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**Letter Report -- Minor Component
Study for Low-Level Radioactive
Waste Glasses**

H. Li

March 1996

**Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830**

**Pacific Northwest National Laboratory
Operated for the U.S. Department of Energy
by Battelle Memorial Institute**

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Pacific Northwest National Laboratory
Richland, Washington 99352

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SUMMARY

During the waste vitrification process, troublesome minor components in low-level radioactive waste streams could adversely affect either waste vitrification rate or melter life-time. Knowing the solubility limits for these minor components is important to determine pretreatment options for waste streams and glass formulation to prevent or to minimize these problems during the waste vitrification. A joint study between Pacific Northwest Laboratory and Rensselaer Polytechnic Institute has been conducted to determine minor component impacts in low-level nuclear waste glass.

This letter report provides the research results obtained from both Laboratories since September 1994. The solubility limits of five minor components (Cl, F, P_2O_5 , SO_3 , and Cr_2O_3) in L6-5412 glass (56.8SiO₂, 5B₂O₃, 20Na₂O, 4CaO, 12Al₂O₃, and 2.2Others, by wt%) were determined for a temperature range from 1300 to 1400 °C, within which the temperature dependence of the solubility for each minor component was minor. Glass major composition effect was also investigated at 1350 °C using L4-9012 glass (56.8SiO₂, 9B₂O₃, 20Na₂O, 12Al₂O₃, and 2.2Others, by wt%). Except for chlorine, results showed that minor component solubility limits were affected by changing glass composition. Comparing with minor component solubilities in L6-5412, substitution of CaO by B₂O₃ increased the solubilities by about 30%, 120%, and 100% for F, P_2O_5 , and Cr_2O_3 , respectively, but decreased the solubility of SO_3 by about 40%. Using L6-5412 glass, potential vitrification problems associated with these minor components were investigated. For glasses containing minor components in excess of the solubility limits, molten glasses exhibited high volatility for Cl, F, and SO_3 , but not for P_2O_5 and Cr_2O_3 , and crystalline phase formation in the bulk glass or phase segregation on the molten glass surface. The effects of the minor components on glass melt viscosity and glass chemical durability (7-day PCT) were also investigated for L6-5412 glass containing the minor components at the solubility limits. Fluorine in glass significantly reduced the melt viscosity and hence the melting temperature decreased by 67 °C and other minor components appeared to slightly increase the melt viscosity, among which chlorine had the most effect, the melting temperature being increased by 23 °C. Effect of minor components on glass chemical durability was measurable but insignificant based on the normalized sodium release, less than 25%.

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1. INTRODUCTION

The recently renegotiated Tri-Party Agreement (TPA, 1994) between the State of Washington Department of Ecology (Ecology), Department of Energy (DOE), and the United States Environmental Protection Agency (EPA) specified vitrification as the encapsulation technology for Hanford's low-level waste (LLW). The TPA specifies that a reference LLW glass formulation that meets complete system requirements be established by June 1996. LLW glass formulation at Pacific Northwest Laboratory, PNL, (Richland, Washington) has been in progress to fulfill the milestone, and to support WHC's (Westinghouse Hanford Company) melter system evaluation (Wilson, 1994).

Hanford Site single-shell tank (SST) and double-shell tank (DST) waste are planned to be separated into low activity (or low-level waste, LLW) and high activity (or high-level waste, HLW) fractions and vitrified for disposal. The LLW is characterized by its high sodium content, averaging about 80% wt% Na_2O in oxide composition. High sodium waste limits the LLW loading in final glass waste forms, primarily by its impact on glass chemical durability. However, some types of wastes have high enough concentrations of minor components, including Cl, F, P_2O_5 , SO_3 , and Cr_2O_3 . These troublesome minor components could cause potential problems in the waste glass vitrification process. These problems are related to volatility or formation of a second phase from these minor components. For example, volatility of halide species can accelerate corrosion of melter off-gas equipment, facility, etc. Formation of crystalline phases in the melt can either promote a phase segregated layer on the melt surface or cause crystal settling at the bottom of melter, which adversely affects waste glass vitrification rate or melter life-time.

This minor component study for LLW glass is an important part of LLW glass formulation program at the PNL. The study addresses critical issues relevant to the glass formulation, and to the melter evaluation, including solubilities of these minor components in LLW glass, glass composition effect on the solubilities, effects of the minor components in glass on waste processibility, and their impacts on chemical durability of final glass waste forms. This letter report summarizes results obtained from this study since September 1994, mainly focusing on a particular glass system, L6-5412. In addition, the glass composition effects on the

minor component solubility limits are under investigation. For L4-9012 glass containing no calcium and 9.0 wt% boron oxide, the minor component solubility values were determined and also included in this report.

2. EXPERIMENTAL PROCEDURES

Solubilities of minor components, Cl, F, P_2O_5 , SO_3 , and Cr_2O_3 , were determined for L6-5412 base glass. A method of single minor component addition into the base glass was used in the current investigation. The melting temperature of L6-5412 glass ($1351^\circ C$) was determined experimentally, at which glass melt viscosity is 10 Pa.s (cf. Figure 27). The minor component solubilities were determined within the base glass melting temperature range, $1300^\circ C$, $1350^\circ C$ and $1400^\circ C$, in ambient air. Table 1 lists L6-5412 glass composition, originally containing a small amount of each minor component of interest.

The minor component loadings covered in this study for L6-5412 glass are in Table 2. Sixty-eight glasses were made. According to glass compositions in Appendix A(1-5), a 500-g batch of each glass was prepared from oxides, carbonates and sodium-containing reagents. Each batch was then mixed in a grinding cell using an Angstrom® grinding machine for 5 min to achieve a homogeneous mixture.

To prepare glass samples, a 130-g batch was transferred into a Pt-10%Rh crucible with a 250 cm^3 capacity. A ratio of the top surface area of batch to the volume of batch was kept at about 2.0 cm^2 for each melt. Each batch was placed immediately in a Deltech® DT-31 furnace at a desired melting temperature. Furnace temperature was controlled by a Honeywell® controller/programmer and monitored by one S-type thermocouple on the controller and a second independent S-type thermocouple. These thermocouples were located in the middle of furnace hot zone. Variation in temperature readout from the two thermocouples was $\pm 1.0^\circ C$ with respect to the present melting temperatures. To check foaming, several early batches were initially melted without a Pt-lid cover on the crucible for the first 5 min. In these cases, initial foaming was negligible; therefore, the remaining batches were melted with a lid on the crucible.

Each melt was held at a preset melting temperature for a total of 2 hr. After the first hour melting, the crucible was taken out of the furnace and the melt was stirred vigorously using a platinum rod to ensure glass homogeneity. Upon melting completion, the molten glass was

partially poured into a steel mold, and then annealed at 520°C for 2 hr in a Thermoline® 2000 furnace, and finally cooled to room temperature, for which the cooling rate was not controlled. The remaining portion of the melt was quenched in air at room temperature. The quenched samples, which were homogeneous, transparent, and free of crystals, were used to determine the solubility limits of the minor components. In some other cases, a whole melt was quenched to evaluate a distribution of crystals from the top to the bottom of the melt.

Final total weight of each glass was recorded. The total weight, including glass, crystals (either in the glass matrix or on the surface of the melt), and a small amount of glass sample taken out by the platinum rod during the melt stirring, was measured using a Mettler® PM4600 balance. The total weight loss was reported in terms of weight percentage of glass obtained against the weight of batched glass :

$$WL \text{ (wt\%)} = 100(W_o - W_m) / W_o \quad (1)$$

where WL is the total weight loss in terms of weight percentage, W_o is the weight of oxides and these minor components calculated from amount of batch material used, and W_m is the weight of glass obtained.

Glass compositions were analyzed using XRF (x-ray fluorescence) spectroscopy and ICP (inductively coupled plasma) spectroscopy. Crystalline phases in glass samples were analyzed using XRD (x-ray diffraction). Some samples were also characterized using SEM/EDS (scanning electron microscopy with energy dispersive spectroscopy). An optical microscope, a LECO® Olympus PGM-3, was used to examine crystals in all glass samples.

Once the solubility limits of the minor components were determined, melt viscosities of the base L6-5412 glass and glasses containing each minor component at its solubility level were measured in the temperature range from 1100 °C to 1450 °C. The viscosity of glass melt was measured using a Brookfield® DV-II viscometer in a Deltech® DT-31 furnace. Spindle factor was determined using standard NBS-711 glass. At 1300°C, the temperature at which these glasses were prepared, viscosity was determined three times: at the beginning, in the middle, and at the end of the viscosity measurement.

The effect of minor components on glass chemical durability in water was studied using the product consistency test (PCT) method (Jantzen and Bibler, 1990). Samples of both L6-5412 glass and glasses containing each of the five minor components at their solubility limits were

used. Samples were prepared by crushing quenched glasses, made at 1350°C, in a tungsten carbide grinding cell using an Angstrom® grinding machine. Particle sizes of pulverized samples were controlled from 75 to 150 µm by using 100 and 200 mesh sieves. To remove fines, the pulverized samples were washed five times using fresh acetone each time, for about 2 min in an ultrasonic bath. The washed powders were kept at 90 °C in a Blue M® OV-490A-2 oven prior to the PCT.

Duplicates were used for the PCT. For each sample, 4.0 g of pulverized glass was weighed using a precision balance, Sartorius® A200S. Deionized water, having a resistivity of 17.1 megohm and pH 6.01, was used as leachant. The leachant of 40.0 g, measured using a Mettler® PM4600 balance, was mixed with 4.0 g powder in a Teflon® container to be used for the test. The ratio of the surface area (SA) of powder to the volume (V) of leachant was hence fixed at ~2000 m²/l. During the test, sample containers were placed in a Blue M® OV-490A-2 oven at the preset temperature, 90°C. The temperature of the oven was monitored by two thermometers, the difference between which was 0.1°C during 7-day PCT.

Before and after the PCT, the pH values of leachates were measured using an Orion® 601A digital ionalyzer calibrated using Fisher® standard buffer solutions with pH7.0 and pH10.0, respectively. To measure the initial pH values for each glass, a separate mixture of powder and water was made with the same SA/V ratio. The measurements were performed after the mixtures were prepared about 10 min. The final pH measurements of leachates were made using the leachates after 7 days.

The concentrations of cations for major glass components plus P, S, and Cr were analyzed using inductively-coupled plasma (ICP). Chlorine and fluorine in solutions were analyzed using ion chromatography (IC) and selective ion electrode (SIE), respectively. First, each solution was filtered using a 0.45 µm filter. For cation analyses, the filtered solutions were then acidified with 0.1 vol% nitric acid to minimize ionic species absorbed by container. For anion analyses, the filtered solutions were not acidified to prevent interference between the acid and elements of interests during the chemical analyses.

Knowing concentrations of each element released into water, normalized elemental mass loss, (NL)_i, was calculated according to (Mendel, 1986) :

$$(NL)_i = C_i / [f_i (SA/V)] \quad (2)$$

where C_i is the concentration (g/m³) of element i in the 0.45 μ m-filtered solution and f_i is the mass fraction of element i in the glass.

3. RESULTS

3.1 Solubility of Minor Components

Chemical analyses were performed for all of 68 glass samples made at three temperatures, 1300, 1350, and 1400°C. Appendixes B(1&2) and C(1-22) tabulate the analytical results for L6-5412 glass and its base glasses spiked with the minor components. The solubility of each minor component was determined by its highest concentration in the quenched glass sample, at which both quenched and annealed glasses were homogeneous, amorphous to x-ray, and had no detectable crystals under an optical microscope (Li, 1994). The solubilities are represented in a form of Cl, F, P₂O₅, SO₃, and Cr₂O₃ in glass network, respectively.

Before presenting the solubility data, it should be noted that in general, the true solubility limits could be higher at temperatures from which the glasses were quenched. A good example can be found in fluorine-spiked glass. The high fluorine-containing melts were transparent, but became either translucent or opalescent once the molten glasses cooled. The results suggest that fluorine is soluble in the melt at higher temperatures, but the glass became over-saturated during cooling. Similar observations were made for other minor component-containing glasses, but the transition from transparent to translucent was difficult to detect in situ. The solubility data provided in this report should be considered as a lower bounds of these limits, providing safe margins for both glass formulation and the actual waste vitrification process. In addition, using the low bounds of solubility limits for glass formulation prevents glasses from minor component-related over-saturation in the glass during glass cooling, which is important since there is little knowledge of how the minor component-crystallized phases impact the waste glass vitrification and chemical durability of the final waste forms.

Figure 1 illustrates solubility limits of the five minor components in L6-5412 glass at 1300, 1350, and 1400°C (see also Table 3). Within experimental error, it appears that melting temperature has a negligible influence on the solubilities within the temperature range studied. Table 3 also includes solubility values (Cl, F, SO₃, and P₂O₅) in L6-5412 glass, which were

independently determined at Rensselaer Polytechnic Institute, RPI, (Crichton and Tomozawa, 1994). For Cl, SO₃, and P₂O₅, the solubility data are in a good agreement with those determined in our laboratory. However, RPI reported significantly higher solubility value for fluorine at 1100 °C. The higher fluorine solubility was related to undetected NaF nuclei in the quenched glass sample. Later, it was confirmed by heat-treating the sample at 480 °C for about 30 min. After the heat-treatment, the sample turned into opal. Hence, the datum reported at 1100°C should not be used as the solubility limit for fluorine.

A solubility limit of each minor component was determined by melting a relatively small quantity, 110 g, of batch for 2 hr. The effect of batch size and melting time on the solubility was further evaluated. Samples were first made from large batch-size melting, ~500 g, for 2 hr at 1300 °C, and then melted in a temperature range between 1100 and 1450 °C for an additional 7hr, during which time molten glasses were continuously stirred by a Pt spindle. These large batches separately contained each minor component according to the concentration level shown in the first row of Table 2. Table 4 compares concentrations of the minor components in glasses made from both large and small batch sizes at 1300 °C. Within experimental uncertainty, results suggested that the solubility limits were unaffected by the batch size and melting time.

3.2 Volatilization of Minor Components

For glasses spiked with minor components in excess of their solubility limits, weight loss of molten glass during melting was significant for certain minor components, including Cl, F, and SO₃. Figure 2(a-c) presents total weight losses for both original L6-5412 glass and glasses containing minor components at 1300, 1350, and 1400 °C, respectively. Volatility of the base glass was negligible as depicted by the dash lines shown in Figure 2(a-c). Chemical composition analyses of L6-5412 glass showed the measured compositions matching those in the batch (cf. Table 1 and Appendix B[1&2]).

