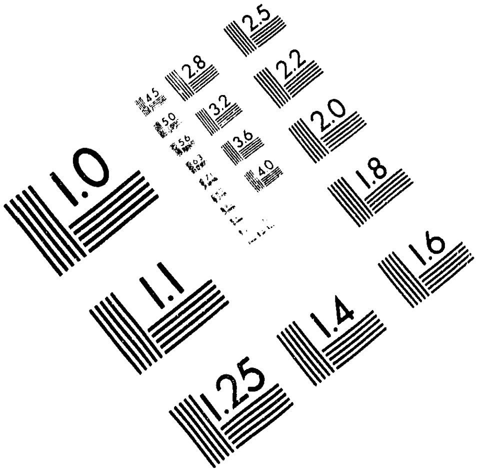

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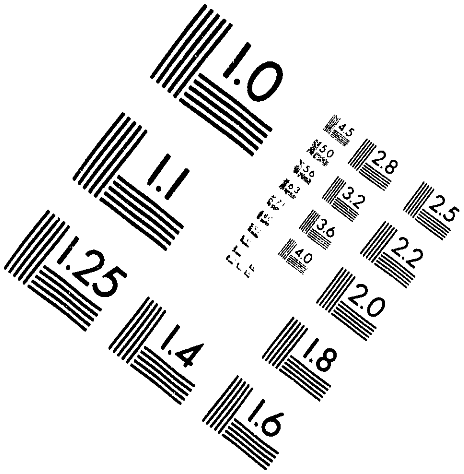

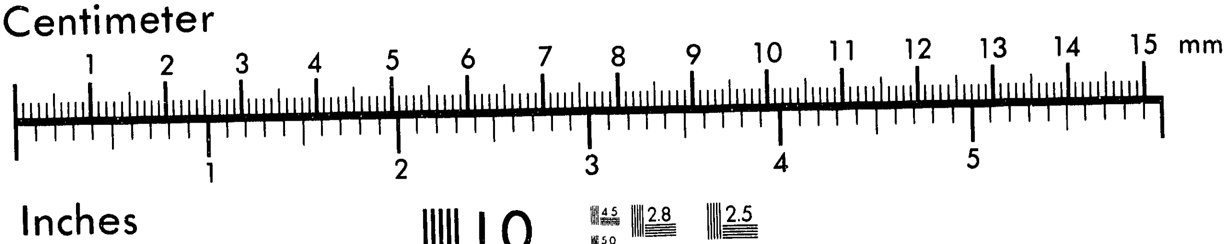

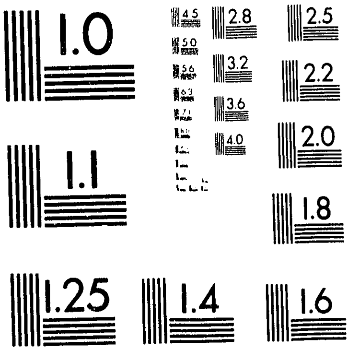

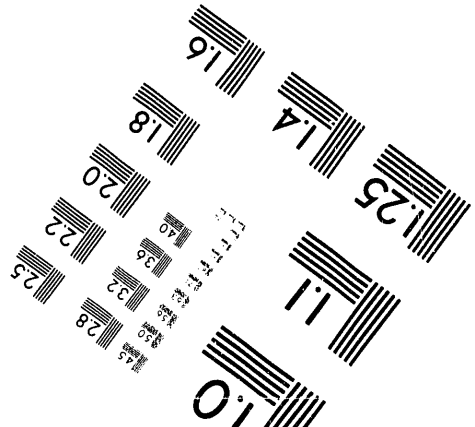

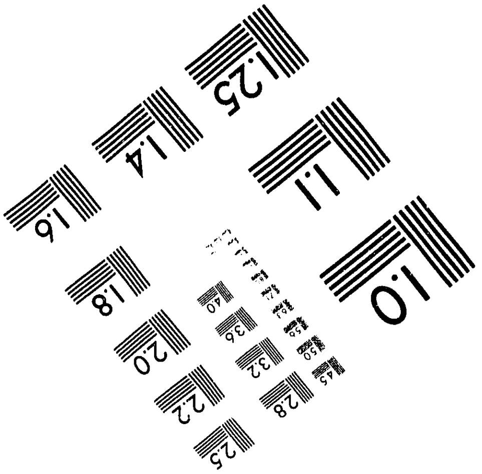

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CRYSTALLIZATION IN SIMULATED GLASSES FROM HANFORD HIGH-LEVEL NUCLEAR WASTE COMPOSITION RANGE

