700-3	700	3
WVCUO-800-3	800	3

Micrographs at two different magnifications of WVCUO sample heat treated at 700°C for 1 hour are given in Figures 5-1 and 5-2. Two types of crystals were observed in this sample. One of them is a large dark particle, approximately 2 micrometers in size, which was identified to be a spinel phase. EDS spectrum of this phase is given in Figure 5-3. The second type of crystals were much smaller in size (0.2 micrometers) and occurred in high concentrations throughout the sample. Examination of the small crystals at high magnifications showed that these crystals occur in clusters. Based upon EDS analysis, the clusters could be iron silicate crystals growing around a spinel phase.

Electron micrographs of WVCUO heat treated at 600°C for 3 hours are given in Figures 5-4 and 5-5. Two different phases can be seen in Figure 5-5. One of the phases is crystalline in nature and is similar to the small crystal clusters discussed above. The other phase is a spherical particle which appeared non-crystalline on visual examination. EDS analysis was done on a similar particle in a sample of WVCUO heat treated at 700°C for 3h and showed the presence of amounts of Ca and P. In addition, crystals of spinel (not shown in the micrographs) were observed in the sample.

STEM analysis was done on WVCUO samples heat treated at 700°C for 3 hours. Electron micrographs at two different magnifications are given in Figures 5-6 and 5-7. As can be seen from the Figures, the main features of interest are the small crystal clusters and the spherical particles. EDS analysis showed the presence of large amounts of P and Ca with smaller amounts of Th and Ce.

An electron micrograph of a crystal with a large aspect ratio observed in the sample of WVCUO heat treated at 800°C for 3 hours is given in Figure 5-8. This crystal was about 0.4 micrometers in width and several micrometers long. The crystal contains large amounts of P and Ca with minor amounts of Th and Ce. A second phase of interest observed in this sample is a large cubic crystal 3.0 micrometers in size. Electron micrograph of this crystal is given in Figure 5-9.

Figure 5-1. Electron Micrograph of WVCUO-700C-1H

Figure 5-2. Electron Micrograph of WVCUO-700C-1H

Figure 5-4. Electron Micrograph of WVCUO-600C-3H

Figure 5-5. Electron Micrograph of WVCUO-600C-3H

Figure 5-6. Electron Micrograph of WVCUO-700C-3H

Figure 5-7. Electron Micrograph of WVCUO-700C-3H

Figure 5-8. Electron Micrograph of WVCUO-800C-3H

Figure 5-9. Electron Micrograph of Cerium-Thorium Oxide Crystal in WVCUO-800C-3H

Main components of this phase are thorium and cerium. This is a cerium-thorium oxide crystal. The large spinel crystals and the smaller crystal clusters also were observed in this sample.

5.3.1.2 Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS)

Samples of WVCUO which were heat treated for 48 hours were analyzed by this technique. The analysis was done to determine the elemental composition of crystalline and other phases in the heat treated samples. Identification of the samples used in EDS analysis are tabulated in Table 5-4.

Two types of particles were observed in WVCUO glass heat treated at 500°C for 48 hours. One of them was crystalline in appearance and its EDS spectrum shows the presence of iron, chromium and nickel. This is an Fe_3O_4 type spinel phase with some of the iron substituted by other transition elements. The other particle was small in size.

Table 5-4. Identification of WVCUO Samples Used in EDS Analysis

<u>Sample Designation</u>	<u>Heat Treatment Temperature (°C)</u>	<u>Heat Treatment Time (h)</u>
WVCUO		
WVCUO-500-48	500	48
WVCUO-600-48	600	48
WVCUO-700-48	700	48
WVCUO-800-48	800	48
WVCUO-900-48	900	48
WVCUO-1000-48	1000	48

Spectra were collected from three different types of phases in WVCUO glass heat treated at 600°C for 48 hours. One type of crystalline phase showed the presence of the transition elements, Fe, Cr, Ni and Mn. This is the spinel phase. A second crystalline phase contained large amounts of thorium and cerium. This is probably a cerium-thorium oxide crystal phase. An EDS spectrum of a third phase indicated the presence of Si, Al, and K in addition to the transition elements.

The WVCUO glass samples heat treated at 700°C for 48 hours had some large crystals in them. These crystals appeared both as single crystals and as clusters. In addition, a number of smaller crystals were observed. EDS spectrum of the crystal cluster showed the presence of the spinel phase. Also, a peak due to rhodium was detected in the spectrum. EDS spectrum of a single big crystal was used to identify these crystals to be the spinel phase. The small particles were analyzed using EDS. The major elements of interest in these particles were thorium, cerium, phosphorous and calcium. Silicon and aluminum also were detected.

Based on the EDS data, three different types of crystals were identified in WVCUO glass heat treated at 800°C for 48 hours. One of the crystalline phases is an iron silicate. An EDS spectrum of the second phase identified it as cerium-thorium oxide. The spinel phase also was detected.

Crystals in the glass sample heat treated at 900°C for 48 hours were analyzed by EDS. Two of the crystalline phases were cerium-thorium oxide and spinel. An EDS spectrum was collected from a distinct particle observed

in the glass. The major component of this phase was Si. Minor amounts of Al, K, Na, Ca and Fe also were detected.

Only two types of crystals were evident during the examination of WVCUO glass heat treated at 1000°C for 48 hours. These crystals were clearly visible, with very sharp boundaries. EDS spectrum of one type of crystal was used to identify them as the spinel phase. The other type of crystal phase was cerium-thorium oxide. The concentration of both types of crystals was low.