High weight loss for some glasses was caused mainly by volatilization of certain minor components, including Cl, F and SO₃. Figure 3(a-c) compares the measured minor component concentrations with those as batched. Two general, distinguished trends are evident. Glasses containing various amounts of either P₂O₅ or Cr₂O₃ had little weight loss during melting at all

three temperatures. Significantly higher weight losses were observed for the glasses having high contents of Cl, F or SO₃. For a glass batch with 5.0 wt% Cl addition, the total weight loss of glass was more than the chlorine loading in the batch, suggesting that other species also volatilized from the melt. Analytical glass composition analyses suggested volatilization of boron and sodium contributed to the weight loss (cf. Appendix A1 and Appendix C1.4).

3.3 Effect of Minor Components on Crystalline Phase Formation

In addition to volatilization of chlorine, fluorine, and sulfate, phase segregation on the surface of molten glass or crystallization in the glass bulk took place once the concentrations of the minor components exceeded their solubility limits in the glass.

3.3.1 Chlorine-Spiked Glass

Figure 4(a-c) illustrates optical micrographs of the vertical cross-sections of quenched glass melts with 5.0 wt% Cl addition, which were melted at 1300, 1350, and 1400°C, respectively. Accumulation of a spherical crystalline phase toward the melt surface is evident, the extent of which increases with decreasing melting temperature.

On the melt surface, a molten salt layer was also observed. Figure 5(a&b) shows a SEM micrograph of the molten salt layer and its EDS pattern, showing the phase high in sodium and chlorine. In the glass matrix shown in Figure 6(a), the crystalline phase precipitates mostly inside of bubbles as depicted in Figure 6(b). Figure 7 illustrates an XRD pattern of the same glass, identifying the crystalline phase in the bulk as NaCl.

3.3.2 Fluorine-Spiked Glass

Glass containing fluorine in excess of its solubility became opalescent and opaque upon cooling from the melting temperature. The spontaneous opacification was directly related to simultaneous nucleation and crystal growth of CaF₂ (Flannery and Wexell, 1986). Figure 8(a&b) illustrates SEM micrograph and EDS pattern of glass spiked with 10.0 wt% F addition and melted at 1300 °C, suggesting the crystals containing Na, Ca and F. The crystalline phases were identified by XRD as NaF and CaF₂ (cf. Figure 9). With lower fluorine additions in the batch, between 3.0 and 2.8 wt%, samples only showed opalescence after heat-treated at 520 °C, suggesting the presence of NaF nuclei in the quenched samples, but not CaF (Flannery and Wexell, 1986).

3.3.3 Phosphate-Spiked Glass

Glass containing phosphate in excess of its solubility also became opalescent and opaque upon the melt cooling. XRD results shown in Figure 10 reveal the glass contained crystalline phases of Na_3PO_4 and $\text{Na}_2\text{Ca}_4(\text{PO}_4)_2\text{SiO}_4$. Possible crystalline phases, such as $\text{Ca}_3(\text{PO}_4)_2$ and $\text{Ca}_3(\text{PO}_4)_2\text{X}(\text{SiO}_4)_2$ (where $\text{X}=1$ or 2) were examined, which were previously reported for aluminoborosilicophosphate glasses (Bogomolova, et al., 1993). No matches were found between standard XRD patterns for the cited crystalline phases and those XRD patterns shown in Figure 10.

In addition to the phosphate-containing crystals in the bulk of glass, phase segregation on the top of the melt was observed at 1300°C for glass spiked with 10.0 wt% P_2O_5 , which is shown in Figure 11. Figure 12(a&b) shows SEM micrographs, comparing the matrix with the phase-separated surface layer. Figure 13(a-c) illustrates EDS patterns for both the matrix (cf. Figure 12a) and two segregated phases (cf. Figures 12b). For the phase-segregated layer, EDS results clearly show one phase enriched in Si and another enriched in Ca and P. At 1350°C or 1400°C , a phase-segregated layer was not observed for melts of the same glass, suggesting the melt was likely outside of a glass immiscibility boundary for this particular glass system (Tomozawa, 1979).

3.3.4 Sulfate-Spiked Glass

Glass containing sulfate in excess of its solubility formed a variety of crystalline phases. Figure 14 shows an optical micrograph of glass with 2.0 wt% SO_3 addition, and melted at 1300°C . In this case, phase segregation was observed in three regions: the meniscus area, at a contacting area near the bottom of crucible wall and the melt, and through the bulk. Figure 15 represents the XRD pattern, identifying the segregated phase in the meniscus area as Na_2SO_4 . Figure 16(a&b) represents SEM micrographs of the melt surface in contact with the Pt-10%Rh crucible wall, revealing two types of segregated phases. In the region shown in Figure 16(a), both sulfate-rich and phosphate-rich phases are evident as revealed by EDS in Figure 17(a). In the area shown in Figure 16(b), the phosphate-rich phase appeared to be dominant as depicted in Figure 17(b). The volume percentage of the crystals in the glass matrix was too small to be detected by XRD, but its presence was confirmed using an optical microscope. The crystalline phase was considered to be a sulfate-rich phase, probably Na_2SO_4 , the same as the segregated

phase in the meniscus area. A spherical crystalline phase, Na_2SO_4 , in the bulk of glass was also reported for silicate glass containing over-saturated sulfate (Sakai, et al., 1994).

Simultaneous sulfate and phosphate phase segregation suggested that an interaction between sulfate and phosphate caused the phosphate-rich phase segregation even below the phosphate solubility limit. Sulfate-induced phosphate segregation has also been observed in high-level waste glass during vitrification when sulfate is over-saturated in the melt (Li, et al., 1994). In addition, Cr-rich phase segregation could be also induced by sulfate segregation, which was observed in LD6-5510 low-level waste glass (56.91 SiO_2 , 20 Na_2O , 5 B_2O_3 , 5 CaO , 10 Al_2O_3 , and 3.09 Others, by wt%). This glass was made from calcined simulant and glass frit, which contains 0.21 wt% SO_3 and 0.04 wt% Cr_2O_3 . During melting at 1300 °C, a molten salt layer of sulfate was formed on the melt surface as depicted in Figure 18(a&b). EDS analyses, shown in Figure 18(c&d), revealed that chromium was also present in the sulfate layer, but not (detectable) in the glass matrix.

3.3.5 Chromium Oxide-Spiked Glass

Crystals in the glass matrix were observed for samples containing chromium oxide in excess of its solubility. Figure 19(a-c) shows SEM micrograph and EDS spectra for the selected area, indicating that the crystal is high in chromium. Figure 20 shows the XRD pattern of the glass with 2 wt% Cr_2O_3 addition, identifying these crystals as chromium oxide.

The presence of Cr_2O_3 crystals raised concern regarding whether or not these crystals would settle to the bottom of crucible during a prolonged melting process. Figure 21(a-c) shows optical micrographs of glass having 2.0 wt% Cr_2O_3 and melted at 1300°C for 40 hr in an alumina crucible covered by an alumina lid. The melt was not stirred during the melting. From the top to the bottom of the melt, a distribution of Cr_2O_3 crystals is fairly uniform, suggesting no crystal settlement during the prolonged melting. These crystals likely precipitated from the glass melt during the sample cooling. It should be, however, noted that chromium oxide could form spinel-like crystals for glass containing higher iron, which might cause crystal settlement.

3.4 Large-Size Batch Pile Melting

The purpose of using relatively larger batch-size melting was to examine whether the change in the melting geometry, in terms of volume of batch to surface area of the melt surface,

had any effects on the minor component solubilities or phase segregation during melting. The first concern has been addressed in Section 3.1, which is relevant for volatile minor components. The second concern was related generally to all minor components. A specific consideration was that by increasing volume of batch without changing the melt top surface area, lower melting point minor component-containing phases might accumulate on the top of the molten glass during the initial melting stage, because as seen in the larger batch, the volume of the segregated phase per top surface area increased.

Several large-size batch melts, about 500 g each, were hence made at 1300 °C. These batches separately contained 1.0% Cl, 2.5% F, 2.5% P₂O₅, 1.0% SO₃, and 0.5% Cr₂O₃ by weight. Each batch had about the same top surface area as the previous one for the smaller batch-size melting. For the batch of L6-5412 glass and one containing 0.5 wt% Cr₂O₃, no phase segregation on the melt surface nor crystals in the bulk were found after one hour. However, for batches containing Cl, F, P₂O₅, and SO₃, small amounts of phase segregation near the top of the molten glass were observed after one hour, which was not previously found during the smaller size batch melting.

For the batch having 1.0 wt% Cl, no crystalline phase was detectable optically in the glass matrix. However, an optical micrograph in Figure 22 shows that the glassy phase, on the crucible wall just above the melt surface, was translucent. Similar observations were made for batches having 2.5 wt% F and 2.5 wt% P₂O₅. Some translucent glassy phases were found on the crucible wall above the melt surface as seen in Figure 23 and 24, respectively. No additional characterizations were made for these glassy phases, in which crystals were considered to be related to those previously identified (cf. Sections 3.3.2 and 3.3.3).

For the batch with 1.0 wt% SO₃ addition, phase segregation was observed in three areas: on the crucible wall, in the meniscus area, and on the contacting surface between the melt and the crucible. Figure 25 illustrates sulfate molten salt segregation in the meniscus area as well as on the crucible wall. Figure 26(a) exhibits the sulfate segregation on the contacting surface area closer to the top of the melt. Figure 26(b) shows a detailed view of the cross-section as identified by an arrow in Figure 26(a), demonstrating that the sulfate crystalline phase imbeds in the glass matrix. The bulk of glass away from the phase-segregated area was free of crystals as confirmed by an optical microscope.

The observed small amount of phase segregation near the vicinity of the meniscus area for some of the minor component-spiked glasses was considered to be related to a slight over-saturation of the minor components in the glass during the early batch melting stage. After grinding the first hour melt together with a small amount of the phase-segregated portion, the glass was remelted for the second hour, during which no phase segregation was observed for any of these glasses. It confirms that the phase segregation was caused by the composition inhomogeneity in the molten glass during the initial melting stage.

3.5 Effect of Minor Components on Glass Melt Viscosity

Figure 27(a-f) illustrates measured viscosities of molten glasses in a temperature range from 1100 to 1450 °C. These glasses had each minor components at their solubility limits (cf. Table 3). In general, variations for repeated measurements, at about 1300 °C, were less than 10% of an average value. Appendix D summarizes the viscosity data. Fluorine was found to reduce the melt viscosity significantly. Other minor components appeared to slightly increase the melt viscosity in the temperature range studied.

For each glass, the melting temperature was determined, corresponding to a melt viscosity of 10 Pa.s, by using the Arrhenius equation to fit the viscosity data within a higher temperature regime as depicted by the solid lines in Figure 27(a-f). At the solubility levels of these minor components, fluorine reduced the melting temperature of the base glass by 67 °C, while chlorine increased the melting temperature by 23 °C. Phosphate and sulfate slightly increased the melting temperature by 10 °C. Within experimental uncertainty, the effect of chromium oxide was negligible.

3.6 Effect of Minor Components on Glass Chemical Durability

Both ion exchange of alkali species in glass with water and glass dissolution into water lead to an increase in leachate pH (Li and Tomozawa, 1995). Figure 28 illustrates the pH values before and after the PCT test (see also Appendix E). The initial pH values of solutions were about 9.5, as compared with ~pH6.0 for deionized water alone. Except for glass spiked with fluorine, the solution pH values were higher than that of the base glass. After the 7-day PCT, solution pH values increased above pH11.0. However, the trend of pH between the base glass

and the glasses spiked with minor components was similar to that of the initial pH values.

Appendix E tabulates the PCT data for L6-5412 glasses made at 1350 °C, which contain the minor components at the solubility limits (cf. Table 3). Figure 29 illustrates the normalized elemental mass loss of Na, B, Si and Al for these glasses. Normalized sodium release is much higher than the normalized releases of the glass network formers, Si, B, and Al. A similar level of the elemental releases for Si, B, and Al is indicative of congruent glass dissolution during the test, while an offset for sodium is primarily related to ion exchange in an earlier stage of the test.

Sodium is considered to be a good indicator for glass susceptibility to water attack based on its high solubility in water, provided that Na is not incorporated in the secondary phase. No secondary phases were found, under an optical microscope, for any samples after 7-day PCT. Relative to the sodium release, $(NL)_{Na}$, of the base glass, the release decreased by ~9 % $(NL)_{Na}$ for F-spiked glass, but increased by 9, 14, 20, and 25 % $(NL)_{Na}$ for SO_3^- , Cl^- , $P_2O_5^-$, and $Cr_2O_3^-$ spiked glasses, respectively. A similar ranking can be also found relative to the boron release of the base glass. Fluorine-spiked glass appears to improve the chemical durability, while the rest of the minor components seem to lower glass chemical durability. Overall, the effects of minor components, at their solubility levels, on glass chemical durability was small for L6-5412 glass. However, solubility of these minor components may vary with base glass composition. An impact of minor components on glass chemical durability for other glass compositions has to be investigated experimentally to achieve better understanding of the functions of these minor components in the glass network.

Comparing trends of the normalized elemental releases with those of the pH values, before and after the test, reveals that they are parallel to one another (cf. Figures 28&29), suggesting an initial pH influence on the glass dissolution. The initial pH differential may be related to the buffering power of these minor components leached out of the glass. The concentrations of the minor components in leachates were found to be higher for glasses spiked with these components (cf. Appendix E2).

The observed initial pH effect may not be generalized for other glasses exhibiting hydrated crystalline surface layers during glass dissolution. For those cases, the elemental releases of alkali species and glass network formers are affected by both the network dissolution

and re-precipitation of some of the saturated glass components in water.

3.7 Effect of Glass Compositions on Minor Component Solubility

In general, a variation in glass composition is expected to affect minor component solubility in glass. To establish a broad database for the minor component solubilities of interest in low-level waste glasses, Table 5 tabulates other selected base glass compositions. The selection was based on three factors: minor component-containing crystalline phases found in L6-5412 glass (cf. sections 3.3.1-3.3.5); chemical durability test results of FY-94 LLW glasses obtained so far from MCC-1 and 7-day PCT; and the test matrix of FY-94 LLW glasses formulated at the Pacific Northwest Laboratory (Kim, 1994). Data obtained for L6-5412 glass showed that the melting temperature had a negligible effect on the solubility levels of these minor components (cf. Figure 1). Hence, the minor component solubilities, for the other remaining base glasses, will be determined only at 1350°C.