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CRYSTALLIZATION IN SIMULATED GLASSES FROM HANFORD HIGH-LEVEL NUCLEAR WASTE COMPOSITION RANGE

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ABSTRACT

Glass crystallization was investigated as part of a property-composition relationship study of Hanford waste glasses. Non-radioactive glass samples were heated in a gradient furnace over a wide range of temperatures. The liquidus temperature was measured, and primary crystalline phases were determined using optical microscopy and Scanning Electron Microscopy with Energy Dispersive Spectrometry (SEM/EDS). Samples have also been heat treated according to a simulated canister centerline cooling curve. The crystalline phases in these samples have been identified by optical microscopy, SEM/EDS, and X-ray diffraction (XRD). Major components of the borosilicate glasses that were melted at approximately 1150°C were SiO_2, B_2O_3, Na_2O, Li_2O, CaO, MgO, Fe_2O_3, Al_2O_3, ZrO_2, and "Others" (sum of minor components). The major crystalline phases identified in this study were zircon, nepheline, calcium silicate, lithium silicate, and a range of solid solutions from clinopyroxenes, orthopyroxenes, olivines, and spinels.

INTRODUCTION

The Hanford Waste Vitrification Plant (HWVP) is being designed to convert selected pretreated Hanford high-level and transuranic wastes to a vitrified form for final disposal in a geologic repository [1]. Composition of the glass product will vary because of differences in composition of the wastes. This will affect the melt and glass properties and, hence, glass processability in the melter and glass product acceptability for isolation in a geologic repository. To produce processable and acceptable glasses from wastes of different composition, a Composition-Property Relationship (CPR) study was started in order to obtain an experimental data base and develop glass and melt property models as a function of glass composition. The composition range of CPR in terms of major oxides is wide enough to cover most of the estimated compositional variability of the waste glasses to be processed in the HWVP. The key properties studied include melt viscosity and electrical conductivity, and glass chemical durability and crystallinity. This paper presents the results regarding the effect of glass composition on crystallinity in glasses from CPR composition range.

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Crystallization has impact on both waste glass processability and acceptability. Significant crystallization should be prevented in the glass melter. A limited concentration of insoluble noble metals, their oxides, and spinel are often unavoidable, and may be acceptable. Crystalline phases in the melter can cause processing problems, such as sludge formation on the melter bottom [2] or even melter electrode shorting if the phases are highly conductive. To avoid crystallization in the melter, the liquidus temperature (T_l) of the glass must be lower than the glass melt minimum temperature; hence, for an HWVP melter, $T_l < 1050°C$. Crystallization during cooling of glass in canisters may decrease glass durability [3], and must be characterized.

EXPERIMENTAL PROCEDURE

Ten major glass components used in CPR study were (the numbers in parenthesis represent the composition range in wt%) SiO_2 (42 to 57), B_2O_3 (5 to 20), Na_2O (5 to 20), Li_2O (1 to 7), CaO (0 to 10), MgO (0 to 8), Fe_2O_3 (0.5 to 15), Al_2O_3 (0 to 17), ZrO_2 (0 to 13), and "Others" (1 to 10). A statistical experimental design technique was used in selecting compositions for testing [4]. A total of 121 glasses, including 11 replicates, were prepared. The "Others" component used in this study was composed of BaO, CdO, CeO_2, Cr_2O_3, Cs_2O, CuO, F, La_2O_3, MnO_2, MoO_3, Nd_2O_3, NiO, P_2O_5, PdO, Pr_6O_{11}, Rb_2O, Rh_2O_3, RuO_2, SO_3, Sm_2O_3, SrO, and Y_2O_3 [4]. Its composition was kept constant except for 12 glasses designed to test the effect of "Others" composition on glass properties.

For each glass, the nine major components were batched as oxides or carbonates, while "Others" were batched together in constant proportions. Each glass was melted at 1150°C for 1 h in a platinum crucible under a lid using an electrically heated resistance furnace. For better homogeneity, the glass was crushed and remelted for 1 h under the same conditions. The molten glass was poured onto a steel plate, air quenched, and crushed into cullet with a maximum diameter of 3 to 4 mm.

The liquidus temperature was measured by heating the glasses, which were initially free of crystals, in a thermal gradient furnace and determining the crystallization front temperature (the highest temperature at which crystals were found). The approximate 11°C/cm temperature gradient usually spanned 100 to 350°C within a temperature range from 500 to 1150°C. Each glass held in a long platinum-gold boat was heat treated for 24 h. Thin sections, prepared from the resulting glass bar, were mounted in polymer resin for optical microscopy and Scanning Electron Microscopy with Energy Dispersive Spectrometry (SEM/EDS).