5.3.1.3 Qualitative X-ray Diffraction (XRD)

Identification of the samples used for qualitative XRD analysis along with the results are given in Table 5-5. Phases were identified by comparison of the measured peak locations (d values) with the reported peak locations. Due to the formation of solid solutions, measured peak locations differ from the reported peak locations for pure crystals. A typical XRD spectrum of a heat treated sample is given in Figure 5-10. A spinel phase (Fe_3O_4 type structure) was observed in all the heat treated samples. Some of the Fe in the spinel are substituted by other transition elements (Cr, Ni, etc). An iron silicate (acmite) was observed in the heat treated glasses. In addition to this, an alumino silicate also was observed. A positive identification of this phase was not possible because the peaks were relatively weak. Also, a cerium-thorium oxide crystal was observed in some samples. Identification of this phase was confirmed by energy dispersive spectroscopy. The XRD spectrum of the glass as received from Catholic University showed the presence of a crystalline spinel phase.

Table 5-5. Crystalline Phase Identified by X-ray Diffraction in Heat-treated Samples of WVCUO

<u>Sample Identification</u>	<u>Crystalline Phases</u>
700°C 384 h	Spinel, acmite, alumino Silicate* Cerium-Thorium Oxide**
800°C 384 h	Spinel, Acmite, Alumino Silicate* Cerium-Thorium Oxide**
850°C 96 h	Spinel, Acmite and an unidentified phase
900°C 384 h	Spinel, Acmite and an unidentified phase

* Due to the large number of peaks observed in the XRD pattern more than one alumino silicate peak locations match the measured peak locations. Also the measured peak intensities were low.

** Identification of this phase was confirmed by energy dispersive spectroscopy.

5.3.1.4 Quantitative X-ray Diffraction Analysis

The WVCUO glass samples on heat treatment at temperatures in the range of 500 to 1000°C developed three or four different crystalline phases. An Fe_3O_4 type spinel phase with some of the iron substituted by other transition elements is present in all the heat treated samples. Also, the peaks due to this particular phase were found to be the strongest in most of the X-ray diffraction data that were collected. Due to these reasons an attempt was made to determine the amount of spinel phase only, in WVCUO glass samples heat treated at 900°C.

Figure 5-10. XRD Spectrum of WVCUO-600C-384H

Identification of the samples used in the analysis along with the analysis results are listed in Table 5-6. Area under the 100 percent peak of the spinel phase was computed, and the weight percent of this phase was determined from the calibration curve given in Figure 3-6. The weight percent values were converted to volume percent by using the density of spinel and glass to be 5.18 g/cm³ and 2.68 g/cm³, respectively.

Table 5-6. Results of Quantitative XRD Analysis			
<u>Sample Designation</u>	<u>Heat Treatment Temperature (°C)</u>	<u>Heat Treatment Time (h)</u>	<u>Vol % Spinel</u>
WVCUO-900-24	900	24	0.13
WVCUO-900-48	900	48	0.89
WVCUO-900-96	900	96	1.15
WVCUO-900-192	900	192	0.70
WVCUO-900-384	900	384	1.17

The internal standard method is the most reliable procedure for the quantitative determination of crystal phases in a sample. In this method the sample is powdered and mixed with a known amount of a standard material, such as silicon. The intensity ratio of the strongest peaks of the standard and the crystalline phase being studied are used to determine the weight percent of the specific crystalline species. In the present study, this method was not used because the glass contains uranium and thorium and the facilities for making and analyzing a large number of powdered glass samples was not available. Errors are expected in the results obtained in the present study due to the following reasons:

The standard used in calibration was Fe₃O₄, but the spinel phase that crystallizes during heat treatment contains Ni, Cr and Mn in addition to Fe. Substitution of iron by other transition elements will change the location of the peaks and also the scattering intensities.

Additionally the composition of the spinel phase may change with heat treatment time and temperature.

Due to the number of different crystalline phases present in the heat treated glasses, a large number of peaks are observed in the X-ray diffraction pattern. Some of these peaks occur at locations very close to the 100 percent peak of the spinel phase. Error in the calculated intensity of the peak being analyzed may occur due to contributions from peaks that belong to other phases.

Intensity of the peaks due to phases other than spinel are relatively low and hence the error in the quantitative XRD analysis of these phases will be even larger. Also, possible non-random orientation of crystals in the bulk sample will lead to error in the analysis. Due to these reasons, the volume percents of crystal phases were determined by optical microscopy in conjunction with image analysis.

5.3.1.5 Optical Microscopy and Image Analysis

Identification of the glass samples which were analyzed along with their thermal histories and analysis results are listed in Table 5-7.

Table 5-7. Results of Image Analysis (WVCUO)

<u>Sample Designation</u>	<u>Heat Treatment Temperature (°C)</u>	<u>Heat Treatment Time (h)</u>	<u>Vol % Crystals</u>
WVCUO-500-48	500	48	1.1
WVCUO-500-96	500	95	1.1
WVCUO-600-3	600	3	0.7
WVCUO-600-6	600	6	1.1
WVCUO-600-12	600	12	0.9
WVCUO-600-24	600	24	1.0
WVCUO-600-48	600	48	1.3
WVCUO-600-96	600	96	1.6
WVCUO-600-192	600	192	1.5
WVCUO-600-384	600	384	2.5
WVCUO-700-1	700	1	0.7
WVCUO-700-3	700	3	2.1
WVCUO-700-12	700	12	2.3
WVCUO-700-24	700	24	3.0
WVCUO-700-48	700	48	3.4
WVCUO-700-96	700	96	3.5
WVCUO-700-192	700	192	4.8
WVCUO-700-384	700	384	4.7
WVCUO-800-1	800	1	2.0
WVCUO-800-3	800	3	1.7
WVCUO-800-12	800	12	3.6
WVCUO-800-24	800	24	3.5
WVCUO-800-48	800	48	4.8
WVCUO-800-96	800	96	3.6
WVCUO-800-192	800	192	3.7
WVCUO-800-384	800	384	8.1
WVCUO-900-3	900	3	1.7
WVCUO-900-6	900	6	1.0
WVCUO-900-12	900	12	1.0
WVCUO-900-24	900	24	2.3
WVCUO-900-48	900	48	3.4
WVCUO-900-96	900	96	2.9
WVCUO-900-192	900	192	4.5
WVCUO-1000-24	1000	24	1.1
WVCUO-1000-48	1000	48	0.7