Solubilities of these minor components were also determined for L4-9012 glass following the same experimental procedures described previously for L6-5412 glass. Using L4-9012 glass composition as a basis, 15 glasses were made according to the test matrix shown in Table 6. The solubility values of all five minor components in L4-9012 glass are summarized in Table 7, in which those in L6-5412 glass are also included for comparison. Within experimental uncertainty, removing calcium from the glass had no effect on chlorine solubility, but increased fluorine solubility by ~30%, and significantly raised phosphate solubility by more than 120%. Chromium oxide solubility was increased by about 100%, although it is not fully understood whether it is related to calcium or to boron. Sulfate solubility, however, decreased by about 40 %, which could be associated with the changes of both calcium and boron (Holmquist, 1966 and Papadopoulos, 1977).

4. DISCUSSIONS

4.1 Minor Components in Glass

4.1.1 Halide Species (Cl, F)

A limited amount of chlorine can be incorporated into silicate glass melt by substitution for bridging oxygen, Si-O-Si or BO, in a form of (Sun and Silverman, 1945) :

where Si-O is the non-bridging oxygen (NBO). The low solubility limit for chlorine lies in its larger ionic radius, 1.81 Å, compared to oxygen, 1.38 Å. According to solubilities obtained for L6-5412 and L4-909 (cf. Table 7), it seems that the variation of boron had no influence on chlorine solubility. Single-bond strengths are 119 and 89 kcal for BO₄ and BO₃, respectively, while that for SiO₄ is 106 kcal (Sun, 1947), which suggests chlorine substitution for bridging oxygen being at least equally difficult for both Si-O bond and B-O bond.

However, fluorine substitution for BO is expected to be easier for its smaller ionic radius, 1.31-1.33 Å. The substitution is similar to the reaction (3) :

This substitution has been confirmed using infrared spectroscopy in alkali silicate glasses (Takusagawa, 1980).

It should be pointed out that NBO is always polarized in a way which provides good screening (or shielding) of the silicon and, therefore, fluorine substitution for NBO is unlikely. Rather, fluorine replaces one of BOs, the polarisability of which to the first Si is weakened by the presence of the second Si (Rabinovich, 1983). Incorporation of chlorine in the glass network may be expected to be analogous to fluorine case, i.e., chlorine substituting for the BO, rather than the NBO as described by Reaction (3).

Although a higher fluorine solubility than that of chlorine in glass is expected, according to this study, fluorine appears to be limited by alkali and alkaline earth ions, such as Na and Ca, in low-level waste glass. The melting temperatures of NaF and CaF₂ are 988°C and 1378°C, respectively (CRC Handbook, 1984). For a silicate melt containing high contents of Na and Ca, formation of CaF₂ crystals is very likely at the temperatures (1300-1400°C), while the formation of NaF is also expected during the melt cooling. According to this study, for L6-5412 glass spiked with a higher amount of fluorine, greater than 3.3 wt% F, CaF₂ and NaF crystals were formed, while CaF₂ resulted in glass-spontaneous opalescence. For the glasses spiked with fluorine in a range from 2.8 to 3.0 wt% F, CaF₂ crystals were not detectable. Instead, NaF nucleation took place when the melt cooled. Therefore, the quenched samples were transparent, but became opalescent after heat treatment at 520°C. Hence, sodium has probably the strongest effect on the fluorine solubility in the low-level waste glasses. When reviewing fluorine

solubilities in L6-5412 and L4-9012 glasses (cf. Table 7), it can be seen that by removing calcium from glass, the increase in fluorine solubility was marginal.

4.1.2 Phosphate

Phosphorous is a glass former. In a variety of phosphorous-containing silicate and borate glass systems, building blocks of glass network may be in the following forms (Carlyle and Smith, 1978, Kosinski, et al., 1988, Kolesova, 1981 and Carter, et al., 1994). :

where $\equiv$ represents three BOs to Si. Therefore, interconnected three-dimensional structures among Si, B, Al, and P are expected. For silicate glass, however, phosphorous is also known as a nucleation agent to promote glass devitrification and amorphous phase separation (Tomoazawa, 1972). One of the crystalline phases found in this study for phosphate-spiked L6-5412 glass was $\text{Na}_2\text{Ca}_4(\text{PO}_4)_2\text{SiO}_4$. The formation of such a complex phase may suggest that the melt was in a state of amorphous phase separation in glass. Several studies also showed that amorphous phase separation promotes crystallization in glass. It was proposed that the amorphous phase separation made the crystallization easier by either letting the liquid-phase composition approach the crystal composition through phase separation (Roy, 1962) or by creating nucleation sites at the interface of glass-in-glass phase separation (Ohlberg, et al., 1962). At the highest P_2O_5 level, the phase separation was indeed observed in this study (cf. Figure 12[b]). It is known that phosphate addition into sodium silicate glass increases the glass immiscibility boundary (Tomoazawa, 1972). Accordingly, it is expected that the solubility of phosphate in low-level waste glass may be limited by formation of phosphate containing crystals, which can be induced by the phase separation. A comparison of the phosphate solubilities between L6-5412 glass with calcium and L4-9012 glass without calcium clearly demonstrates that a great increase in phosphate solubility once calcium is removed from glass.

4.1.3 Sulfate

For sulfur gas, SO_3 , or a mixture of SO_2 and O_2 , is bubbled into a molten soda-silicate glass, the reactions for silica-soda and sulfate-soda may be (Papadopoulos, 1973):

where K_1 and K_2 are the equilibrium constants, which are expressed as:

$$K_1 = a(\text{NBO}) / [a(\text{BO}) a(\text{FO})] \quad (7a)$$

$$K_2 = a(\text{NaSO}_4) / [P(\text{SO}_3) a(\text{Na}_2\text{O})] = a(\text{NaSO}_4) / [P(\text{SO}_3) a^2(\text{Na}^+) a(\text{FO})] \quad (8a)$$

where $a(i)$ and $P(i)$ are the activity and the partial vapor pressure of species i of interest, respectively, NBO is the nonbridging oxygen, Si-O, BO is the bridging oxygen, Si-O-Si, and FO is the free oxygen, O^{2-} .

By substituting $\gamma(i)C(i)$ for $a(i)$ in Equation (7a) and (8a), where $\gamma(i)$ and $C(i)$ are the activity coefficient and concentration of the species i of interest, respectively, solubility of sulfate in glass can be expressed as :

$$C(\text{SO}_3) = C(\text{Na}_2\text{SO}_4) = \xi P(\text{SO}_3) [C(\text{Na}^+)C^2(\text{NBO})/C(\text{BO})] \quad (9)$$

where ξ is equal to $(K_2/K_1)\{[\gamma^2(\text{Na}^+)\gamma^2(\text{NBO})]/[\gamma(\text{BO})\gamma(\text{Na}_2\text{SO}_4)]\}$, which is assumed to be invariant with glass compositions of interest. According to Equation (9), the sulfate solubility in silicate glass, under a given vapor pressure, $P(\text{SO}_3)$, is sensitive to the concentrations of both NBO and BO in glass.

Sulfate solubilities determined for L6-5412 and L4-9012 glasses (cf. Table 7) are in good qualitative agreement with Equation (9). Relative to L6-5412, $C(\text{BO})$ in L4-9012 glass was higher as a result of the increase of B_2O_3 , from 5 to 9 wt%, while $C(\text{NBO})$ was lower with a removal of CaO. Applying the same methodology to glass formulation, a better glass composition than L4-9012 glass may be formulated by using less Al_2O_3 (9 wt%) to increase sulfate solubility and at the same time not to significantly affect the other minor component solubilities.

Regarding sulfate concentration in excess of its solubility in glass, the excessive amount of SO_4^{2-} in Reaction (8) will segregate from the molten glass. Where the viscosity of molten glass is low, ~ 4 Pa.s, the segregated sulfate tends to accumulate mostly on the surface, forming a layer. The evaporation of the sulfate layer may be expressed by the reaction (Holmquist, 1966):

and then

Gaseous SO_2 tends to escape from the melt if the partial pressure product, $(P_{\text{SO}_2})(P_{\text{O}_2})^{1/2}$, above the melt is low according to Reaction (11), which in turn reduces the solubility of sulfate in the

melt. This may explain the high sulfate volatility of L6-5412 glass containing sulfate above its solubility.

In general, sulfate solubility decreases with increasing melting temperature for a given closed system in which partial pressures of SO_2 and O_2 are held constant (Holmquist, 1966). In this study, the furnace atmosphere was not controlled. Within experimental uncertainty, the solubility of sulfate obtained in L6-5412 glass appeared to be constant for a temperature range from 1300 to 1400°C. The effect of small amount of iron (0.005 wt% Fe_2O_3) and chromium (0.036 wt% Cr_2O_3) on sulfate solubility is unknown. At present, it is assumed that their influence was negligible.

The sulfate solubility determined in this study is an apparent value since sulfate in the is not in an equilibrium state with the atmosphere above the melt. Under either oxidizing or reducing conditions, a diffusion coefficient, D (cm^2/s) of SO_2 in borosilicate melt was reported (Schreiber, et. al, 1988) :

$$\log D = -3.08 - (3300/T) \quad (12)$$

where T is the temperature (K). The above equation was actually fit to the diffusion data for a temperature range between 1050 and 1150°C. Assuming the same equation valid at higher temperatures, 1300°C, the diffusion distance, d , of SO_2 in the melt can be approximated, by $d = (Dt)^{1/2}$, to be 2.2 mm for $t = 2$ hr and 4.6 mm for $t = 9$ hr. Accordingly, it is expected that SO_3 decreases with increasing melting time. However, from comparison of solubility values between 2 h-melt and 9 h-melt (cf. Table 4), it appears that at the solubility level, sulfate in the glass was stable thermally. The stability of sulfate dissolved in glass suggests that sulfate could be in equilibrium with bubbles in the melt. These fine bubbles are difficult to diffuse from a high viscous melt, which provide a local environment for the stability of sulfate dissolved in the glass network. However, at 1500°C, severe reboiling of glass containing sulfate at its low-temperature solubility limit was observed as shown in Figure 30. The sulfate reboiling at 1500 °C was indicative of its solubility reduction, which generates O_2 and SO_2 gas according to Reaction (11). The stable foam observed here is believed to be nucleated from small bubbles that pre-exist in the melt (Kim and Hrma, 1991 & 1992).

4.1.4 Chromium Oxide

It has been postulated that Cr^{3+} is in a form of chromic complex retained in a silicate ring composed of three bridging oxygens (BO or O^{b}), and three nonbridging oxygens (NBO or O^-). The redox equilibrium between Cr^{3+} and Cr^{6+} in the melt is hence expressed by the reaction (Singh and Nath, 1981) :

or

Reaction (13) shows that Cr^{3+} can be retained in the melt if oxygen partial pressure is low or the melt is in a reducing state. For a silicate glass with 20 mol % Na_2O melted at 1400°C , the $\text{Cr}^{6+}/\text{Cr}^{3+}$ ratio was reported to be about 0.006, suggesting that most of chromium in the melt was in Cr^{3+} state (Paul, 1990). For the low-level waste glass investigated here, only Cr_2O_3 was precipitated from the glass matrix; the glass looked greenish, suggesting that the melt is in a reducing state.

The ratio of $\text{Cr}^{6+}/\text{Cr}^{3+}$ is known to be dependent on oxygen partial pressure above glass melt, and glass composition or glass basicity (Kramer, 1991). The ratio is also influenced strongly by other redox species in the melt. For the glass composition investigated here, both iron oxide and sulfate could interact with Cr_2O_3 . However, the concentration of iron (0.005 wt % Fe_2O_3) in this case was too low and hence the iron effect is considered to be negligible. Sulfate (0.32 wt %), on the other hand, was comparable to the solubility of Cr_2O_3 (0.46 wt %). Its influence on the chromium redox ratio, $\text{Cr}^{6+}/\text{Cr}^{3+}$, may not be neglected. Common redox couples were studied previously (Tress, 1960). Internal oxygen pressure of sulfur was reported to be greater than that of chromium oxide and hence chromium is oxidized by sulfate (Tress, 1960).

There is a lack of study of the composition effect on the solubility of total chromium content in glass. Based on Reaction (13), chromium dissolved in the silicate network depends on the concentrations of both bridging oxygen and nonbridging oxygen. Hence, it is expected that the solubility of total chromium oxide varied with glass composition. The composition effect

can be seen by comparing its solubility in L6-5412 glass with that in L4-9012 glass (cf. Table 7).

4.2 Effect of Batch Size on Segregation of Minor Component-Containing Phases

Batch melting 1) converts the solid powder materials into a liquid eventually free from undissolved crystals as well as free from precipitated crystalline phases; and 2) eliminates chemical and thermal variations in the molten glass. In laboratory-scale testing, glass is made by melting a small quantity of batch materials in a crucible. Although no cold-cap scenario can be applied to the crucible melting, a variation in batch size, especially increasing the batch size, tends to favor segregation of minor component-containing phases during an early stage of batch melting as observed in this study (cf. Figures 22-26).

Previously published data showed that batch-free time (BFT) of silicate glass, which is defined by 99% completion of batch melting, has a relationship of (Bunting and Bieler, 1969):

$$\text{BFT} = C_1 (M/A) + C_2 \quad (14)$$

where M is the mass of glass produced from batch materials; A is the surface area through which the heat is conducted; and C_1 and C_2 are the constants related to batch composition and the complex processes of melting, respectively. For a given batch composition and fixed melting conditions, BFT increases with the ratio of (M/A).

Figure 31(a-f) shows a process of the large batch pile melting of L4-9012 glass with 1.0 wt% SO_3 addition at 1350°C. To take each micrograph, the crucible was taken out of the furnace and then immediately quenched in water. In a very early stage, reaction of batch materials occurred only on the surface while no reaction took place beneath the crust as shown in Figure 31(a), which was verified by inserting a Pt-rod into the batch pile. After 5 min melting, the whole batch was near a molten stage, which was confirmed from examining the inside of the melt by breaking some very large and thick foams on the melt surface. On the melt surface, a yellowish sulfate segregation was readily seen both near the meniscus area and on the surface as shown in Figure 31(b). It appeared that the sulfate segregation was reaching towards the meniscus area with melting time as revealed by the increase of the sulfate band shown in Figure 31(c). However, the segregated sulfate later decreased at longer melting time as depicted in Figure 31(d&e), and then completely disappeared after 120 min as illustrated in Figure 31(f).

After 120 min, the molten glass was quenched and removed from the crucible. Optical examination of the bulk glass showed no crystals.