Crystallization was also characterized for samples subjected to simulated canister centerline cooling. A glass sample held at 1150°C for 30 min in a high-purity alumina crucible was cooled following the canister centerline cooling time-temperature schedule that was obtained from numerical simulation as well as empirical data [4]. The alumina crucible with glass was then cut vertically, and thin sections were prepared for optical microscopy and SEM.

The thin sections from liquidus temperature glass samples were observed using an optical microscope with both reflected and transmitted light to evaluate the type of crystalline phases in the glass and to determine the crystallization front temperature. The chemical composition of the crystalline phases was qualitatively determined by SEM/EDS. Canister centerline-cooled glasses were examined by X-ray diffraction (XRD) in addition to optical microscopy and SEM/EDS to identify crystalline phases and to determine their semi-quantitative volume fractions.

The primary phase of crystallization was defined as the crystalline phase other than spinel with the highest liquidus temperature. If the glass liquidus temperature was outside of the sample's temperature range, the measurement was repeated until the crystallization front temperature was within the temperature range tested. However, no attempt was made to rerun the test if the hot end temperature was ≥ 1110°C or cold end temperature ≤ 700°C.

The liquidus temperature for spinels and clinopyroxenes was fitted to the first-order mixture model of the form [4], $T_l = \Sigma b_i m_i$ ($i = 1...10$), where m_i is the mass fraction of the i-th oxide component and b_i is the i-th component coefficient. The number of data points for other phases was not large enough to fit the model.

RESULTS AND DISCUSSION

Out of 110 glasses (excluding 11 replicates from the 121 glasses tested), 9 glasses did not precipitate any crystalline phase other than spinel during 24 h gradient temperature heat treatment, and 58 glasses precipitated at least one type of crystalline phase during canister centerline cooling. Figure 1 shows the liquidus temperatures of major crystalline phases identified in CPR glasses. As stated earlier, glasses with $T_l \geq 1050°C$ can cause problems because they can precipitate crystals during melting. Figure 2 shows the distribution of samples according to crystalline phases identified in canister centerline cooled glasses.

All 11 replicate glasses (six different compositions with one to five replicates) exhibited the same crystallinity. The liquidus temperature of the primary phase was within 30°C. The liquidus temperature of spinel crystals in replicate samples showed a somewhat larger scatter—the difference between maximum and minimum within samples of the same composition was 64°C. This difference can be attributed to the difficulties encountered during the crystallization front temperature determination for the spinel crystals. Spinel crystals were difficult to distinguish from RuO_2, which were similar in size, and from residual intermediate reaction products, which were probably formed in the early stages of melting.

The noble metals and their oxides, mostly RuO_2, were present as undissolved particles and sometimes as small needles that crystallized from RuO_2 dissolved in the glass. In some glasses, spinels or other crystals were nucleated on RuO_2. Also, spinel crystals in some glasses provided nucleation sites for other crystals, such as clinopyroxenes, as observed previously by Jantzen and Bickford [5-7]. The major crystalline phases identified in CPR glasses are discussed in the following paragraphs.

Spinel and Hematite

All oxide minerals with a spinel ($MgAl_2O_4$) structure are called spinels. The spinel structure allows complete solid solutions between many different spinels. Spinels identified in CPR glasses were those containing Fe, Cr, and Ni, namely magnetite (Fe_3O_4), chromite ($FeCr_2O_4$), and trevorite ($NiFe_2O_4$), which form solid solutions of the type $(Ni,Fe)(Fe,Cr)_2O_4$. Most common was magnetite (Fe_3O_4) with Ni and Cr as minor elements; although Fe_2O_3 was used as a glass component, Fe^{2+} was produced by reduction at high temperatures. Hematite (Fe_2O_3) was the only iron oxide identified in CPR glasses other than spinels.

Extremely small volume fractions (< 0.01%) of spinel-type crystals were observed in most samples, but this level of crystallinity is typical for air-quenched samples, probably a residue from melting reactions. The residual spinel had a characteristic appearance of dissolving crystals (round edges).