The glass crystallizes in the temperature range of 600 - 900°C. A few large crystals of spinel and cerium-thorium oxide were observed in the glasses heat treated at 1000°C. The glass samples heat treated at 900°C contained mainly large crystals with a few small crystals. The samples heat treated in the temperature range of 600-800°C contained some large crystals and a large number of small crystals. The area of the large crystals were of the order of $5 \times 10^{-5} \text{ mm}^2$ whereas the small crystals had an average area of $5 \times 10^{-7} \text{ mm}^2$. The samples heat treated at 500°C contained some large crystals. It is possible that these crystals did not form during the heat treatment because the untreated glass also contained some large crystals. An untreated, remelted sample of WVCUO contained a few isolated large crystals (approximately 0.4 volume percent). An untreated sample of WVCUO-18 (which was remelted for 18 hours at 1100°C) contained approximately 1.6 volume percent crystals. It was concluded that this residual crystallization is a property of this glass composition. Selected optical micrographs of the heat treated glass samples are given in Figures 5-11 to 5-32. All the samples were photographed using reflected light optics.

5.3.2 Analysis of Partially Reduced Glass WVCU10

Samples of glass WVCU10 which were given isothermal heat treatments were analyzed in the same way as WVCUO samples.

Figure 5-11. Optical Micrograph of WVCUO Glass Heat-treated for 48 Hours at 500 °C (400X)

Figure 5-12. Optical Micrograph of WVCUO Glass Heat-treated for 96 Hours at 500 °C (400X)

Figure 5-13. Optical Micrograph of WVCUO Glass Heat-treated for 3 Hours at 600 °C (400X)

Figure 5-14. Optical Micrograph of WVCUO Glass Heat-treated for 6 Hours at 600 °C (400X)

Figure 5-15. Optical Micrograph of WVCUO Glass Heat-treated for 192 Hours at 600 °C (400X)

Figure 5-16. Optical Micrograph of WVCUO Glass Heat-treated for 384 Hours at 600 °C (400X)

Figure 5-17. Optical Micrograph of WVCUO Glass Heat-treated for 1 Hour at 700 °C (400X)

Figure 5-18. Optical Micrograph of WVCUO Glass Heat-treated for 3 Hours at 700 °C (400X)

Figure 5-19. Optical Micrograph of WVCUO Glass Heat-treated for 96 Hours at 700 °C (400X)

Figure 5-20. Optical Micrograph of WVCUO Glass Heat-treated for 192 Hours at 700 °C (400X)

Figure 5-21. Optical Micrograph of WVCUO Glass Heat-treated for 384 Hours at 700 °C (400X)

Figure 5-22. Optical Micrograph of WVCUO Glass Heat-treated for 1 Hour at 800 °C (400X)

Figure 5-23. Optical Micrograph of WVCUO Glass Heat-treated for 3 Hours at 800 °C (400X)

Figure 5-24. Optical Micrograph of WVCUO Glass Heat-treated for 6 Hours at 800 °C (400X)

Figure 5-25. Optical Micrograph of WVCUO Glass Heat-treated for 192 Hours at 800 °C (400X)

Figure 5-26. Optical Micrograph of WVCUO Glass Heat-treated for 384 Hours at 800 °C (400X)

Figure 5-27. Optical Micrograph of WVCUO Glass Heat-treated for 3 Hours at 900 °C (400X)

Figure 5-28. Optical Micrograph of WVCUO Glass Heat-treated for 6 Hours at 900 °C (400X)

Figure 5-29. Optical Micrograph of WVCUO Glass Heat-treated for 48 Hours at 900 °C (400X)

Figure 5-30. Optical Micrograph of WVCUO Glass Heat-treated for 192 Hours at 900 °C (400X)

Figure 5-31. Optical Micrograph of WVCUO Glass Heat-treated for 24 Hours at 1000 °C (400X)

Figure 5-32. Optical Micrograph of WVCUO Glass Heat-treated for 48 Hours at 1000 °C (400X)

5.3.2.1 Scanning Transmission Electron Microscopy

Identification of WVCU10 samples used in analysis by Scanning Transmission Electron Microscopy (STEM) are given in Table 5-8. Analysis using STEM was performed only on samples which were heat treated for short periods of time (1 to 3 hours).

Table 5-8. Identification of WVCU10 Samples Used in Analysis by Scanning Transmission Electron Microscopy		
<u>Sample Designation</u>	<u>Heat Treatment Temperature (°C)</u>	<u>Heat Treatment Time (h)</u>
WVCUO		
WVCU10-600-3	600	3
WVCU10-700-1	700	1
WVCU10-700-3	700	3
WVCU10-800-3	800	3
WVCU10-900-3	900	3

Electron micrographs of WVCU10 heat treated at 700°C for 1 hr are given in Figures 5-33 and 5-34. Two different types of crystals can be seen in Figure 5-33. EDS analysis was done on the cubic crystals which were approximately 0.5 micrometers in size. The EDS spectrum collected from a typical cubic crystal shows that this is the spinel phase. As compared to the oxidized glass given the same heat treatment these crystals are slightly larger in size. The second type of crystals were needle like in appearance, and an EDS spectrum collected from this phase shows that it contains large amounts of P and Ca with minor amounts of Th and Ce.