The larger batch pile melting described above reveals the process of the sulfate segregation. Before homogeneous molten glass was formed, molten sulfate accumulated towards the melt top surface and was then transported into the meniscus area. During this stage, the melt viscosity was high and the segregation toward the surface might be facilitated by evolution of gases from decomposition of carbonates in the batch. Once the melt was in a glassy state, the melt viscosity was lower and sulfate segregation toward the surface was believed to be faster. The rate of sulfate accumulation was faster than that of sulfate volatilization from the surface. During the second stage, a very low viscous molten sulfate layer formed on the surface, an indication of sulfate segregation reaching a plateau. Later, the decrease of sulfate segregation is associated with sulfate volatilization since the melting was in ambient air, and the partial vapor pressure product of $P_{SO_2}P_{O_2}^{1/2}$ is low, promoting sulfate evaporation according to Reaction (11). For this third stage, sulfate in the bulk of the melt seems to be soluble in the glass network. The sulfate segregation scenario described here is considered to be generally applicable to the observations previously discussed in Section 3.4 for melting larger batches containing spiked chlorine, fluorine, and sulfate. Therefore, for large batch pile melting, the segregation is considered to be related to the minor component saturation as a result of batch composition inhomogeneity in an initial melting stage.

4.3 Effect of Minor Components on Glass Melt Viscosity

Viscous flow in the glass melt relates to physical shear movement between network building blocks and is a measure of an average bond strength of the glass network. In this sense, glass containing higher concentration of NBO has lower viscosity. Hence, glass viscosity is composition-dependent.

This study demonstrates that minor components either decrease or increase the glass melt viscosity. For fluorine-spiked glass, fluorine substitution for oxygen bonded to either silicon or boron weakens the strength of the network, resulting in lower melt viscosity. On the other hand, incorporation of chlorine appears to make the network more rigid, contributing to a higher melt viscosity. Increasing melt viscosity with the addition of chlorine was previously reported (Eitel,

1976), and attributed to volatility of Na from the melt. In this study, analytical data showed that sodium concentrations in glasses are close to those as-batched (cf. Appendixes A1 and C1.1). The observed increase of the melt viscosity for chlorine-spiked glass is not due to the sodium loss. Phosphorous contributes to the network formation, which forms a bond with Si, B, Al and O. Incorporation of P₂O₅ into the network should yield higher viscosity. The viscosity of phosphate-spiked glass was found to be relatively higher than that of the base glass, but nearly identical to that of sulfate-spiked glass. The structural role of sulfate in glass and its influence on the melt viscosity is not well understood. Again, for the sulfate-spiked glass at its solubility limit, no sodium loss was evident and the observed in melt viscosity was not associated with sodium volatility. Incorporation of chromium oxide (0.5 wt%) into L6-5412 glass appears to have no effect on the viscosity. For L4-9012 glass spiked with chromium at its solubility limit, 1.0 wt%, the glass melt viscosity decreased, which translates to 25 °C reduction of the glass melting temperature (cf. Figure 32).

Although compositions of the base glass (L6-5412) are modified with additions of these minor components, the ratio between a network former (SiO₂, B₂O₃, and Al₂O₃) and a network modifier (Na₂O, CaO, and K₂O) is not changed in all cases. Therefore, it must be concluded that the effects of minor components on the base glass melt viscosity are related to the structural variations in these glasses, resulting from incorporation of these minor components.

4.4 Effect of Minor Components on Glass Chemical Durability

For alkali-containing silicate glasses, a glass network reacting with water proceeds through ion exchange, network hydrolysis, and subsequent network dissolution. A dominating process of glass leaching during the period of 7-day PCT is dependent on the pH level of the solution or water.

At a lower solution pH level, less than pH8.5, the ion exchange between alkali ions in glass and water proceeds according to (Charles, 1958) :

where M⁺ is the alkali ion, and (g) and (l) refer to glass and solution, respectively. The reaction increases the pH of the solution and at the same time produce silanol group, ≡Si-OH, in the glass. For this study, the initial solution pH at room temperature was above 9.0 as a result of

ion exchange, which was promoted by a high ratio, 2000 m², of the sample surface areas to the volume of leachant. At a higher solution pH level, greater than pH9, dissolved silicon, in a form of Si(OH)₄, can further disassociate into HSiO₃⁻ and then into SiO₃²⁻. Accordingly, the solubility of silica in leachate increases sharply with increasing pH beyond pH8.5 (Iler, 1979). In this study, as in other waste glasses (Feng, 1991, and Li and Tomozawa, 1995), once the PCT was initiated at 90°C, the network dissolution is considered to be dominant through the test period. The leaching process can be summarized as free hydroxyl, formed by Reaction (15), attacking siloxane bonds at the leachate/glass interface according to (Charles, 1958) :

and then dissolution of the leached layer via the reaction of nonbridging oxygen (NBO), $\equiv\text{Si-O}^-$ according to (Charles, 1958) :

Accordingly, chemical durability results obtained in this study reflect the susceptibility of the glass network to water attack since Reaction (17) played a dominant role for 7-day PCT. The dominant role of the network dissolution via Reaction (17) can explain parallel trends between the glass elemental releases and that of the solution pH. In this study, no surface precipitation products were observed on the surfaces of glass particles, further confirming the dominant role of glass network dissolution in 7-day PCT.

According to PCT results obtained in this study, minor components dissolved in L6-5412 glass had a measurable effect on glass chemical durability. Presently, it is not well understood how these minor components alter the glass structure in such a way that the initial ion exchange seems to be enhanced in most of cases, except for fluorine-spiked glass. Further investigations on the structural roles of these minor components in low-level waste glasses are necessary. In general, the effect of minor components on glass chemical durability is glass composition-dependent, since their solubilities vary with glass composition as demonstrated in this study (cf. Table 7). Therefore, it would be premature to reach a general conclusion regarding an impact of the minor components on low-level waste glass chemical durability.

4.5 Suggestions on Glass Structure Study of Low-Level Waste Glasses

Based on experimental results obtained so far from the minor component study, it is evident that incorporation of these minor components affects the base glass properties (viscosity and chemical durability), and that a variation of glass composition significantly influences the minor component solubility limits in general. To optimize LLW glass formulation in terms of waste glass processability, it is ideal to formulate glass having high solubilities of these minor components. On the other hand, an impact of minor components on glass chemical durability must be also considered. Both aspects are directly related to the changes of glass structure with variations of both glass major and minor components. To optimize LLW glass formulation, it is important to study the changes of the glass structure with the addition of the minor components. Better understanding of the glass chemistry can in turn provide feedback to formulate glass candidates which can tolerate relatively high concentrations of the minor components without compromising chemical durability of the glass waste form.

For low-level waste glasses, correlations between glass properties and minor components in the glass are not well understood. However, the glass compositions are much simpler than those of high-level waste glasses, making the low-level waste glass structure study feasible. Several analytical characterization techniques have been widely used to study glass structures for many commercial glass systems, including silicates, borates and borosilicate. These include ultra-violet absorption spectroscopy, x-ray photoelectron spectroscopy, nuclear magnetic resonance, infrared and raman spectroscopy. To demonstrate the usefulness of these analytical techniques in the glass structure study, several previously reported studies are provided as follows.

Ultra-violet absorption spectroscopy was used to study chromium in binary alkali borate glasses (Paul and Douglas, 1967). Results showed that concentration of Cr^{6+} in borate glass decreased when non-bridging oxygen concentration was reduced, which was characterized by the UV absorption peak changes in terms of its intensity and position near 360 nm wavelength. In addition, the study also revealed non-linear correlation between the non-bridging oxygen (NBO) concentration and that of Cr^{6+} .

Nonbridging and bridging oxygens in sodium silicate glasses incorporated with Al_2O_3 and B_2O_3 were studied by Smets and Lommen (1981), using X-ray photoelectron spectroscopy,

which is often referred as to ESCA (electron spectroscopy for chemical analysis). For $0.2\text{Na}_2\text{O}-x\text{B}_2\text{O}_3-(0.8-x)\text{SiO}_2$ glass, it was found that the substitution of B_2O_3 for SiO_2 decreased NBO concentration in the glass if $x\text{B}_2\text{O}_3/0.2\text{Na}_2\text{O} < 1.0$. However, for $x\text{B}_2\text{O}_3/0.2\text{Na}_2\text{O} \geq 1.0$, a small amount of residual NBO remained in the glass. In contrast, for $0.2\text{Na}_2\text{O}-x\text{Al}_2\text{O}_3-(0.8-x)\text{SiO}_2$ glass, NBOs completely disappeared in the glass when $x\text{Al}_2\text{O}_3/0.2\text{Na}_2\text{O}$ is greater than 0.75. For the boron case, the existence of residual NBOs may be explained by the results reported by Greenblatt and Bray (1967). Using nuclear magnetic resonance (NMR), Greenblatt and Bray studied borate glasses containing various amounts of alkali oxides, either Li_2O or Na_2O or PbO . Their results for $x\text{Na}_2\text{O}-(1-x)\text{B}_2\text{O}_3$ glass showed that the ratio of four-coordinated boron, BO_4 , to three coordinated boron, BO_3 , increased with the increase of Na_2O if $x/(1-x) \leq 0.5$ (where x is in the mole fraction). For the case of $x/(1-x) \geq 0.5$, the ratio of BO_4/BO_3 decreased with the further increase of Na_2O . Accordingly, it appears that in a lower Na_2O regime, Na_2O is completely consumed by the reaction of $\text{BO}_3 \Rightarrow \text{BO}_4$. The reaction is reversed after Na_2O reached a certain level. Similar cases were found for $x\text{Li}_2\text{O}-(1-x)\text{B}_2\text{O}_3$ and $x\text{PbO}-(1-x)\text{B}_2\text{O}_3$ glasses. Combining results of ESCA and NMR discussed above, a non-linear relationship appears to exist between Na_2O concentration and boron structure. Therefore, the effect of alkali ions in the low-level waste glasses on the glass properties would be expected to be also non-linear.

Infrared and Raman spectroscopy have been widely used to study glass structure in borate, silicate, and phosphate glasses (Kolesova, 1981, Kosinski, et al., 1988, and Takusagawa, 1980). In addition, water in glass can be quantitatively measured using IR spectroscopy. The effect of water on chemical durability of high-level waste glasses was studied by Li and Tomozawa (1995). The results showed that water in glass increased glass dissolution slightly using 7-day PCT test.

Many of the analytical instruments are available at Pacific Northwest Laboratory, including Fourier transform infrared (FTIR) spectrophotometer, Raman spectrometer, Ultraviolet/visible absorption (UV/VIS) spectrophotometer, Nuclear magnetic resonance (NMR) spectrometer. Combining experiences/knowledge gained in the minor component study for low-level waste glass with the resources available, PNL has a advantageous position to study the glass structures for low-level waste glasses, which will provide one of important feedbacks for the glass formulation.

5. CONCLUSIONS

Solubility limits of minor components, Cl, F, P_2O_5 , SO_3 , and Cr_2O_3 , in a temperature range from 1300 to 1400°C were determined for L6-5412 glass. Temperature dependency of the solubilities was found to be negligible in this case. Glass composition effect on the solubilities was investigated using L4-9012 glass having zero CaO, but higher B_2O_3 . Results showed increases in solubilities of F, P_2O_5 , and Cr_2O_3 , but decrease of SO_3 solubility. Changing glass composition appears not to affect chlorine solubility. Overall, present data suggest that minor component solubilities are strongly influenced by glass composition.

Using L6-5412 glass, impacts of minor components in glass, in excess of their solubility limits, were investigated in terms of volatility, phase segregation, and crystallization. This study found that for L6-5412 glass, the minor component volatility was in the order of $Cl > SO_3 > F$ (cf. Figure 2). Comparing with the weight loss for the base glass during melting, P_2O_5 and Cr_2O_3 showed no volatilization. For glass containing minor components in excess of their solubility limits, a variety of phase segregation and crystallization in the molten glass was identified. Study also revealed that sulfate segregation could promote phosphate segregation, demonstrating a possibility that solubility of one minor component could be influenced by the presence of another minor component. A similar interaction between over-saturated sulfate and chromium was also observed in another low-level waste glass.

Glass melt viscosities were measured for L6-5412 glass containing minor components at their solubility levels. Fluorine significantly reduced the melt viscosity, while Cl, P_2O_5 and SO_3 increased the melt viscosity, among which chlorine had the most effect. Chromium oxide in glass appeared to have the least impact on the viscosity at low solubility (0.5 wt%). However, for L4-9012 glass, 1.0 wt% Cr_2O_3 is soluble in glass and it reduce the melt viscosity.

In general, the effect of minor components at their solubility levels on glass chemical durability was measurable for L6-5412 glass. Since solubility is composition-dependent, further investigation will be conducted to examine the above finding.

6. FUTURE WORK

Solubility limits will be determined at Pacific Northwest Laboratory (PNL) using the remaining selected glasses, while Rensselaer Polytechnic Institute (RPI) is also investigating the

composition effect using a large test matrix, the most of which is, however, within the composition envelope as used at PNL. Effects of minor components on both glass melt viscosity and chemical durability will be investigated; PNL will cover both aspects and RPI will focus on glass chemical durability. The effect of furnace atmospheres on glass volatility will be also studied at RPI; a study related to minor component phase boundary is currently under investigation at RPI.

7. REFERENCES

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Table 1. Composition of L6-5412 Base Glass

Oxide	wt%	Others	wt%
SiO ₂	56.78	Bi ₂ O ₃	0.014
B ₂ O ₃	5.00	Cl	0.092
Na ₂ O	20.00	Cr ₂ O ₃	0.036
CaO	4.00	F	0.213
Al ₂ O ₃	12.00	Fe ₂ O ₃	0.005
Others	2.22	K ₂ O	0.327
		MnO	0.007
		Nd ₂ O ₃	0.012
		P ₂ O ₅	1.187
		SO ₃	0.320
		ZrO ₂	0.005
SUM:	100.00	SUM :	2.217

Table 2. Minor Component Loading in L6-5412 Base Glass

Unit : wt%				
Cl	F	P ₂ O ₅	SO ₃	Cr ₂ O ₃
1	2.5	2.5	1	0.5
1.2	2.8	3.0	1.2	0.8
2.0	3.0	5.0	1.5	1.0
5.0	5.0	7.5	2.0	2.0
	10.0	10.0		

Chemicals used for minor component :
NaCl, NaF, NaPO₃, Na₂SO₄ and Cr₂O₃

Table 3. Measured Minor Component Solubility Limits in L6-5412 Glass

unit : wt %				
Minor Component	Method	1300 C	1350 C	1400 C
Chlorine, Cl (1)	XRF	0.56 (0.03)	0.57 (0.03)	0.52 (0.03)
	(3)	0.66 (0.05)		
Fluorine, F (1)	XRF	0.77 (0.02)	0.92 (0.02)	0.91 (0.02)
	(3)	2.79 (0.27) at 1100 C		
Phosphate, P ₂ O ₅ (1)	XRF	1.94 (0.16)	2.10 (0.16)	2.28 (0.17)
	(3)	1.95 (0.15)		
Sulfate, SO ₃ (1)	XRF	0.75 (0.06)	0.75 (0.07)	0.75 (0.07)
	(3)	0.60 (0.08) at 1200 C		
Chromium Oxide, Cr ₂ O ₃ (2)	ICP	0.46	0.48 (0.02)	0.48 (0.02)

(1) All values in aparenthese are one standard deviation, except for Cr₂O₃ case.