Out of 27 glasses with Fe_2O_3 > 8 wt%, 20 formed spinel within 24 h of isothermal heat treatment. The remaining 7 glasses that did not form spinel were

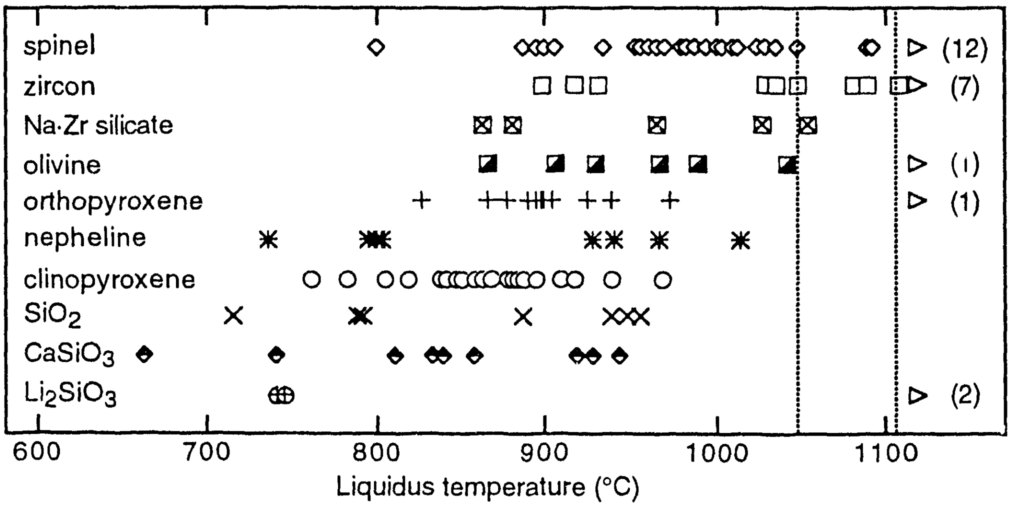

Figure 1. Liquidus temperatures of major crystalline phases in CPR glasses (figures in parenthesis represent the number of samples with $T_l \geq 1110°C$).

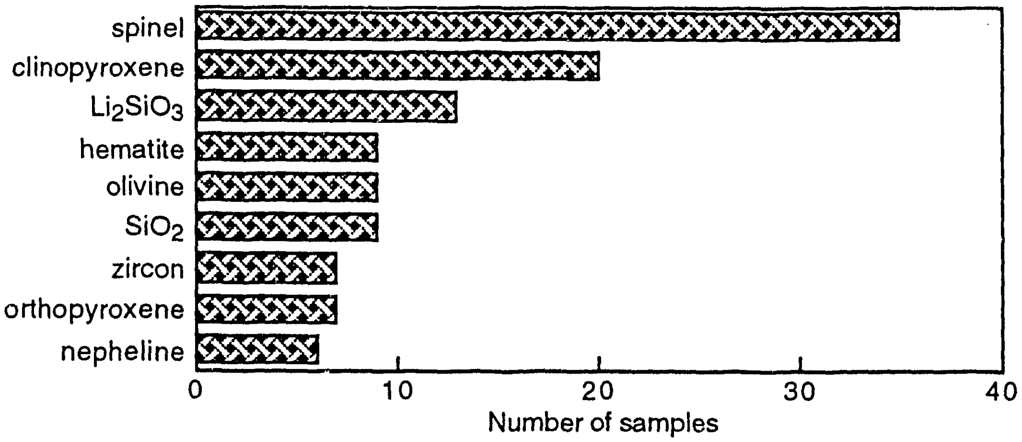

Figure 2. Number of glass samples with crystalline phases identified after canister centerline cooling (some samples formed two or more phases).

usually high in alkali oxides (Na_2O and Li_2O) and always low in Al_2O_3 (< 3.2 wt%). Spinel precipitated in 18 out of 36 glasses with 2 wt% < Fe_2O_3 < 8 wt%, but only in seven out of 47 glasses with $Fe_2O_3 \leq 2$ wt%. The latter glasses had low alkali and high "Others" concentrations. The liquidus temperature of spinel was higher than 900°C in all glasses but one (T_l = 800°C), and in some glasses reached above 1110°C, the maximum temperature commonly used in the gradient furnace. Only 1 glass precipitated hematite as a primary phase with T_l = 1070°C.

In canister centerline-cooled samples, all glasses with Fe_2O_3 > 11 wt% (13 glasses) formed at least one of the Fe-containing oxides (spinel and hematite) and at least one other phase. Glasses with 15 wt% Fe_2O_3 (the maximum value) always formed hematite. The lowest concentration of Fe_2O_3 that resulted in hematite precipitation was 11 wt%. Spinel precipitated in 11 glasses out of 30 with 4 wt% < Fe_2O_3 < 11 wt%, but only in 5 out of 67 with Fe_2O_3 ≤ 4 wt%. These 5 glasses contained relatively high Al_2O_3 (≥ 8 wt%) and high "Others" (≥ 7 wt%).