Micrographs at two different magnifications of sample WVCU10 heat treated at 600°C for 3 hours are given in Figures 5-35 and 5-36. Crystal clusters (about 1.5 micrometers size) can be seen in both micrographs. EDS spectra collected from the center of the crystal cluster shows it contains large amounts of Fe with minor amounts of Cr, Ni, and Mn. This is probably the spinel phase. EDS spectrum of a typical crystal which is seen around the central spinel phase shows that the elements present in this phase are Fe and Si with small amounts of Al and Ca. These crystals could be an iron silicate phase (eg. acmite). An EDS spectrum was collected from a large cubic crystal (not shown in the micrographs) and shows the presence of large amounts of Fe and Cr with minor amounts of Ni. This is the spinel phase which was observed in all the samples.

An electron micrograph of a sample of WVCU10 heat treated at 700°C for 3 hours is given in Figure 5-37. The only phase seen in this micrograph are cubic crystals, approximately 0.4 to 0.5 micrometers in size. An EDS spectrum collected from this phase indicated that this phase is a spinel.

Micrographs of WVCU10 heat treated at 800°C for 3 hours are given in Figures 5-38 and 5-39. Two types of crystals can be seen in Figure 5-38. The cubic crystals are about 0.4 to 0.5 micrometers in size and EDS analysis shows the presence of Fe, Ni, Mn and Cr. The crystal contains large amounts of P and Ca with minor amounts of Th and Ce.

The cubic spinel phase can be clearly seen in electron micrographs of WVCU10 sample heat treated at 900°C for 3 hours. The micrographs are given in Figures 5-40 and 5-41.

Figure 5-33. Electron Micrograph of WVCU10-700C-1H

Figure 5-34. Electron Micrograph of WVCU10-700C-1H

Figure 5-35. Electron Micrograph of Crystal Clusters in WVCU10-600C-3H

Figure 5-36. Electron Micrograph of a Crystal Cluster in WVCU10-600C-3H

Figure 5-37. Electron Micrograph of WVCU10-700C-3H

Figure 5-38. Electron Micrograph of WVCU10-800C-3H

Figure 5-39. Electron Micrograph of WVCU10-800C-3H

Figure 5-40. Electron Micrograph of WVCU10-900C-3H

Figure 5-41. Electron Micrograph of WVCU10-900C-3H

5.3.2.2 Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS)

SEM and EDS analysis was performed on samples which were heat treated for long periods of time (24-48 hours). Identification of the samples used in the EDS analysis are given in Table 5-9.

Table 5-9. Identification of WVCU10 Samples Used in EDS Analysis

<u>Sample Designation</u>	<u>Heat Treatment Temperature (°C)</u>	<u>Heat Treatment Time (h)</u>
WVCU10		
WVCU10-500-48	500	48
WVCU10-600-48	600	48
WVCU10-700-48	700	48
WVCU10-800-48	800	48
WVCU10-900-48	900	48
WVCU10-1000-24	1000	24

EDS spectra were collected from four different phases observed in a WVCU10 sample heat treated at 500°C for 48 hours. One of the phases was a large cubic crystal, and the EDS spectrum of this phase shows that it is an Fe_3O_4 type spinel phase with part of the Fe substituted by other transition elements like Cr and Ni. EDS spectrum of a small cubic crystal shows it contains large amounts of Fe with minor amounts of Cr, Mn and Ni. This is also a spinel crystal. The main difference between the large and the small spinel crystals is that the large crystals contain a larger amount of chromium. EDS spectrum collected from another crystalline particle showed it contained a large amount of Rh and Ru. An EDS spectrum collected from a distinct particle seen in the sample identified large amounts of Ce and La. Particles with this composition were not observed in any other sample.

An EDS spectrum of a large spinel crystal observed in the sample of WVCU10 heat treated for 48 hours at 600°C shows the presence of Rh in addition to the transition elements. It is possible that Rh acts as nucleation sites for the formation of spinel crystals. EDS spectrum of a small crystal shows the presence of the transition elements along with Si, Al, Ca and K. Since the crystal was really small in size it is possible that contributions from the glass matrix gave rise to the peaks due to Si, Al, K and Ca. EDS spectrum of a particle in the same sample shows the particle contains large amounts of Rh. One particle was composed almost entirely of sulfur. Sulfur particles were not observed in any other sample.

EDS spectra of two large crystals in the sample of WVCU10 heat treated at 700°C for 48 hours were taken. One of the crystals is the spinel phase.

The other crystal is a cerium -thorium oxide. Compared to the same type of crystal in the oxidized glass, this crystal contains a larger amount of thorium and a very small amount of cerium.

EDS spectra were collected from four different phases in WVCU10 glass heat treated at 800°C for 48 hours. Spectra of a large spinel phase and of a small spinel crystal showed varying amounts of Fe, Ni, and Cr.

The EDS spectrum collected from a large cubic crystal identified it to be cerium-thorium oxide. EDS spectrum of another particle shows the presence of P, Ca and Si in addition to Th and Ce.

Two thorium containing phases observed in WVCU10 samples heat treated at 900°C for 48 hours could not be identified. A spinel phase was also observed.

WVCU10 glass heat treated at 1000°C for 24 hours contained very few crystals. EDS spectra were collected from two distinct particles which were observed in the sample. EDS spectrum of one particle shows the presence of Si, Al and K. The other particle contained Si, Fe, Al, Mg and very small amounts of Mn.