(2) For Cr₂O₃, values in apparenthese are differences between two fussion methods used in ICP.

(3) Values shaded were determined using microprobe by a subcontractor at RPI, Troy, NY .

Table 4. Comparison of Minor Component Solubility Limits
between 2 h-Melt and 9 h-Melt for L6-5412 Glass

M.C.	t = 2 h	t = 9 h
Cl	0.56	0.59
F	0.77	0.78
P2O5	1.94	1.72
SO3	0.75	0.83
Cr2O3	0.46	0.54

Table 5. Base Glass Compositions Selected for Minor Component Study

Unit: wt%				
Glass	L6-5412	L4-9012	L4-909	L5-0912
Tm (oC) *	1351	1345	—	1387
MCC-1 (Na, g/m ²) #	—	3.78	3.33	11.05
PCT (Na, g/m ²) #	0.351	0.30	0.60	0.95
Oxide	wt%	wt%	wt%	wt%
SiO ₂	56.78	56.78	59.78	56.78
B ₂ O ₃	5.00	9.00	9.00	
Na ₂ O	20.00	20.00	20.00	20.00
CaO	4.00			9.00
Al ₂ O ₃	12.00	12.00	9.00	12.00
Others	2.22	2.22	2.22	2.22
SUM:	100.00	100.00	100.00	100.00

Others	L6-5412	L4-9012	L4-909	L5-0912
Bi ₂ O ₃	0.014	0.014	0.014	0.014
Cl	0.092	0.092	0.092	0.092
Cr ₂ O ₃	0.036	0.036	0.036	0.036
F	0.213	0.213	0.213	0.213
Fe ₂ O ₃	0.005	0.005	0.005	0.005
K ₂ O	0.327	0.327	0.327	0.327
MnO	0.007	0.007	0.007	0.007
Nd ₂ O ₃	0.012	0.012	0.012	0.012
P ₂ O ₅	1.187	1.187	1.187	1.187
SO ₃	0.320	0.320	0.320	0.320
ZrO ₂	0.005	0.005	0.005	0.005
SUM :	2.217	2.217	2.217	2.217

* Melting temperatures were determined according to the glass melt viscosity of 10 Pa.s, which was experimentally measured.

Data are from the PNL internal memo (D.S. Kim, 1994).

Table 6. Minor Component Loading in L4-9012 Based Glasses

Unit : wt%

Cl	F	P2O5	SO3	Cr2O3
1.0	3.0	5.0	1.0	0.5
1.2	(3.8)	(5.8)	1.5	1.0
1.5	4.0	6.0	1.8	1.2
	5.0	7.0		

Note:

(1) Chemicals used for minor components are NaCl, NaF, NaPO3, Na2SO4 and Cr2O3.

(2) Values in parenthese are to be used to further narrow down the solubility limits of these minor components of interest.

Table 7. Measured Minor Component Solubility Limits in L4-9012 Glass

Unit: wt%

Glass	L6-5412	L4-9012
	B ₂ O ₃ : 5 wt% CaO : 4 wt%	B ₂ O ₃ : 9 wt% CaO : 0 wt%
Chlorine, Cl	0.57	0.49
Fluorine, F	0.92	1.18 < X < 1.45
Phosphate, P ₂ O ₅	2.10	4.72 < X < 5.72
Sulfate, SO ₃	0.75	0.47
Chromium Oxide, Cr ₂ O ₃	0.48	1.04

Note: The solubility values are for the glasses melted at 1350 C.

Figure 1. Measured solubility limits of minor components in L6-5412 glass melted at 1300, 1350 and 1400 °C.

Figure 2. Total weight loss of L6-5412 based glasses spiked with minor components and melted at (a) 1300 °C, (b) 1350 °C and (c) 1400 °C.

Figure 3. Comparison of concentrations of minor components for L6-5412 glass between the measured and as-batched, (a) 1300, (b) 1350, and (c) 1400 °C.

Figure 4. Optical micrographs of cross sections of quenched glasses melted at (a) 1300 °C, (b) 1350 °C and (c) 1400 °C for L6-5412 glass spiked with 5.0 wt%Cl (mag. 8X).

Figure 5. (a) SEM micrograph of a molten salt layer, X#2, and (b) its corresponding EDS pattern, X#2, for glass spiked with 5.0 wt%Cl and melted at 1300 °C.

Figure 6. (a) SEM micrograph of a cross section of a glass spiked with 5.0 wt%Cl and melted at 1300 °C and (b) its corresponding EDS pattern, X#3.

Figure 7.-X-ray diffraction pattern and identification of the crystalline phase for L6-5412 glass spiked with 5 wt%Cl and melted at 1300 °C.

Figure 8. (a) SEM micrograph of L6-5412 glass spiked with 10.0 wt%F and melted at 1300 °C and (b) its corresponding EDS pattern, X#3 (Note: the black spots are the voids caused by ion beam heating on these crystals).

Figure 9. X-ray diffraction pattern and identification of the crystalline phases for L6-5412 glass spiked with 10.0 wt%F and melted at 1300 °C.

Figure 10. X-ray diffraction pattern and identification of the crystalline phases for L6-5412 glass spiked with 10.0 wt% P_2O_5 and melted at 1300 °C.

Figure 11. Optical micrograph of L6-5412 glass spiked with 10.0 wt% P_2O_5 and melted at 1300 °C, showing a phase segregated layer at the top of the melt (mag. 200X).

Figure 12. SEM micrographs of for L6-5412 glass spiked with 10.0 wt%P₂O₅ and melted at 1300 °C, showing (a) homogeneous matrix, X#1, and (b) phase separation at the top of the melt, X#3 and X#4.

(a)

(b)

(c)

Figure 13. EDS patterns corresponding to the areas, X#1, 2, and 3 shown in Figure 12.

Figure 14. Optical micrograph of L6-5412 glass spiked with 2.0 wt%SO₃ and melted at 1300 °C, showing phase segregation in a meniscus area (mag. 8X).

Figure 15. X-ray diffraction pattern and identification of the crystalline phases for the segregated phases in the meniscus area (Note: L6-5412 glass spiked with 2.0 wt%SO₃ and melted at 1300 °C was used in this case).

(a)

(b)

Figure 16. SEM micrographs of L6-5412 glass spiked with 2.0 wt%SO₃ and melted at 1300°C, showing (a) plate-like, X#1, and (b) rod-like crystalline phases, X#2.

(a)

(b)

Figure 17. EDS patterns of (a) plate-like and (b) rod-like crystalline phases shown in Figure 16.

Figure 18. SEM characterizations of sulfate segregation on the molten glass surface for LD6-5510 glass, showing (a) SEM micrograph of sulfate segregation, (b) detailed morphology of the segregated phases, and (c-d) the related EDS patterns as identified by X#7 and X#8 in (b).

(a)

Figure 19. (a) SEM micrograph and (b-c) its corresponding EDS patterns, X#1 and X#2, for L6-5412 glass spiked with 2.0 wt%Cr₂O₃ and melted at 1300°C.

Figure 20. X-ray diffraction pattern and identification of the crystalline phase for L6-5412 glass spiked with 2.0 wt%Cr₂O₃ and melted at 1300 °C.

Figure 21. Optical micrographs of L6-5412 glass spiked with 2.0 wt% Cr_2O_3 and melted at 1300 °C for 40 hr, showing crystals in (a) the top, (b) the middle and (c) the bottom portions of the glass matrix (mag. 8X).

Figure 22. Optical micrograph of a large batch, ~ 500 g, melted at 1300°C for 1 h for L6-5412 spiked with 1.0 wt% Cl, showing some translucent glassy phase just above the surface of the melt (meg. 4X).

Figure 23. Optical micrograph of a large batch, ~500 g, melted at 1300 °C for 1 h for L6-5412 spiked with 2.5 wt% F, showing some opal glassy phase just above the surface of the melt (meg. 4X).

Figure 24. Optical micrograph of a large batch, ~500 g, melted at 1300 °C for 1 h for L6-5412 spiked with 2.5 wt% P_2O_5 , showing some translucent glassy phase just above the surface of the melt (meg. 4X).

Figure 25. Optical micrograph of a large batch, ~500 g, meted at 1300 °C for 1 h for L6-5412 spiked with 1.0 wt% SO_3 , showing sulfate segregation near the meniscus area, and just above the surface of the melt (meg. 4X).

Figure 26. Detailed optical micrographs of Figure 25, showing (a) the phase segregation also in a contacting area between the melt and crucible wall (meg. 4X) and (b) segregated sulfate crystals imbeded in the glass as indicated by the arrow in (a) (meg. 100X).

Figure 27. Melt viscosity measured in the temperature range from 1100 °C to 1450 °C for (a) L6-5412, and (b-f) L6-5412 based glasses spiked with each minor component at its solubility limit.

Figure 28. Leachate pH values measured before and after 7-day PCT for L6-5412 glass and its based glasses spiked with minor components at their solubility limits.

Figure 29. Normalized elemental mass loss measured after 7-day PCT for L6-5412 glass and its based glasses spiked with minor components at their solubility limits.

Figure 30. Optical micrograph of L6-5412 glass containing 0.75 wt% SO_3 and melted at 1500 °C, showing severe reboiling phenomenon.

Figure 31. Optical micrographs of L4-9012 glass spiked with 1.0 wt% SO_3 and melted at 1350 °C, showing the sulfate segregation and volatilization processes during melting (Note: RB - reacted batch materials, B - unreacted batch materials, S - segregated sulfate, G - glass, and C - crucible wall).

Figure 32. Comparison of glass melt viscosities in a temperature range from 1100 to 1450 °C for L4-9012 glass and its base glass spiked with Cr₂O₃ at its solubility limit, 1.0 wt%.

Appendix A

Compositions of L6-5412 Based Glasses Spiked with Minor Components

Appendix A1. Compositions of L6-5412 Based Glasses Spiked with Chlorine

unit: wt%				
Cl	1.0	1.2	2.0	5.0
SiO ₂	56.26	56.15	55.70	53.99
B ₂ O ₃	4.95	4.94	4.90	4.75
Na ₂ O	19.82	19.78	19.62	19.02
CaO	3.96	3.96	3.92	3.80
Al ₂ O ₃	11.89	11.87	11.77	11.41
Others	3.11	3.30	4.08	7.02
SUM	100.00	100.00	100.00	100.00
Others				
Bi ₂ O ₃	0.014	0.014	0.014	0.014
Cl	1.000	1.200	2.000	5.000
Cr ₂ O ₃	0.035	0.035	0.035	0.034
F	0.211	0.211	0.209	0.203
Fe ₂ O ₃	0.005	0.005	0.005	0.005
K ₂ O	0.324	0.323	0.321	0.311
MnO	0.007	0.007	0.007	0.007
Nd ₂ O ₃	0.012	0.012	0.012	0.011
P ₂ O ₅	1.176	1.174	1.164	1.129
SO ₃	0.317	0.316	0.314	0.304
ZrO ₂	0.005	0.005	0.005	0.005
SUM	3.100	3.59	4.084	7.020

Appendix A2. Compositions of L6-5412 Based Glasses Spiked with Fluorine

unit: wt%					
F	2.5	2.8	3.0	5.0	10.0
SiO ₂	55.48	55.31	55.19	54.06	51.21
B ₂ O ₃	4.89	4.87	4.86	4.76	4.51
Na ₂ O	19.54	19.48	19.44	19.04	18.04
CaO	3.91	3.90	3.89	3.81	3.61
Al ₂ O ₃	11.72	11.69	11.66	11.42	10.82
Others	4.46	4.75	4.95	6.91	11.81
SUM	100.00	100.00	100.00	100.00	100.00
Others					
Bi ₂ O ₃	0.014	0.014	0.014	0.014	0.013
Cl	0.090	0.090	0.089	0.088	0.083
Cr ₂ O ₃	0.035	0.035	0.035	0.034	0.032
F	2.500	2.800	3.000	5.000	10.000
Fe ₂ O ₃	0.005	0.005	0.005	0.005	0.004
K ₂ O	0.319	0.318	0.318	0.311	0.295
MnO	0.007	0.007	0.007	0.007	0.006
Nd ₂ O ₃	0.012	0.012	0.012	0.011	0.011
P ₂ O ₅	1.160	1.156	1.154	1.130	1.070
SO ₃	0.312	0.312	0.311	0.304	0.288
ZrO ₂	0.005	0.005	0.005	0.005	0.004
SUM	14.58	14.52	14.48	16.908	16.807

Appendix A3. Compositions of L6-5412 Based Glasses Spiked with Phosphate

unit: wt%					
P2O5	2.5	3.0	5.0	7.5	10.0
SiO2	56.03	55.74	54.59	53.15	51.72
B2O3	4.93	4.91	4.81	4.68	4.55
Na2O	19.73	19.63	19.23	18.72	18.22
CaO	3.95	3.93	3.85	3.74	3.64
Al2O3	11.84	11.78	11.54	11.23	10.93
Others	3.52	4.01	5.99	8.46	10.94
SUM	100.00	100.00	100.00	100.00	100.00
Others					
Bi2O3	0.014	0.014	0.014	0.013	0.013
Cl	0.091	0.090	0.089	0.086	0.084
Cr2O3	0.035	0.035	0.034	0.033	0.032
F	0.210	0.209	0.205	0.200	0.194
Fe2O3	0.005	0.005	0.005	0.004	0.004
K2O	0.323	0.321	0.314	0.306	0.298
MnO	0.007	0.007	0.007	0.007	0.006
Nd2O3	0.012	0.012	0.011	0.011	0.011
P2O5	2.500	3.000	5.000	7.500	10.000
SO3	0.316	0.314	0.307	0.299	0.291
ZrO2	0.005	0.005	0.005	0.004	0.004
SUM	3.516	4.014	5.991	8.454	10.939