Overall, the chance of forming spinel crystals decreased as the concentration of Fe_2O_3 decreased, but spinel could precipitate at Fe_2O_3 concentrations as low as 2 wt%. Generally, for a given concentration of Fe_2O_3, the chance of spinel crystallization increased as the concentration of Al_2O_3 increased and the alkali concentration decreased. The "Others" mix, containing small amounts of Cr and Ni, promoted spinel formation at low Fe_2O_3 concentrations.

The first-order component coefficients for the liquidus temperature of spinel, obtained by fitting the first-order mixture model to the experimental data, are given in Table 1, and a plot of predicted versus measured liquidus temperature is in Figure 3. Data from glasses with different "Others" composition were not included in the calculation because Cr_2O_3 and NiO in "Others" affected the liquidus temperature of spinel and clinopyroxene. The fitting for the liquidus temperature of spinel was poor, which was expected considering the large scatter of experimental data in replicate glasses. The maximum deviation of predicted values from experimental values (68°C) was close to the scatter of experimental data in replicate glasses.

Table 1 indicates that T_l of spinel is most strongly increased by the presence of MgO and Fe_2O_3. The strong effect of MgO is surprising because Mg was never detected in spinel crystals. Interestingly, the low "Others" coefficient suggests a decrease in liquidus temperature with increasing "Others," although "Others" promotes the formation of spinel at low Fe_2O_3 concentrations.

Clinopyroxene

Pyroxenes are the most common form of single-chain silicates and consist of two sub-groups: clinopyroxenes (monoclinic) and orthopyroxenes (orthorhombic) [8]. Generalized chemical composition of clinopyroxenes may be written $M_1M_2(Si_2O_6)$, where M_1 represents Na, Ca, or Li and M_2 represents Fe^{3+}, Fe^{2+}, Mg, Al, or Cr. A wide range of cation substitutions is possible between clinopyroxene members to form a complete solid solution series.

Clinopyroxenes were formed as primary phases in 24 glasses, and their liquidus temperature ranged from 760 to 970°C. Three glasses precipitated a Zr-containing phase along with clinopyroxene with almost identical T_l (within ~15°C). Glasses with Fe_2O_3 > 12 wt% did not form clinopyroxene as a primary phase, but usually formed orthopyroxene. When Fe_2O_3 > 7 wt% and CaO > 3 wt%, the clinopyroxene solid solutions contained hedenbergite ($CaFeSi_2O_6$) as a major component. Acmite ($NaFeSi_2O_6$) was found as a major phase only when Na_2O > 10 wt%. Most clinopyroxene phases found in glasses with 2 wt% ≤ Fe_2O_3 < 7 wt% were comprised of diopside ($CaMgSi_2O_6$) with hedenbergite as a minor phase.

Twelve glasses formed clinopyroxene crystals during canister centerline cooling. All of these glasses contained either high Fe_2O_3 (>7 wt%) or relatively high MgO (>5 wt%), or both. As in the liquidus temperature samples, hedenbergite was a major component when the Fe_2O_3 concentration was high, and diopside was a major component when the Fe_2O_3 concentration was low and the MgO concentration high. Interestingly, acmite was not observed in canister centerline-cooled samples. No glasses with B_2O_3 > 12 wt% precipitated clinopyroxenes, and 7 out of 12 glasses with clinopyroxene had 5 wt% B_2O_3 (the minimum value). Accordingly, B_2O_3 tends to suppress formation of clinopyroxene group crystals.

Table 1. First-Order Mixture Model Coefficients for Liquidus Temperature (°C).

Component	Spinel	Clinopyroxene
SiO_2	960	989
B_2O_3	841	388
Na_2O	93	-17
Li_2O	182	-286
CaO	1599	1195
MgO	2959	2343
Fe_2O_3	2181	1569
Al_2O_3	1495	1319
ZrO_2	1238	1560
Others	697	1168