5.3.2.3 Qualitative X-ray Diffraction (XRD)

Identification of the samples used in qualitative XRD analysis along with the results are given in Table 5-10. Phases were identified by comparison of the measured peak locations (d values) with the reported peak locations. Due to the formation of solid solutions, measured peak locations differ from the reported peak locations for pure crystals. A spinel phase (Fe_3O_4 type structure) was observed in all the heat treated samples of WVCU10. Some of the Fe in the spinel phase are substituted by other transition elements (Cr, Ni etc). A sample heat treated at 900°C showed the presence of only two phases; spinel and cerium-thorium oxide. Acmite is probably present in the samples heat treated at 600, 700 and 800°C, but, a positive identification of this phase could not be made due to very low peak intensities.

Table 5-10. Crystalline Phases Identified by X-Ray Diffraction in Heat-Treated Samples of WVCU10

<u>Sample Identification</u>	<u>Crystalline Phases</u>
600°C 192 h	Spinel, Acmite
700°C 192 h	Spinel, Acmite*, Cerium-Thorium Oxide*
800°C 192 h	Spinel, Acmite, Cerium-Thorium Oxide*
900°C 384 h	Spinel and Cerium-Thorium Oxide

*Since the intensity of the peaks were low a positive identification could not be made.

5.3.2.4 Optical Microscopy and Image Analysis

Identification of the glass samples which were analyzed along with their thermal histories and analysis results are listed in Table 5-11.

The glass crystallizes in the temperature range of 500 - 900°C. Samples heat treated in the temperature range of 500 - 800°C contained a large number of small crystals and a few large crystals. The small crystals had an average area of approximately $7 \times 10^{-7} \text{ mm}^2$ and the large crystals had areas about one to two orders of magnitude larger. The small crystals were identified by x-ray diffraction and energy dispersive spectroscopy to be an Fe_3O_4 type spinel phase. The large crystals were mainly spinel and cerium-thorium oxide. The glass samples heat treated at 900°C contained mainly large crystals with a few small crystals. Glass samples which were heat treated at 1000°C for 24 hours and 48 hours contained only a few large crystals (0.4 volume percent). An untreated sample of WVCU10 contained 1.0 volume percent crystals. Selected optical micrographs of the heat treated glass samples are given in Figures 5-42 to 5-61. All the samples were photographed using reflected light optics.

Table 5-11. Results of Image Analysis (WVCU10)

<u>Sample Designation</u>	<u>Heat Treatment Temperature (°C)</u>	<u>Heat Treatment Time (h)</u>	<u>Vol % Crystals</u>
WVCU10	Untreated Glass Sample		1.0
WVCU10-500-48	500	48	3.0
WVCU10-500-96	500	96	5.4
WVCU10-600-1	600	1	3.7
WVCU10-600-3	600	3	3.9
WVCU10-600-6	600	6	4.0
WVCU10-600-12	600	12	5.5
WVCU10-600-24	600	24	6.4
WVCU10-600-48	600	48	5.6
WVCU10-600-96	600	96	5.1
WVCU10-600-192	600	192	4.3
WVCU10-700-1	700	1	3.6
WVCU10-700-3	700	3	3.1
WVCU10-700-6	700	6	3.0
WVCU10-700-12	700	12	4.6
WVCU10-700-24	700	24	4.2
WVCU10-700-48	700	48	3.5
WVCU10-700-96	700	96	5.5
WVCU10-700-192	700	192	5.6
WVCU10-800-1	800	1	2.5
WVCU10-800-3	800	3	3.0
WVCU10-800-6	800	6	2.5
WVCU10-800-12	800	12	2.5
WVCU10-800-24	800	24	2.9
WVCU10-800-48	800	48	5.0
WVCU10-800-96	800	96	4.4
WVCU10-800-192	800	192	4.6
WVCU10-900-1	900	1	1.1
WVCU10-900-3	900	3	1.4
WVCU10-900-6	900	6	1.5
WVCU10-900-12	900	12	1.3
WVCU10-900-24	900	24	2.2
WVCU10-900-48	900	48	3.7
WVCU10-900-96	900	96	4.8
WVCU10-900-192	900	192	4.3
WVCU10-1000-24	1000	24	0.3
WVCU10-1000-96	1000	48	0.4

Figure 5-42. Optical Micrograph of WVCU10 Glass Heat-treated for 1 Hour at 600 °C (400X)

Figure 5-43. Optical Micrograph of WVCU10 Glass Heat-treated for 3 Hours at 600 °C (400X)

Figure 5-44. Optical Micrograph of WVCU10 Glass Heat-treated for 96 Hours at 600 °C (400X)

Figure 5-45. Optical Micrograph of WVCU10 Glass Heat-treated for 192 Hours at 600 °C (400X)

Figure 5-46. Optical Micrograph of WVCU10 Glass Heat-treated for 1 Hours at 700 °C (400X)

Figure 5-47. Optical Micrograph of WVCU10 Glass Heat-treated for 3 Hours at 700 °C (400X)

Figure 5-48. Optical Micrograph of WVCU10 Glass Heat-treated for 96 Hours at 700 °C (400X)

Figure 5-49. Optical Micrograph of WVCU10 Glass Heat-treated for 192 Hours at 700 °C (400X)

Figure 5-50. Optical Micrograph of WVCU10 Glass Heat-treated for 1 Hour at 800 °C (400X)

Figure 5-51. Optical Micrograph of WVCU10 Glass Heat-treated for 3 Hours at 800 °C (400X)

Figure 5-52. Optical Micrograph of WVCU10 Glass Heat-treated for 6 Hours at 800 °C (400X)

Figure 5-53. Optical Micrograph of WVCU10 Glass Heat-treated for 12 Hours at 800 °C (400X)