Appendix A4. Compositions of L6-5412 Based Glasses Spiked with Sulfate

unit: wt%				
SO3	1.0	1.2	1.5	2.0
SiO2	56.39	56.28	56.11	55.82
B2O3	4.97	4.96	4.94	4.92
Na2O	19.86	19.82	19.76	19.66
CaO	3.97	3.96	3.95	3.93
Al2O3	11.92	11.89	11.86	11.80
Others	2.89	3.08	3.37	3.87
SUM	100.00	100.00	100.00	100.00
Others				
Bi2O3	0.014	0.014	0.014	0.014
Cl	0.092	0.091	0.091	0.090
Cr2O3	0.035	0.035	0.035	0.035
F	0.212	0.211	0.211	0.210
Fe2O3	0.005	0.005	0.005	0.005
K2O	0.325	0.324	0.323	0.321
MnO	0.007	0.007	0.007	0.007
Nd2O3	0.012	0.012	0.012	0.012
P2O5	1.179	1.176	1.173	1.167
SO3	1.000	1.200	1.500	2.000
ZrO2	0.005	0.005	0.005	0.005
SUM	2.886	3.080	3.375	3.868

Appendix A5. Compositions of L6-5412 Based Glasses Spiked with Chromium Oxide

unit: wt%				
Cr2O3	0.5	0.8	1.0	2.0
SiO2	56.52	56.35	56.23	55.66
B2O3	4.98	4.96	4.95	4.90
Na2O	19.91	19.85	19.81	19.61
CaO	3.98	3.97	3.96	3.92
Al2O3	11.94	11.91	11.88	11.76
Others	2.67	2.96	3.16	4.14
SUM	100.00	100.00	100.00	100.00
Others				
Bi2O3	0.014	0.014	0.014	0.014
Cl	0.092	0.091	0.091	0.090
Cr2O3	0.500	0.800	1.000	2.000
F	0.212	0.212	0.211	0.209
Fe2O3	0.005	0.005	0.005	0.005
K2O	0.325	0.324	0.324	0.320
MnO	0.007	0.007	0.007	0.007
Nd2O3	0.012	0.012	0.012	0.012
P2O5	1.181	1.178	1.175	1.164
SO3	0.318	0.317	0.317	0.314
ZrO2	0.005	0.005	0.005	0.005
SUM	2.57	2.964	3.161	4.139

Appendix B

Compositions of L6-5412 Glass Measured by ICP and XRF

Appendix B1. Compositions of L6-5412 Glass Measured by ICP/AES Method

Unit: wt%			
Oxide	1300 C	1350 C	1400 C
SiO ₂	55.31	54.63	54.64
B ₂ O ₃	4.84	4.86	4.81
Na ₂ O	19.96	19.07	19.66
CaO	3.95	3.99	4.11
Al ₂ O ₃	11.63	11.43	11.49
Others			
Bi ₂ O ₃	0.000	0.000	0.000
Cl	0.054	0.049	0.053
Cr ₂ O ₃	0.030	0.040	0.040
F			
Fe ₂ O ₃	0.060	0.037	0.040
K ₂ O	0.000	0.000	0.000
MnO	0.010	0.020	0.013
Nd ₂ O ₃	0.023	0.020	0.040
P ₂ O ₅	1.090	1.150	1.200
SO ₃	0.270	0.280	0.270
ZrO ₂	0.010	0.000	0.010
SUM	97.24	95.58	96.38

(1) Zero value indicates that that elemental concentration in solution is below its detection limit.

(2) For major components, P₂O₅, SO₃ and Cr₂O₃, their deviations in concentrations from the two fusion methods were equal to or less than +/- 0.06%.

(3) Chlorine was determined by XRF.

Appendix B2. Compositions of L6-5412 Glass Measured by XRF Method

Unit : wt%

Oxide	1300 C		1350 C		1400 C	
	(+/ -)		(+/ -)		(+/ -)	
SiO ₂	56.69	4.06	56.48	4.06	52.84	3.64
B ₂ O ₃ #	6.21	0.62	3.74	0.37	3.67	0.37
Na ₂ O#	21.30	2.13	21.30	2.13	17.93	1.79
CaO	4.32	0.31	4.28	0.29	4.20	0.29
Al ₂ O ₃	11.88	0.89	12.58	0.94	10.60	0.81
Others						
Bi ₂ O ₃	0.017	0.001	0.017	0.001	0.015	0.001
Cl	0.054	0.006	0.049	0.006	0.053	0.006
Cr ₂ O ₃	0.037	0.003	0.036	0.003	0.036	0.003
F						
Fe ₂ O ₃	0.048	0.003	0.033	0.002	0.028	0.002
K ₂ O	0.336	0.024	0.346	0.025	0.318	0.023
MnO	0.009	0.001	0.008	0.001	0.010	0.001
Nd ₂ O ₃	0.010	0.001	0.011	0.001	0.011	0.001
P ₂ O ₅	1.123	0.137	1.198	0.137	1.056	0.137
SO ₃	0.310	0.037	0.292	0.035	0.305	0.035
ZrO ₂	0.014	0.001	0.014	0.001	0.013	0.001
SUM	102.37		100.38		91.08	

Concentrations of B₂O₃ and Na₂O were determined by ICP.
 (+/-) One standard deviation

Appendix C

Measured Compositions of L6-5412 Based Glasses Spiked with Minor Components

Appendix C1.1 Measured Composition of L6-5412 Glass Spiked with 1.0 wt% Cl

Oxide	1300 C		1350 C		1400 C	
	(+/-)		(+/-)		(+/-)	
SiO ₂	56.26	2.78	55.62	2.78	56.05	2.78
B ₂ O ₃ #	4.70	0.47	4.72	0.47	4.63	0.46
Na ₂ O#	22.10	2.21	19.10	1.91	20.70	2.07
CaO	4.23	0.21	4.16	0.21	4.17	0.21
Al ₂ O ₃	11.49	0.66	10.92	0.62	11.75	0.66
Others						
Bi ₂ O ₃						
Cl	0.556	0.030	0.569	0.030	0.522	0.028
Cr ₂ O ₃	0.042	0.001	0.042	0.001	0.041	0.001
F						
Fe ₂ O ₃	0.056	0.003	0.067	0.003	0.054	0.003
K ₂ O	0.269	0.014	0.267	0.014	0.283	0.016
MnO	0.014	0.001	0.013	0.001	0.013	0.001
Nd ₂ O ₃ #	0.088	0.009	0.091	0.009	0.110	0.010
P ₂ O ₅	0.884	0.119	0.882	0.117	0.983	0.121
SO ₃	0.340	0.035	0.320	0.035	0.290	0.035
ZrO ₂	0.018	0.001	0.015	0.001	0.014	0.001
SUM	101.045		96.786		99.612	

Concentrations of B₂O₃ and Na₂O were determined by ICP.
 (+/-) One standard deviation

Appendix C1.2 Measured Composition of L6-5412 Glass Spiked with 1.2 wt%Cl

Oxide	1300 C		1350 C		1400 C	
	(+/-)		(+/-)		(+/-)	
SiO ₂	57.33	2.78	51.34	2.57	56.26	2.78
B ₂ O ₃ #	5.44	0.54	5.60	0.56	4.99	0.50
Na ₂ O#	21.10	2.11	20.40	2.04	23.20	2.32
CaO	4.37	0.22	4.16	0.21	4.31	0.21
Al ₂ O ₃	11.96	0.68	9.81	0.59	11.24	0.64
Others						
Bi ₂ O ₃						
Cl	0.684	0.036	0.582	0.031	0.554	0.030
Cr ₂ O ₃	0.037	0.001	0.035	0.001	0.035	0.001
F						
Fe ₂ O ₃	0.083	0.004	0.059	0.003	0.066	0.003
K ₂ O	0.276	0.014	0.263	0.014	0.272	0.014
MnO	0.012	0.001	0.010	0.001	0.010	0.001
Nd ₂ O ₃						
P ₂ O ₅	0.868	0.119	0.784	0.112	0.784	0.115
SO ₃	0.265	0.035	0.285	0.032	0.295	0.032
ZrO ₂	0.009	0.001	0.009	0.000	0.009	0.000
SUM	102.435		93.335		102.033	

Concentrations of B₂O₃ and Na₂O were determined by ICP.
 (+/-) One standard deviation

Appendix C1.3 Measured Composition of L6-5412 Glass Spiked with 2.0 wt% Cl

Oxide	1300 C		1350 C		1400 C	
	(+/-)		(+/-)		(+/-)	
SiO ₂	57.33	4.06	59.47	4.28	58.40	4.28
B ₂ O ₃ #	4.96	0.50	4.57	0.46	4.89	0.49
Na ₂ O#	19.14	1.91	18.60	1.86	18.33	1.83
CaO	4.48	0.32	4.56	0.32	4.51	0.32
Al ₂ O ₃	11.71	1.40	12.79	1.40	13.17	1.44
Others						
Bi ₂ O ₃	0.021	0.002	0.021	0.002	0.020	0.001
Cl	0.852	0.070	0.781	0.066	0.837	0.069
Cr ₂ O ₃	0.037	0.003	0.035	0.003	0.036	0.003
F						
Fe ₂ O ₃	0.068	0.005	0.040	0.003	0.064	0.005
K ₂ O	0.322	0.027	0.317	0.027	0.324	0.028
MnO	0.006	0.002	0.006	0.002	0.008	0.002
Nd ₂ O ₃						
P ₂ O ₅	1.352	0.367	1.444	0.390	1.650	0.390
SO ₃	0.432	0.100	0.300	0.100	0.267	0.100
ZrO ₂	0.013	0.001	0.013	0.001	0.013	0.001
SUM	100.728		102.957		102.524	

Concentrations of B₂O₃ and Na₂O were determined by ICP.
 (+/-) One standard deviation

Appendix C1.4 Measured Composition of L6-5412 Glass Spiked with 5.0 wt%Cl

Oxide	1300 C		1350 C		1400 C	
		(+/-)		(+/-)		(+/-)
SiO ₂	59.47	4.28	58.83	4.06	60.97	4.28
B ₂ O ₃ #	3.86	0.39	3.86	0.39	4.03	0.40
Na ₂ O#	15.77	1.58	17.66	1.77	16.04	1.60
CaO	4.44	0.31	4.38	0.31	4.55	0.32
Al ₂ O ₃	12.56	0.94	12.91	0.96	12.17	0.91
Others						
Bi ₂ O ₃	0.021	0.002	0.021	0.002	0.019	0.001
Cl	0.843	0.060	0.829	0.059	0.823	0.059
Cr ₂ O ₃	0.034	0.002	0.034	0.002	0.035	0.003
F						
Fe ₂ O ₃	0.030	0.002	0.063	0.003	0.065	0.003
K ₂ O	0.249	0.018	0.243	0.018	0.258	0.018
MnO	0.008	0.001	0.009	0.001	0.009	0.001
Nd ₂ O ₃ #	0.011	0.001	0.012	0.001	0.013	0.001
P ₂ O ₅	1.059	0.142	1.162	0.140	0.912	0.137
SO ₃	0.082	0.030	0.095	0.030	0.062	0.030
ZrO ₂	0.012	0.001	0.000	0.000	0.000	0.000
SUM	98.458		100.106		99.948	

Concentrations of B₂O₃ and Na₂O were determined by ICP.
 (+/-) One standard deviation

Appendix C2.1 Measured Composition of L6-5412 Glass Spiked with 2.5 wt% F

Oxide	1300 C		1350 C		1400 C	
		(+/-)		(+/-)		(+/-)
SiO ₂	55.41	2.78	55.41	2.78	57.55	3.00
B ₂ O ₃ #	4.19	0.42	4.19	0.42	3.93	0.39
Na ₂ O#	21.00	2.10	20.20	2.20	23.50	2.35
CaO	4.17	0.21	4.17	0.21	4.28	0.21
Al ₂ O ₃	11.19	0.64	11.05	0.64	11.92	0.68
Others						
Bi ₂ O ₃						
Cl	0.038	0.005	0.049	0.005	0.045	0.005
Cr ₂ O ₃	0.038	0.001	0.038	0.001	0.039	0.001
F	0.770	0.015	0.920	0.018	0.910	0.018
Fe ₂ O ₃	0.107	0.006	0.063	0.003	0.057	0.003
K ₂ O	0.279	0.014	0.278	0.014	0.276	0.014
MnO	0.012	0.001	0.009	0.001	0.010	0.001
Nd ₂ O ₃						
P ₂ O ₅	0.878	0.117	1.015	0.119	0.852	0.119
SO ₃	0.245	0.030	0.302	0.032	0.280	0.032
ZrO ₂	0.035	0.001	0.035	0.001	0.036	0.001
SUM	98.352		97.727		103.687	

Concentrations of B₂O₃ and Na₂O were determined by ICP.
 (+/-) One standard deviation

Appendix C2.2 Measured Composition of L6-5412 Glass Spiked with 2.8 wt%F

Oxide	1300 C		1350 C		1400 C	
	(+/-)		(+/-)		(+/-)	
SiO ₂	57.76	3.00	56.69	2.78	55.84	2.78
B ₂ O ₃ #	4.54	0.45	4.70	0.47	4.51	0.45
Na ₂ O#	19.60	1.96	22.00	2.20	20.20	2.02
CaO	4.37	0.22	4.38	0.22	4.34	0.22
Al ₂ O ₃	11.28	0.66	11.47	0.66	11.20	0.64
Others						
Bi ₂ O ₃						
Cl	0.039	0.005	0.047	0.005	0.035	0.005
Cr ₂ O ₃	0.034	0.001	0.034	0.001	0.034	0.001
F	1.090	0.022	1.100	0.022	1.060	0.021
Fe ₂ O ₃	0.064	0.003	0.053	0.003	0.041	0.003
K ₂ O	0.296	0.016	0.307	0.016	0.289	0.016
MnO	0.009	0.001	0.008	0.001	0.009	0.001
Nd ₂ O ₃						
P ₂ O ₅	0.687	0.117	0.937	0.119	0.880	0.119
SO ₃	0.277	0.032	0.275	0.032	0.297	0.032
ZrO ₂	0.008	0.000	0.008	0.000	0.008	0.000
SUM	100.053		102.011		98.740	

Concentrations of B₂O₃ and Na₂O were determined by ICP.
 (+/-) One standard deviation

Appendix C2.3 Measured Composition of L6-5412 Glass with 3.0 wt%F

Oxide	1300 C		1350 C		1400 C	
	(+/-)		(+/-)		(+/-)	
SiO ₂	56.48	2.78	54.13	2.78	57.33	2.78
B ₂ O ₃ #	4.35	0.43	5.28	0.53	5.35	0.53
Na ₂ O#	22.20	2.22	22.10	2.21	21.80	2.18
CaO	4.30	0.21	4.24	0.21	4.37	0.22
Al ₂ O ₃	11.22	0.64	11.41	0.64	12.41	0.70
Others						
Bi ₂ O ₃						
Cl	0.055	0.006	0.048	0.005	0.027	0.005
Cr ₂ O ₃	0.031	0.001	0.031	0.001	0.031	0.001
F	1.090	0.022	1.140	0.023	1.100	0.022
Fe ₂ O ₃	0.044	0.003	0.054	0.003	0.039	0.001
K ₂ O	0.296	0.016	0.278	0.014	0.298	0.016
MnO	0.006	0.001	0.006	0.001	0.005	0.001
Nd ₂ O ₃						
P ₂ O ₅	0.944	0.119	0.891	0.117	0.882	0.119
SO ₃	0.300	0.032	0.280	0.032	0.257	0.032
ZrO ₂	0.028	0.001	0.028	0.001	0.028	0.001
SUM	101.339		99.915		103.926	