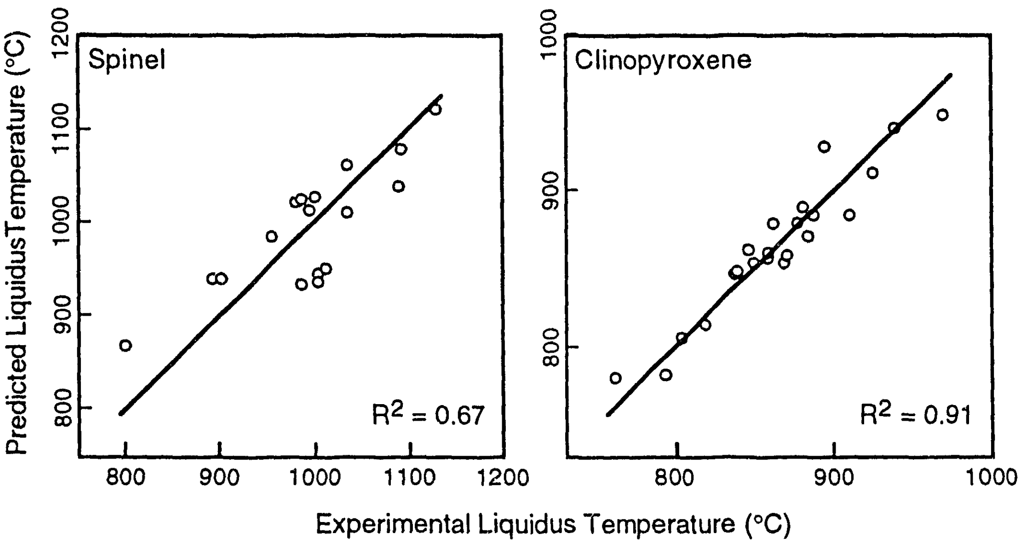

Figure 3. Predicted versus measured liquidus temperature of spinel and clinopyroxene for the first-order mixture model.

Among 24 glasses that formed clinopyroxene as the primary phase, only 6 precipitated clinopyroxene during canister centerline cooling, 17 did not precipitate any crystals other than spinel, and 1 glass precipitated lithium silicate. Out of 12 glasses that formed clinopyroxene during canister centerline cooling, clinopyroxene was the primary phase only in 6 glasses, although Fe_2O_3 concentration was very high (>14 wt%) in 4 of the remaining 6 glasses.

First-order component coefficients for liquidus temperature of clinopyroxene group crystals are in Table 1, and a plot of predicted versus measured values are in Figure 3. The fit was very good, with the maximum difference between predicted and experimental values < 20°C except for 1 glass (36°C), but glasses with altered "Others" were excluded. As Table 1 shows, alkali oxides and B_2O_3 decrease the liquidus temperature of clinopyroxene, Li_2O having the strongest effect. All remaining components tend to increase T_l. As in spinel crystals, MgO was most effective in increasing T_l, which agrees with the observation that MgO was the major element in most of the clinopyroxenes identified in this study. The effect of ZrO_2 was as strong as Fe_2O_3, although ZrO_2 was not a major component in clinopyroxenes.

Orthopyroxene and Olivine

Orthopyroxenes are represented by magnesium–iron pyroxenes (orthoenstatite–orthoferrosilite series), $(Mg,Fe)SiO_3$ [8], and olivines by forsterite-fayalite series, $(Mg,Fe)_2SiO_4$, which belong to island silicates [9]. In orthopyroxenes and olivines, the cations Mg^{2+} and Fe^{2+} are mutually replaceable, forming complete solid solutions within each series.

Twelve glasses precipitated orthopyroxene crystals as their primary phase with T_l ranging from 826 to 973°C for all but one sample. This high ZrO_2 (8 wt%) glass formed $ZrSiO_4$ and orthopyroxene up to > 1118°C, which mostly settled at the bottom of the boat (the other 11 glasses contained ≤ 4.4 wt% ZrO_2). The unusually high T_l of this glass was probably caused by liquid-liquid segregation. The orthopyroxene phase was close to $MgSiO_3$ composition in only 2 glasses, both containing 8 wt% MgO. One glass with 5 wt% MgO and 11.4 wt% Fe_2O_3 formed a solid solution of $FeSiO_3$ and $MgSiO_3$. The remaining 9 glasses with Fe_2O_3 > 7 wt% and MgO < 1 wt% formed an orthopyroxene phase that was close to $FeSiO_3$ with Ni and Cr as minor elements.

Olivine was the primary phase in 8 glasses, out of which seven had 8 wt% MgO and one 5 wt% MgO; Fe_2O_3 was between 2 and 14 wt%. The composition was close to Mg_2SiO_4 with Fe and Ni as minor components, with T_l ranging from 866 to 1042°C except in 1 glass with T_l > 1118°C.