Figure 5-54. Optical Micrograph of WVCU10 Glass Heat-treated for 192 Hours at 800 °C (400X)

Figure 5-55. Optical Micrograph of WVCU10 Glass Heat-treated for 1 Hour at 900 °C (400X)

Figure 5-56. Optical Micrograph of WVCU10 Glass Heat-treated for 3 Hours at 900 °C (400X)

Figure 5-57. Optical Micrograph of WVCU10 Glass Heat-treated for 6 Hours at 900 °C (400X)

Figure 5-58. Optical Micrograph of WVCU10 Glass Heat-treated for 48 Hours at 900 °C (400X)

Figure 5-59. Optical Micrograph of WVCU10 Glass Heat-treated for 96 Hours at 900 °C (400X)

Figure 5-60. Optical Micrograph of WVCU10 Glass Heat-treated for 192 Hours at 900 °C (400X)

Figure 5-61. Optical Micrograph of WVCU10 Glass Heat-treated for 96 Hours at 1000 °C (400X)

5.3.3 Analysis of Samples Given Non-Isothermal Heat Treatment

In this section analysis done on two types of heat treated glass samples are presented. One type of heat treatment was cooling at a specified cooling rate from a starting temperature of 1100°C. The other type is a heat treatment schedule which closely approximated the canister cooling curves. Volume percent of crystals in the heat treated glasses were determined by reflected light optical microscopy in conjunction with image analysis. Crystal phases were identified by X-ray diffraction and energy dispersive spectroscopy.

5.3.3.1 Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS)

Identification of the samples used in this analysis are given in Table 5-12.

Table 5-12. Identification of Samples Used in SEM Analysis (Non-Isothermal Heat Treatments)

<u>Sample ID</u>	<u>Base Glass</u>	<u>Heat Treatment Schedule</u>
WVCUO-CR.-COOL	WVCUO	Cooled at 1.48°C per minute from 1100°C
WVCUO-TC2312	WVCUO	Canister Cooling curve TC2312*
WVCUO-18-TC1804	WVCUO-18	Canister Cooling curve TC1804*
WVCUO-TC1811	WVCU10	Canister Cooling curve TC1811*

* TC1804, TC1811, and TC2312 refer to canister cooling curves recorded during West Valley Melter Run TC-4.

Three EDS spectra were collected from WVCUO sample which was cooled at 1.48°C per minute from a starting temperature of 1100°C. EDS spectra collected from one of the big crystals showed the presence of Fe, Cr, Ni and minor amounts of Mn. This is the Fe_3O_4 type spinel phase with a large amount of Fe replaced by Cr and Ni. Small amounts of Rh also were detected. A large number of small crystals were observed in the sample. The crystals were too small in size, and hence the spectrum collected contained contributions from the surroundings of this phase. The main components in this phase are Fe, Mn, Cr and Ni. A big particle observed in the sample showed the presence of Si, Al, Fe, K and Na.

EDS spectra were collected from a sample of WVCUO which underwent heat treatment to simulate canister cooling curve TC2312. The sample contained both big and small crystals. The smaller crystals were numerous and uniform throughout the sample. The bigger crystals occurred both as single crystals and crystal clusters. EDS spectrum of one type of big crystal shows the spinel phase. The other type of big crystal showed the presence of thorium and cerium. An EDS spectrum typical of the small crystals shows that they contain large amounts of Fe with minor amounts of Mn, Cr, Ni and Ti.

Another sample used in EDS analysis was glass WVCUO-18 given heat treatment to simulate canister cooling curve TC1804. Two types of crystals were found in this sample. One contained thorium and cerium. The other crystal is the spinel phase and contains Fe, Mn, Cr, Ni and Ti. EDS spectrum was collected from a particle which was observed in the sample. The particle contained Si, Al, Fe, K and Na.

EDS spectra were collected from a sample of WVCU10 heat treated to simulate canister cooling curve TC1811. This sample also contained small and large crystals. Some large crystals are spinel. A crystal cluster phase contains Th, Ce, Si, Fe, P, Ca and Al. EDS spectrum of a small crystal showed it to be also a spinel crystal. The difference between the small and the large spinel crystals is that the large crystals contain a large amount of chromium whereas the small crystals are composed almost entirely of Fe.

5.3.3.2 Qualitative X-ray Diffraction (XRD)

X-ray diffraction data were collected from samples of WVCUO and WVCU10 that were given heat treatments to simulate canister cooling curves TC2312 and TC1804. A spinel phase and one cerium-thorium oxide phase were identified in both heat treated samples. The main phases identified from the XRD data were the spinel and cerium-thorium oxide. It is possible that acmite also is present in the sample. However, the peak intensities were too low to make a positive identification of this phase. Positive identification of only the spinel phase could be made from this data.

5.3.3.3 Optical Microscopy and Image Analysis

Identification of the samples used in this analysis are given in Table 5-13. Samples of WVCUO and WVCUO-18 given the same heat treatments appeared similar on qualitative examination of the sections. Based on the size, most of the crystals could be classified into two groups. The small crystals had an average area of approximately $5.0 \times 10^{-7} \text{ mm}^2$. The other type of crystals, which will be referred to as the big crystals, were one to two orders of magnitude bigger than the small crystals. The small crystals observed in samples of WVCU10 were slightly larger than the small crystals seen in WVCUO samples.