Concentrations of B₂O₃ and Na₂O were determined by ICP.
 (+/-) One standard deviation

Appendix C2.4 Measured Composition of L6-5412 Glass Spiked with 5.0 wt%F

Oxide	1300 C		1350 C		1400 C	
	(+/ -)		(+/ -)		(+/ -)	
SiO ₂	55.19	3.85	57.98	4.06	55.62	3.85
B ₂ O ₃ #	4.19	0.42	4.19	0.42	4.44	0.44
Na ₂ O#	18.00	1.80	19.14	1.91	19.55	1.95
CaO	4.27	0.29	4.34	0.31	4.28	0.29
Al ₂ O ₃	11.94	0.89	12.81	0.96	11.98	0.91
Others						
Bi ₂ O ₃	0.018	0.001	0.018	0.001	0.017	0.001
Cl	0.041	0.005	0.037	0.005	0.032	0.005
Cr ₂ O ₃	0.034	0.002	0.034	0.002	0.033	0.002
F	1.970	0.039	1.910	0.038	1.890	0.038
Fe ₂ O ₃	0.054	0.003	0.061	0.003	0.058	0.003
K ₂ O	0.318	0.023	0.330	0.024	0.340	0.024
MnO	0.007	0.001	0.007	0.001	0.008	0.001
Nd ₂ O ₃ #	0.012	0.001	0.010	0.001	0.010	0.001
P ₂ O ₅	1.045	0.135	1.345	0.154	1.373	0.149
SO ₃	0.210	0.032	0.265	0.035	0.210	0.032
ZrO ₂	0.013	0.001	0.013	0.001	0.013	0.001
SUM	97.307		102.481		99.857	

Concentrations of B₂O₃ and Na₂O were determined by ICP.
 (+/-) One standard deviation

Appendix C2.5 Measured Composition of L6-5412 Glass Spiked with 10.0 wt% F

Oxide	1300 C		1350 C		1400 C	
	(+/ -)		(+/ -)		(+/ -)	
SiO ₂	54.55	3.21	55.19	3.21	50.70	3.00
B ₂ O ₃ #	4.19	0.42	4.41	0.44	4.22	0.42
Na ₂ O#	18.60	1.86	20.49	2.05	19.01	1.90
CaO	4.48	0.32	4.42	0.31	4.39	0.31
Al ₂ O ₃	12.04	1.42	12.66	1.40	10.64	1.32
Others						
Bi ₂ O ₃	0.015	0.001	0.014	0.015	0.001	0.000
Cl	0.049	0.015	0.051	0.014	0.027	0.000
Cr ₂ O ₃	0.038	0.003	0.036	0.003	0.037	0.003
F	4.170	0.083	4.160	0.083	4.03	0.081
Fe ₂ O ₃	0.068	0.005	0.052	0.004	0.102	0.008
K ₂ O	0.323	0.028	0.332	0.028	0.302	0.025
MnO	0.009	0.002	0.007	0.002	0.010	0.002
Nd ₂ O ₃						
P ₂ O ₅	1.054	0.344	1.123	0.344	1.421	0.367
SO ₃	0.182	0.000	0.205	0.092	0.192	0.085
ZrO ₂	0.014	0.001	0.015	0.001	0.014	0.001
SUM	99.776		103.171		95.094	

Concentrations of B₂O₃ and Na₂O were determined by ICP.
 (+/-) One standard deviation

Appendix C3.1 Measured Composition of L6-5412 Based Glass with 2.5 wt%P2O5

Oxide	1300 C		1350 C		1400 C	
	(st. div.)		(st. div.)		(st. div.)	
SiO ₂	57.98	3.00	58.19	3.00	55.62	2.78
B ₂ O ₃ #	5.54	0.55	4.89	0.49	5.38	0.54
Na ₂ O#	20.80	2.08	24.00	2.40	24.30	2.43
CaO	4.30	0.21	4.37	0.22	4.28	0.21
Al ₂ O ₃	11.73	0.66	11.20	0.64	11.20	0.64
Others						
Bi ₂ O ₃						
Cl	0.062	0.006	0.052	0.005	0.042	0.005
Cr ₂ O ₃	0.035	0.001	0.037	0.001	0.035	0.001
F						
Fe ₂ O ₃	0.039	0.001	0.044	0.003	0.040	0.001
K ₂ O	0.283	0.145	0.296	0.016	0.299	0.016
MnO	0.012	0.001	0.012	0.001	0.010	0.001
Nd ₂ O ₃						
P ₂ O ₅	1.943	0.156	2.103	0.160	2.278	0.167
SO ₃	0.357	0.035	0.347	0.035	0.357	0.035
ZrO ₂	0.014	0.001	0.014	0.001	0.014	0.001
SUM	103.088		105.559		103.861	

Concentrations of B₂O₃ and Na₂O were determined by ICP.
(+/-) One standard deviation

Appendix C3.2 Measured Composition of L6-5412 Glass with 3.0 wt%P2O5

Unit : wt%

Oxide	1300 C		1350 C		1400 C	
		(+/-)		(+/-)		(+/-)
SiO2	50.27	2.57	55.62	2.78	54.98	2.78
B2O3#	5.22	0.52	5.57	0.56	5.47	0.55
Na2O#	23.00	2.30	19.60	1.96	20.60	2.06
CaO	4.16	0.21	4.28	0.21	4.27	0.21
Al2O3	9.28	0.57	11.07	0.64	11.07	0.64
Others						
Bi2O3						
Cl	0.059	0.006	0.048	0.005	0.045	0.005
Cr2O3	0.032	0.001	0.032	0.001	0.035	0.001
F						
Fe2O3	0.076	0.004	0.054	0.003	0.050	0.003
K2O	0.295	0.016	0.283	0.014	0.293	0.016
MnO	0.014	0.001	0.013	0.001	0.013	0.001
Nd2O3						
P2O5	2.296	0.167	2.200	0.165	2.516	0.176
SO3	0.340	0.035	0.330	0.035	0.340	0.035
ZrO2	0.030	0.001	0.030	0.001	0.030	0.001
SUM	95.065		99.137		99.716	

Concentrations of B2O3 and Na2O were determined by ICP.
 (+/-) One standard deviation

Appendix C3.3 Measured Composition of L6-5412 Glass Spiked with 5.0 wt%P2O5

Oxide	1300 C		1350 C		1400 C	
		(+/-)		(+/-)		(+/-)
SiO2	56.91	4.06	53.27	3.64	55.84	3.85
B2O3#	4.22	0.42	4.35	0.43	4.41	0.44
Na2O#	20.22	2.02	19.55	1.95	18.33	1.83
CaO	4.25	0.29	4.13	0.29	4.25	0.29
Al2O3	12.53	0.93	11.19	0.85	12.15	0.91
Others						
Bi2O3	0.014	0.001	0.012	0.001	0.013	0.001
Cl	0.055	0.006	0.048	0.006	0.046	0.005
Cr2O3	0.036	0.003	0.034	0.002	0.034	0.002
F						
Fe2O3	0.061	0.003	0.058	0.003	0.054	0.003
K2O	0.312	0.023	0.311	0.022	0.330	0.024
MnO	0.007	0.001	0.008	0.001	0.005	0.001
Nd2O3#	0.019	0.002	0.011	0.001	0.011	0.001
P2O5	5.614	0.412	4.972	0.367	5.637	0.412
SO3	0.380	0.042	0.330	0.040	0.335	0.040
ZrO2	0.011	0.001	0.011	0.001	0.011	0.001
SUM	104.634		98.270		101.458	

Concentrations of B2O3 and Na2O were determined by ICP.
 (+/-) One standard deviation

Appendix C3.4 Measured Composition of L6-5412 Glass Spiked with 7.5 wt% P2O5

Oxide	1300 C		1350 C		1400 C	
	&	(%)	&	(%)	@	(%)
SiO2	47.40		48.24		50.86	2.4
B2O3	4.21		4.35		4.44	0.5
Na2O	17.24		17.33		18.67	
CaO	3.54		3.69		3.80	4.4
Al2O3	10.42		10.79		11.19	1.6
Others						
Bi2O3	0.000		0.059		0.074	
Cl						
Cr2O3	0.048		0.045		0.046	13.0
F						
Fe2O3	0.072		0.065		0.044	20.7
K2O						
MnO	0.012		0.032		0.015	13.3
Nd2O3	0.075		0.063		0.096	
P2O5	6.526		6.778		7.244	0.5
SO3	0.249		0.306		0.269	12.3
ZrO2	0.012		0.026		0.024	
SUM	89.808		91.772		96.764	

& Values were determined by ICP using sodium fussion method, in which Na2O and ZrO2 were determined using potassium fussion method.

@ Values were determined by ICP using both sodium and potassium fussion methods.

(%) Deviation percentage was determined as : $100\% \times |Cs - Cp| / 0.5 \times (Cs + Cp)$, where Cs and Cp are the concentrations measured using sodium and potassium fussion methods.

Appendix C3.5 Measured Composition of L6-5412 Glass Spiked with 10.0 wt% P2O5

Oxide	1300 C		1350 C		1400 C	
	(+/ -)		(+/ -)		(+/ -)	
SiO2	54.34	3.85	51.13	3.64	50.49	3.64
B2O3#	3.45	0.34	4.38	0.44	4.54	0.00
Na2O#	18.33	1.83	18.06	1.81	19.01	0.00
CaO	4.14	0.29	4.03	0.28	4.02	0.28
Al2O3	11.58	1.30	12.21	1.32	11.24	1.34
Others						
Bi2O3	0.014	0.001	0.014	0.001	0.014	0.001
Cl	0.066	0.016	0.036	0.015	0.069	0.015
Cr2O3	0.033	0.003	0.033	0.003	0.031	0.003
F						
Fe2O3	0.076	0.006	0.066	0.005	0.047	0.004
K2O	0.300	0.025	0.336	0.028	0.311	0.027
MnO	0.008	0.002	0.006	0.002	0.005	0.002
Nd2O3						
P2O5	10.632	0.917	9.945	0.894	10.540	0.917
SO3	0.574	0.110	0.447	0.105	0.439	0.107
ZrO2	0.014	0.001	0.014	0.001	0.014	0.001
SUM	103.559		100.705		100.763	

Concentrations of B2O3 and Na2O were determined by ICP.
(+/ -) One standard deviation

Appendix C4.1 Measured Composition of L6-5412 Glass Spiked with 1.0 wt%SO₃

Unit : wt%

Oxide	1300 C		1350 C		1400 C	
	(+/-)		(+/-)		(+/-)	
SiO ₂	53.70	3.85	55.84	3.85	57.12	4.06
B ₂ O ₃ #	3.51	0.35	4.03	0.40	3.64	0.36
Na ₂ O#	21.30	2.13	18.74	1.87	17.93	1.79
CaO	4.09	0.28	4.24	0.29	4.35	0.31
Al ₂ O ₃	12.05	0.91	12.83	0.96	12.32	0.93
Others						
Bi ₂ O ₃	0.012	0.001	0.012	0.001	0.011	0.001
Cl	0.056	0.006	0.055	0.006	0.045	0.005
Cr ₂ O ₃	0.032	0.002	0.033	0.002	0.033	0.002
F						
Fe ₂ O ₃	0.068	0.004	0.073	0.004	0.055	0.003
K ₂ O	0.319	0.023	0.343	0.024	0.345	0.024
MnO	0.008	0.001	0.010	0.001	0.009	0.001
Nd ₂ O ₃ #	0.013	0.001	0.013	0.001	0.012	0.001
P ₂ O ₅	1.082	0.135	1.185	0.140	1.244	0.144
SO ₃	0.749	0.062	0.754	0.065	0.749	0.065
ZrO ₂	0.012	0.001	0.012	0.001	0.012	0.001
SUM	96.995		98.156		97.874	

Concentrations of B₂O₃ and Na₂O were determined by ICP.
(+/-) One standard deviation

Appendix C4.2 Measured Composition of L6-5412 Glass Spiked with 1.2 wt%SO₃

Unit : wt%

Oxide	1300 C		1350 C		1400 C	
	(+/-)		(+/-)		(+/-)	
SiO ₂	56.48	2.78	57.55	2.78	55.84	2.78
B ₂ O ₃ #	5.80	0.58	5.15	0.52	5.31	0.53
Na ₂ O#	19.60	1.96	20.80	2.08	21.10	2.11
CaO	4.38	0.22	4.44	0.22	4.42	0.22
Al ₂ O ₃	11.05	0.64	10.92	0.64	10.98	0.64
Others						
Bi ₂ O ₃						
Cl	0.046	0.005	0.047	0.005	0.065	0.006
Cr ₂ O ₃	0.035	0.001	0.037	0.001	0.037	0.001
F						
Fe ₂ O ₃	0.069	0.003	0.046	0.003	0.053	0.003
K ₂ O	0.290	0.157	0.284	0.157	0.305	0.157
MnO	0.013	0.001	0.012	0.001	0.013	0.001
Nd ₂ O ₃						
P ₂ O ₅	1.001	0.124	0.829	0.119	0.956	0.121
SO ₃	0.787	0.055	0.852	0.057	0.777	0.052
ZrO ₂	0.012	0.001	0.012	0.001	0.012	0.001
SUM	99.560		100.975		99.865	

Concentrations of B₂O₃ and Na₂O were determined by ICP.
 (+/-) One standard deviation

Appendix C4.3 Measured Composition of L6-5412 Glass Spiked with 1.5 wt% SO₃

Unit : wt%

Oxide	1300 C		1350 C		1400 C	
	@	(%)	&	(%)	@	(%)
SiO ₂	54.07	0.2	51.28		54.27	0.1
B ₂ O ₃	4.49	3.6	4.24		4.58	0.9
Na ₂ O	19.66		19.12		18.88	
CaO	4.04	3.4	3.80		4.20	5.1
Al ₂ O ₃	11.79	0.0	11.24		11.89	0.7
Others						
Bi ₂ O ₃	0.000		0.000		0.071	
Cl						
Cr ₂ O ₃	0.057	52.6	0.044		0.076	54.3
F						
Fe ₂ O ₃	0.054	37.0	0.055		0.052	
K ₂ O						
MnO	0.008	40.0	0.000		0.010	73.7
Nd ₂ O ₃	0.054		0.051			
P ₂ O ₅	1.162	1.2	1.176		1.276	15.6
SO ₃	0.876	4.7	0.728		0.916	20.7
ZrO ₂	0.016		0.027		0.054	
SUM	96.274		91.761		96.269	

& Values were determined by ICP using sodium fussion method,

@ Values were determined by ICP using both sodium and potassium fussion methods.