Among the canister centerline-cooled samples, nine formed olivine, five orthopyroxene, and one formed both. Among 9 glasses that formed olivine, olivine was the primary phase in seven; zircon was the primary phase in the remaining 2 glasses, which were high in ZrO_2. One glass, which had olivine as the primary phase, precipitated krinovite ($NaMg_2CrSi_3O_{10}$) instead of olivine when canister centerline cooled. Out of 12 glasses with orthopyroxene as the primary phase, five formed orthopyroxene during canister centerline cooling, five (with Fe_2O_3 > 8 wt%) formed various crystals, such as hematite, spinel, lithium silicate and clinopyroxene, and two (with Fe_2O_3 < 8 wt%) did not form any crystals at all.

Zirconium-Containing Crystals

Glasses that precipitated Zr-containing primary phases ($ZrSiO_4$, ZrO_2, $Ca_2ZrSi_4O_{12}$, or sodium-zirconium silicate) had at least 3.9 wt% ZrO_2. In 17 out of 18 glasses with ZrO_2 > 7 wt%, one of Zr-containing phases, mostly zircon ($ZrSiO_4$), was the primary phase with T_l > 1000°C in 15 glasses (T_l > 1110°C in seven). The remaining 1 glass, which contained 13 wt% ZrO_2, did not precipitate any crystals. Out of 12 glasses with 3.9 wt% ≤ ZrO_2 < 7 wt%, only four had a Zr-containing primary phase; in three of these four, clinopyroxene precipitated along with Zr-containing crystals with almost the same T_l as mentioned earlier. In 1 glass, with both maximum ZrO_2 (13 wt%) and maximum CaO (10 wt%), a massive crystallization of $Ca_2ZrSi_4O_{12}$ occurred along with a small amount of $ZrSiO_4$ (T_l > 1118°C). Sodium-zirconium silicate was found in 5 glasses with Na_2O > 11 wt% and a T_l ranging from 860 to 1055°C. In 1 glass with a low concentration of SiO_2 (42.1 wt%), the primary phase was ZrO_2 with T_l > 1118°C.

In canister centerline-cooled samples, no Zr-containing crystalline phases were found when the ZrO_2 concentration was < 5 wt%, but at least one Zr-containing crystalline phase was found in 7 out of 24 glasses with ZrO_2 ≥ 5 wt%. The major phase in most of these glasses was $ZrSiO_4$. Crystallization of ZrO_2 was observed in 2 glasses with low SiO_2 ($\leq$ 44 wt%). The glass with $Ca_2ZrSi_4O_{12}$ as the primary phase also precipitated $Ca_2ZrSi_4O_{12}$ during canister centerline cooling. Five glasses with a sodium-zirconium silicate primary phase did not form any Zr-containing phase during canister centerline cooling. Because sodium-zirconium silicate was identified only in liquidus temperature samples, its structural information and exact composition could not be obtained; XRD analysis was performed only for canister centerline cooled samples.

The samples with ZrO_2 > 10 wt%, but T_l < 1110°C, did not show any Zr-containing crystalline phase after canister centerline cooling. This indicates that zircon crystallization was too slow to precipitate from glasses with as much as 13 wt% ZrO_2 and T_l < 1110°C. One glass with 13 wt% ZrO_2 did not crystallize during canister centerline cooling nor during 24 h isothermal heat treatment; this glass was high in both B_2O_3 (20 wt%) and Na_2O (19 wt%).

Aluminum-Containing Crystals

Nepheline ($NaAlSiO_4$) was the primary phase in 8 glasses; its T_l range was between 736 and 1015°C. All these glasses were high in both Na_2O (> 10 wt%) and Al_2O_3 ($\geq$ 9 wt%). The liquidus temperature seemed to decrease as the B_2O_3 concentration increased. One glass with 7 wt% Li_2O and 8 wt% Na_2O formed lithium-aluminum silicate (a primary phase) with T_l = 815°C.

Six glasses precipitated nepheline during canister centerline cooling. All belonged to the group of 8 glasses which contained high Al_2O_3 (>8 wt%) and high Na_2O (18 wt%). One of the remaining 2 glasses out of this group of 8 glasses had a low T_l (736°C), and the other was free of crystals after both canister centerline cooling and 24 h isothermal heat treatment. Glasses with high CaO in addition to high Al_2O_3 and Na_2O crystallized gehlenite ($Ca_2Al_2SiO_7$) in addition to nepheline. Among 8 glasses with nepheline as the primary phase, four with T_l > 920°C precipitated nepheline and 4 glasses with T_l < 810°C did not form any crystals during canister centerline cooling.