Table 5-13. Results of Image Analysis

<u>Sample Designation</u>	<u>Heat Treatment Schedule</u>	<u>Vol % Crystals</u>
WVCUO-TC1804	TC1804	5.1
WVCUO-TC1811	TC1811	4.8
WVCUO-TC2312	TC2312	4.8
WVCUO-18-TC1804	TC1804	3.8
WVCUO-18-TC1811	TC1811	3.2
WVCUO-18-TC2312	TC2312	6.1
WVCU10-TC1804	TC1804	5.6
WVCU10-TC1811	TC1811	7.5
WVCU10-TC2312	TC2312	4.0
WVCUO-CR.-COOL	Cooled at 1.48°C per minute from 1100°C	1.6
WVCUO-18-CR.-COOL	Cooled at 1.48°C per minute from 1100°C	2.4

* TC1804, TC1811, and TC2312 are notations for canister cooling curves.

WVCUO and WVCUO-18 samples cooled at 1.48°C per minute contained the big crystals and a very small number of small crystals. Samples of all glasses given heat treatment which simulated TC1804 contained mainly large crystals with a few small crystals. Heat treatment which simulated TC1811 produced some big crystals and a large number of small crystals. TC2312 heat treatment produced mainly big crystals in samples WVCUO, WVCUO-18 and WVCU10. Canister cooling curves TC1811 and TC2312 are very similar. But, heat treatment to simulate TC1811 produced a large number of small crystals whereas TC2312 heat treatment produced mainly big crystals. The reason for the difference in the microstructures developed during these two heat treatments is not known. Optical micrographs of the samples are given in Figures 5-62 to 5-72.

Figure 5-62. Optical Micrograph of WVCUO-TC1804

Figure 5-63. Optical Micrograph of WVCUO-18-TC1804

Figure 5-64. Optical Micrograph of WVCU10-TC1804

Figure 5-65. Optical Micrograph of WVCU10-TC1811

Figure 5-66. Optical Micrograph of WVCUO-TC1811

Figure 5-67. Optical Micrograph of WVCUO-18-TC1811

Figure 5-68. Optical Micrograph of WVCUO-TC2312

Figure 5-69. Optical Micrograph of WVCUO-18-TC2312

Figure 5-70. Optical Micrograph of WVCUO-CR Cool

Figure 5-71. Optical Micrograph of WVCUO-18-CR Cool

Figure 5-72. Optical Micrograph of WVCU10-TC2312

Volume fractions of the total crystal content present in the heat treated glass samples were determined by image analysis. Results of the analysis are tabulated in Table 5-13.

A cooling rate of 1.48°C per minute, from a starting temperature of 1100°C, was predicted to induce total volume percent crystals of 2 percent or less in glass sample WVCUO. Glass samples WVCUO and WVCUO-18 were heat treated at this cooling rate. The crystal content in the heat treated samples of WVCUO and WVCUO-18 were 1.6 and 2.4 volume percent respectively.

5.4 Determination of T-T-T Diagrams

Quantitative T-T-T diagrams were determined for glasses WVCUO and WVCU10. T-T-T diagrams were based on total amount of crystallization, observed in isothermally heat treated glass samples, as determined by image analysis.

5.4.1 T-T-T Diagram for Glass WVCUO

Plots of volume percent crystals versus heat treatment time for WVCUO samples are given in Figures 5-73 to 5-76 for 600, 700, 800 and 900°C, respectively. Volume percent crystals in the heat treated glass samples are tabulated in Table 5-7. Plots of volume percent crystals versus log time are given in Figures 5-77 to 5-80. From these plots heat treatment times required to obtain 1.5, 2.0 and 3.0 volume percent crystals at 600, 700, 800 and 900°C were obtained. Time of heat treatment to obtain 2.0 volume percent crystals at 600°C was obtained by extrapolating the data given in Figure 5-77, assuming a linear relationship between volume percent crystals versus log heat treatment time. Heat treatment times for different amounts of crystallization are given in Table 5-14. From these data, a T-T-T diagram for glass WVCUO was constructed and is given in Figure 5-81; i.e., T-T-T curves were drawn for 1.5, 2 and 3 volume percent crystallization.

Based on the results of image analysis, the approximate liquidus temperature was estimated to be 1000°C for glass WVCUO. The critical cooling rate to obtain less than 2 volume percent crystallization was determined from the T-T-T diagram. From a starting temperature of 1100°C, the critical cooling rate was estimated to be 1.48°C per minute. The mechanical construction which gave this cooling rate is presented in Figure 4-6.

As seen in Figures 5-73 to 5-80, there is some scatter in the data. This could in part be due to the residual crystallization present in untreated samples and also to minor inhomogeneities in the samples used for heat treatment.

5.4.2 T-T-T Diagram for Glass WVCU10

Plots of volume percent crystals versus heat treatment time for WVCU10 samples are given in Figures 5-82 to 5-85 for 600, 700, 800 and 900°C respectively. Volume percent crystals in the heat treated glass samples are tabulated in Table 5-11. Plots of volume percent crystals versus log time are given in Figures 5-86 to 5-89. From these plots heat treatment times required to obtain 4.0 and 4.5 volume percent crystals at 600, 700, 800 and 900°C were obtained. Heat treatment times for different amounts of crystallization are given in Table 5-15. From these data, a T-T-T diagram for glass WVCU10 was constructed and is given in Figure 5-90; i.e., T-T-T curves were drawn for 3 and 4 percent crystallization.

Table 5-14. Estimated Heat Treatment Times for 1.5, 2.0, and 3.0 Volume Percent Crystallization in WVCUO

Heat Treatment Temperature (°C)	Volume Percent Crystallization	Heat Treatment Time (h)
600	1.5	86.8
600	2.0	1036.1
700	1.5	2.8
700	2.0	5.7
700	3.0	22.7
800	1.5	2.2
800	2.0	3.9
800	3.0	12.0
900	1.5	3.7
900	2.0	8.8
900	3.0	50.5

Based on the results of image analysis, liquidus temperature of glass WVCU10 was estimated to be 1000°C or less. Some scatter is observed in the data of volume percent crystallization versus heat treatment time. This could be due to the residual crystal content of the glass and also due to sample to sample variations. Another reason for this scatter could be error in the analysis technique. Most of the samples contained a large number of very small crystals ($\sim$ area 0.5×10^{-7} mm²). This size is approximately the lower detection limit of the system, using the highest magnification available, and hence some error is expected. An accurate determination of this error could not be made, but was estimated to be less than one percent.