(%) Deviation percentage was determined as : $100\% \times |Cs - Cp| / 0.5 \times (Cs + Cp)$,

where Cs and Cp are the concentrations measured using sodium and potassium fussion methods.

Appendix C4.4 Measured Composition of L6-5412 Glass Spiked with 2.0 wt% SO₃

Unit : wt%

Oxide	1300 C		1350 C		1400 C	
		(+/-)		(+/-)		(+/-)
SiO ₂	53.06	3.85	53.06	3.85	50.27	3.64
B ₂ O ₃ #	4.73	0.47	4.06	0.41	4.70	0.47
Na ₂ O#	19.68	1.97	20.76	2.08	20.62	2.06
CaO	4.34	0.31	4.20	0.29	4.18	0.29
Al ₂ O ₃	13.53	1.42	11.36	1.36	11.96	1.34
Others						
Bi ₂ O ₃	0.013	0.001	0.013	0.001	0.014	0.001
Cl	0.039	0.014	0.045	0.014	0.026	0.000
Cr ₂ O ₃	0.034	0.003	0.031	0.003	0.032	0.003
F						
Fe ₂ O ₃	0.072	0.006	0.063	0.005	0.060	0.005
K ₂ O	0.299	0.025	0.317	0.027	0.353	0.029
MnO	0.006	0.002	0.007	0.002	0.006	0.002
Nd ₂ O ₃	0.000	0.000	0.000	0.000	0.000	0.000
P ₂ O ₅	0.641	0.000	0.917	0.344	1.237	0.344
SO ₃	0.852	0.125	0.724	0.120	0.597	0.115
ZrO ₂	0.010	0.001	0.009	0.001	0.010	0.001
SUM	97.300		95.551		94.078	

Concentrations of B₂O₃ and Na₂O were determined by ICP.
 (+/-) One standard deviation

Appendix C5.1 Measured Composition of L6-5412 Glass Spiked with 0.5 wt% Cr₂O₃

Unit : wt%

Oxide	1300 C & (%)	1350 C @ (%)	1400 C @ (%)
SiO ₂	51.80	53.28 2.0	53.01 1.0
B ₂ O ₃	4.33	4.75 2.0	4.50 0.0
Na ₂ O	20.97	19.63	19.26
CaO	3.86	4.02 1.6	4.05 6.3
Al ₂ O ₃	11.41	11.76 2.0	11.71 1.0
Others			
Bi ₂ O ₃	0.000	0.020	0.000
Cl			
Cr ₂ O ₃	0.460	0.480 4.0	0.476 4.2
F			
Fe ₂ O ₃	0.055	0.055 47.0	0.064 34.4
K ₂ O			
MnO	0.014	0.015 13.0	0.017 0.0
Nd ₂ O ₃	0.175	0.078	0.049
P ₂ O ₅	0.965	1.170 4.0	1.154 1.3
SO ₃	0.287	0.323 25.0	0.289 26.2
ZrO ₂	0.060	0.015	0.041
SUM	94.382	95.594	94.610

& Values were determined by ICP using sodium fussion method,
in which Na₂O and ZrO₂ were determined using potassium fussion method.

@ Values were determined by ICP using both sodium and potassium fussion methods.

(%) Deviation percentage was determined as : $100\% \cdot [Cs - Cp] / 0.5 \cdot (Cs + Cp)$,

where Cs and Cp are the concentrations measured using sodium and potassium fussion methods.

Appendix C5.2 Measured Composition of L6-5412 Glass Spiked with 0.8 wt%Cr₂O₃

Unit : wt%

Oxide	1300 C		1350 C		1400 C	
		(+/-)		(+/-)		(+/-)
SiO ₂	55.19	2.78	54.55	2.78	54.34	2.78
B ₂ O ₃ #	4.57	0.46	5.60	0.56	4.99	0.50
Na ₂ O#	20.00	2.00	20.80	2.08	21.80	2.18
CaO	4.27	0.21	4.21	0.21	4.21	0.21
Al ₂ O ₃	10.58	0.62	10.69	0.62	11.24	0.64
Others						
Bi ₂ O ₃						
Cl	0.065	0.006	0.059	0.006	0.048	0.005
Cr ₂ O ₃	0.791	0.039	0.795	0.039	0.794	0.039
F						
Fe ₂ O ₃	0.079	0.004	0.057	0.003	0.080	0.004
K ₂ O	0.279	0.145	0.289	0.157	0.283	0.145
MnO	0.015	0.003	0.017	0.003	0.014	0.003
Nd ₂ O ₃						
P ₂ O ₅	0.694	0.117	0.756	0.117	0.926	0.119
SO ₃	0.332	0.350	0.242	0.325	0.220	0.325
ZrO ₂	0.011	0.001	0.011	0.001	0.011	0.001
SUM	96.882		98.088		98.959	

Concentrations of B₂O₃ and Na₂O were determined by ICP.
 (+/-) One standard deviation

Appendix C5.3 Measured Composition of L6-5412 Glass Spiked with 1.0 wt%Cr₂O₃

Oxide	1300 C		1350 C		1400 C	
	(+/-)		(+/-)		(+/-)	
SiO ₂	54.98	3.85	54.13	3.85	54.77	3.85
B ₂ O ₃	4.60	0.46	4.15	0.42	4.48	0.45
Na ₂ O	20.76	2.08	19.55	1.95	19.82	1.98
CaO	4.21	0.29	4.18	0.29	4.17	0.29
Al ₂ O ₃	12.15	0.91	11.92	0.91	12.11	0.91
Others						
Bi ₂ O ₃	0.009	0.001	0.009	0.001	0.010	0.001
Cl	0.054	0.006	0.049	0.006	0.041	0.005
Cr ₂ O ₃	0.959	0.067	0.972	0.069	0.973	0.069
F						
Fe ₂ O ₃	0.064	0.003	0.059	0.003	0.081	0.004
K ₂ O	0.349	0.025	0.340	0.024	0.304	0.022
MnO	0.016	0.002	0.016	0.002	0.017	0.002
Nd ₂ O ₃	0.010	0.001	0.012	0.001	0.022	0.002
P ₂ O ₅	1.196	0.142	1.244	0.142	1.237	0.144
SO ₃	0.305	0.037	0.227	0.035	0.247	0.035
ZrO ₂	0.012	0.001	0.012	0.001	0.015	0.001
SUM	99.680		96.870		98.286	

Concentrations of B₂O₃ and Na₂O were determined by ICP.
 (+/-) One standard deviation

Appendix C5.4 Measured Composition of L6-5412 Glass Spiked with 2.0 wt% Cr₂O₃

unit : wt%

Oxide	1300 C		1350 C		1400 C	
	(+/-)		(+/-)		(+/-)	
SiO ₂	52.63	3.85	54.98	4.06	55.19	4.06
B ₂ O ₃	4.54	0.45	4.57	0.46	4.31	0.43
Na ₂ O	18.06	1.81	20.89	2.09	20.49	2.05
CaO	4.23	0.29	4.20	0.29	4.17	0.29
Al ₂ O ₃	12.04	1.42	11.87	1.38	11.64	1.42
Others						
Bi ₂ O ₃	0.013	0.001	0.013	0.001	0.013	0.001
Cl	0.076	0.017	0.055	0.017	0.035	0.016
Cr ₂ O ₃	1.771	0.124	1.805	0.127	1.824	0.129
F						
Fe ₂ O ₃	0.063	0.005	0.090	0.007	0.097	0.007
K ₂ O	0.292	0.024	0.340	0.028	0.337	0.028
MnO	0.011	0.000	0.011	0.000	0.011	0.000
Nd ₂ O ₃	0.000	0.000	0.000	0.000	0.000	0.000
P ₂ O ₅	1.100	0.344	1.031	0.344	1.237	0.344
SO ₃	0.405	0.105	0.350	0.102	0.195	0.097
ZrO ₂	0.012	0.001	0.012	0.001	0.012	0.001
SUM	95.235		100.215		99.569	

Concentrations of B₂O₃ and Na₂O were determined by ICP.

(+/-) One standard deviation

Appendix D

Melt Viscosity of L6-5412 and Its Based Glasses Spiked
with Minor Components at Their Solubility Limit Levels

Appendix D. Melt Viscosity of L6-5412 and Its Based Glasses Spiked with Minor Components at Their Solubility Limit Levels

L6-5412		L6-5412Cl1		L6-5412F2.5		L6-5412P2.5		L6-5412S1		L6-5412Cr0.5	
Temp. (C)	Viscosity (Pa.s)	Temp. (C)	Viscosity (Pa.s)	Temp. (C)	Viscosity (Pa.s)	Temp. (C)	Viscosity (Pa.s)	Temp. (C)	Viscosity (Pa.s)	Temp. (C)	Viscosity (Pa.s)
1287	15.03	1287	16.65	1287	9.02	1287	15.97	1286	16.24	1288	15.27
1238	22.00	1238	25.42	1238	13.25	1238	21.27	1237	24.61	1239	23.32
1189	34.58	1188	40.11	1189	20.30	1188	38.34	1188	38.40	1189	36.69
1238	22.82	1238	26.30	1238	13.43	1237	25.13	1237	24.84	1238	23.90
1288	15.36	1287	17.70	1288	9.58	1287	16.74	1286	16.59	1288	15.95
1338	10.95	1337	12.81	1338	7.05	1337	11.86	1336	11.74	1338	11.19
1388	7.81	1387	9.10	1388	5.18	1387	8.42	1386	8.36	1389	7.86
1438	5.78	1437	6.88	1438	3.98	1437	6.15	1436	6.33	1439	5.81
1289	16.50	1288	19.78	1289	11.16	1288	17.79	1287	18.37	1289	16.88
1140	65.40	1139	78.39	1140	38.80	1139	70.01	1139	72.66	1140	68.75
1090	113.52	1089	136.84	1090	66.93	1089	123.79	1089	129.06	1089	118.78

Appendix E

PCT Data of L6-5412 and Its Based Glasses Spiked with Minor Components at Their Solubility Limits

**Appendix E1 pH Values Before and After the PCT Test for L6-5412 and
Its Based Glasses Containing Minor Components at Their Solubility Limits.**

Glass	before PCT	after PCT	
		No.1	No.2
L6-5412	9.55	11.10	11.14
L6-5412Cl	9.69	11.22	11.22
L6-5412F	9.36	11.03	10.99
L6-5412P	9.93	11.21	11.16
L6-5412S	9.75	11.24	11.21
L6-5412Cr	9.92	11.33	11.33

Appendix E2 Concentration and Normalized Elemental Mass Loss Determined by 7 Days PCT Test for L6-5412 and Its Based Glasses Containing the Minor Components at Their Solubility Limits.

Glass	Element	Ci (mg/L)		(NL)i (g/m ²)		Method
		No.1	No.2	No.1	No.2	
L6-5412	Si	60.44	60.50	0.114	0.114	ICP
	B	3.99	4.02	0.128	0.129	ICP
	Na	103.88	104.48	0.350	0.352	ICP
	Ca	1.34	1.41	0.023	0.025	ICP
	Al	13.36	13.41	0.105	0.106	ICP
	Cl	0.37	0.33	0.201	0.179	IC
	F	0.39	0.36	0.092	0.085	SIE
	P	0.15	0.17	0.014	0.016	ICP
	S	0.31	0.31	0.121	0.121	ICP
	Cr	0.00	0.00	0.000	0.000	ICP
L6-5412Cl	Si	66.21	64.67	0.125	0.122	ICP
	B	4.55	4.48	0.147	0.145	ICP
	Na	117.00	115.82	0.396	0.392	ICP
	Ca	1.10	1.00	0.019	0.018	ICP
	Al	14.91	14.62	0.118	0.116	ICP
	Cl	2.27	2.89	0.020	0.026	IC
	F	0.44	0.46	0.104	0.108	SIE
	P	0.25	0.24	0.024	0.023	ICP
	S	0.37	0.38	0.145	0.149	ICP
	Cr	0.00	0.00	0.000	0.000	ICP
L6-5412F	Si	56.26	56.08	0.107	0.106	ICP
	B	3.88	3.91	0.126	0.127	ICP
	Na	93.04	94.76	0.315	0.321	ICP
	Ca	1.01	0.95	0.018	0.017	ICP
	Al	12.56	12.54	0.099	0.099	ICP
	Cl	0.53	0.49	0.291	0.269	IC
	F	4.80	4.80	0.306	0.306	SIE
	P	0.16	0.16	0.016	0.016	ICP
	S	0.25	0.30	0.098	0.118	ICP
	Cr	0.00	0.00	0.000	0.000	ICP
L6-5412P	Si	76.76	75.31	0.146	0.143	ICP
	B	5.19	5.09	0.168	0.165	ICP
	Na	125.52	121.56	0.426	0.413	ICP
	Ca	0.52	0.52	0.009	0.009	ICP
	Al	17.86	17.49	0.142	0.139	ICP
	Cl	—	—	—	—	—
	F	—	—	—	—	—
	P	0.86	0.82	0.051	0.048	ICP
	S	0.36	0.42	0.142	0.165	ICP
	Cr	0.00	0.00	0.000	0.000	ICP
L6-5412S	Si	61.69	61.28	0.117	0.116	ICP
	B	4.17	4.13	0.135	0.134	ICP
	Na	111.94	111.30	0.379	0.377	ICP
	Ca	1.34	1.38	0.024	0.024	ICP
	Al	13.75	13.68	0.109	0.108	ICP
	Cl	—	—	—	—	—
	F	—	—	—	—	—
	P	0.17	0.17	0.016	0.016	ICP
	S	1.30	1.35	0.216	0.224	ICP
	Cr	0.00	0.00	0.000	0.000	ICP
L6-5412Cr	Si	72.49	72.06	0.137	0.136	ICP
	B	5.17	5.14	0.167	0.166	ICP
	Na	130.15	129.08	0.441	0.437	ICP
	Ca	0.71	0.71	0.012	0.012	ICP
	Al	15.57	15.47	0.123	0.122	ICP
	Cl	—	—	—	—	—
	F	—	—	—	—	—
	P	0.38	0.38	0.037	0.037	ICP
	S	0.37	0.35	0.145	0.137	ICP
	Cr	0.19	0.19	0.028	0.028	ICP