Table 5-15. Estimated Heat Treatment Times for 4.0 and 4.5 Volume Percent Crystallization in WVCU10.

Heat Treatment Temperature (°C)	Volume Percent Crystallization	Heat Treatment Time (h)
500	4.0	~60.0
500	4.5	~89.0
600	4.0	2.7
600	4.5	9.3
700	4.0	13.2
700	4.5	38.9
800	4.0	39.8
800	4.5	125.9
900	4.0	251.0
900	4.5	

The data at 500°C is very approximate because only two samples were heat treated at this temperature.

Figure 5-73. Heat Treatment Time versus Crystallization in WVCUO at 600°C

Figure 5-74. Heat Treatment Time versus Crystallization in WVCUO at 700°C

WVCUO Heat Treated at 800 C

Figure 5-75. Heat Treatment Time versus Crystallization in WVCUO at 800°C

Figure 5-76. Heat Treatment Time versus Crystallization in WVCUO at 900°C

WVCUO Heat Treated at 600 C

Figure 5-77. Log Time versus Crystallization in WVCUO at 600°C

Figure 5-78. Log Time versus Crystallization in WVCUO at 700°C

WVCUO Heat Treated at 800 C

Figure 5-79. Log Time versus Crystallization in WVCUO at 800°C

Figure 5-80. Log Time versus Crystallization in WVCUO at 900°C

TTT Diagram for Glass - WVCUO

Figure 5-81. TTT Diagrams for Glass WVCUO

Figure 5-82. Heat Treatment Time versus Crystallization in WVCU10 at 600°C

Figure 5-83. Heat Treatment Time versus Crystallization in WVCU10 at 700°C

Figure 5-84. Heat Treatment Time versus Crystallization in WVCU10 at 800°C

WVCU10 Heat Treated at 900 C

Figure 5-85. Heat Treatment Time versus Crystallization in WVCU10 at 900°C

Figure 5-86. Log Time versus Crystallization in WVCU10 at 600°C

WVCU10 Heat Treated at 600 C

Figure 5-87. Log Time versus Crystallization in WVCU10 at 700°C

Figure 5-88. Log Time versus Crystallization in WVCU10 at 800°C

WVCU10 Heat Treated at 900 C

Figure 5-89. Log Time versus Crystallization in WVCU10 at 900°C

TTT Diagram for Glass - WVCU10

Figure 5-90. TTT Diagram for Glass WVCU10

6.0 SUMMARY AND CONCLUSIONS

Samples of a fully simulated reference borosilicate glass were prepared with different oxidation states. The oxidation state of the glass melt was controlled by remelting in a controlled atmosphere furnace. Samples were prepared in which the Fe^{++} to total iron ratio varied from 0.0 to 0.48. Glass transition temperature decreased with an increase in the amount of Fe^{++} .

A procedure was developed for the determination of the Fe^{++} to total iron ratio in fully simulated nuclear waste glasses which contain more than one polyvalent ion. This procedure involved the analysis of the Mossbauer spectra of these glass samples. The samples used in the development of this procedure covered a Fe^{++} to total iron ratio of 0.1 to 0.64. Over this range, a one-to-one correlation was observed in the results obtained by wet chemical analysis and Mossbauer spectroscopy.

Crystallization behavior of the fully oxidized glass WVCUO (all the iron in Fe^{+++} state) and a partially reduced glass WVCU10 (Fe^{++} to total iron ratio of 0.1) were studied. The samples were crystallized using isothermal and non-isothermal heat treatment schedules. The non-isothermal heat treatment schedules closely approximated the canister cooling curves received from West Valley Nuclear Services Company.

Heat treated glass samples were analyzed by optical microscopy, image analysis, scanning transmission electron microscopy, scanning electron microscopy, energy dispersive spectroscopy and X-ray diffraction. Untreated samples of all the glasses which were used in the crystallization studies showed a small amount of residual crystallization at 1100°C. Compared to the fully oxidized glass WVCUO, the temperature of maximum crystallization was lower in the partially reduced glass, WVCU10. An Fe^3O_4 type spinel phase with part of the Fe replaced by Cr, Ni and Mn was observed in all the samples. Compared to the oxidized glass, the spinel phase was richer in iron in the reduced glass. Also, a cerium-thorium oxide crystal was observed in a number of samples. Cerium content of this crystal was higher in the oxidized glass samples when compared to the partially reduced glass. A crystal containing calcium and phosphorous was observed in some of the heat treated glass samples.

Some of the samples, heat treated according to canister cooling curves, showed larger amounts of crystallization. Some of the canister cooling curves involve both heating and cooling cycles and hence the samples were subjected to a two stage heat treatment schedule. This might act as a nucleation heat treatment followed by a crystal growth step in which case the total crystal content of the heat treated samples will be higher than that observed for continuous cooling or isothermal heat treatments.

Time-Temperature-Transformation (T-T-T) diagrams were determined for the fully simulated reference borosilicate glass melts WVCUO and WVCU10. The nose of the T-T-T curve is at a lower temperature for the partially reduced glass, WVCU10. Also, in most samples the total crystal content was higher in the WVCU10 sample when compared to WVCUO sample given the same heat treatment.