Lithium Silicate

Lithium silicate (Li_2SiO_3) was the primary phase in only 4 glasses; all contained 7 wt% Li_2O (the highest concentration used). The liquidus temperature was low (741 and 745°C) in 2 glasses and high (T_l > 1150°C) in the other two.

Crystals of Li_2SiO_3 were identified in 13 canister centerline-cooled samples; 11 of them contained 7 wt% Li_2O and $B_2O_3 \leq 6$ wt%, one contained 6.3 wt% Li_2O, and one had 9.5 wt% B_2O_3 along with 7 wt% Li_2O. Among 14 glasses with 7 wt% Li_2O and B_2O_3 > 6 wt%, Li_2SiO_3 was found in only 1 glass. This might suggest that B_2O_3 suppresses Li_2SiO_3 crystallization in high Li_2O glasses. Out of 4 glasses with Li_2SiO_3 as the primary phase, three precipitated Li_2SiO_3 during canister centerline cooling (the other did not precipitate any crystals).

Calcium Silicate

Calcium silicate was the primary phase in 9 glasses with T_l between 663 and 943°C. This phase was never observed in the canister centerline-cooled samples, and so structural information could not been obtained. Judging from the relative peaks of Ca and Si in the qualitative EDS spectra, it is likely that the composition was $CaSiO_3$. All 9 glasses had CaO > 3.5 wt%, and six of them had CaO $\geq$ 7 wt%. An interesting feature in these 9 glasses was a small or zero MgO content ($\leq$ 0.5 wt%). During canister centerline cooling, one (with 14 wt% Fe_2O_3) of these 9 glasses formed clinopyroxene and the other eight (with $Fe_2O_3 \leq 4.5$ wt%) did not precipitate any crystals.

Silicon Dioxide

Silicon dioxide (SiO_2) was the primary phase in 6 glasses with T_l from 788 to 957°C. These glasses contained high SiO_2 (> 52 wt%) and were generally low in Fe_2O_3 (≤ 2 wt% except one glass with 10.5 wt%) and ZrO_2 (< 1.8 wt%). Nine canister centerline-cooled glasses formed SiO_2 without any noticeable compositional dependence (SiO_2 ranged from 42 to 56 wt%). The primary phase was SiO_2 in only two out of these nine samples. Four glasses out of six with primary SiO_2 were crystal-free after canister centerline cooling.

Effect of Different "Others"

Four glasses were tested with the same nominal composition, but different "Others" composition. The primary phase in the glass with regular (unaltered) "Others" was clinopyroxene with T_l = 860°C (average value from three replicate glasses). Three glasses with altered "Others" had a higher Cr_2O_3 content and formed clinopyroxene as the primary or a secondary phase with T_l in the range of 880 to 945°C. Two glasses had Cr_2O_3 as the primary phase with T_l = 944 and 1036°C. After canister centerline cooling of these 4 glasses, Cr_2O_3 crystallization was observed only in the glass with the highest Cr_2O_3 concentration (0.89 wt%).

Nepheline was the primary phase (T_l = 795°C) in 2 glasses with the same nominal composition but different "Others". One glass with higher Cr_2O_3 and NiO precipitated spinel during canister centerline cooling while its counterpart with regular "Others" remained crystal-free.

Lithium-aluminum silicate was found along with Cr_2O_3 after canister centerline cooling in 2 glasses with Al_2O_3 > 16 wt%, 6.9 wt% Li_2O, and 2.97 or 1.17 wt% Cr_2O_3. The corresponding glasses with regular "Others" (0.09 and 0.07 wt% Cr_2O_3 in glass, respectively) were crystal-free, which suggests that small additions of insoluble oxides, such as Cr_2O_3, can cause precipitation of other crystalline phases.

Orthopyroxene was the primary phase in a glass with 2.38 wt% Cr_2O_3 and 3.26 wt% P_2O_5, whereas clinopyroxene was the primary phase in the glass of the same nominal composition and regular "Others" (0.21 wt% Cr_2O_3 and 0.16 wt% P_2O_5). After canister centerline cooling, Cr_2O_3 and Li_3PO_4 were identified in the glass with high Cr_2O_3 and P_2O_5, but spinel was seen in the glass with regular "Others."

Crystal-Free Glasses (Except Spinel)

Nine glasses did not precipitate any crystalline phase other than spinel during 24 h gradient furnace heat treatment. Generally these glasses showed a high sum of B_2O_3, Na_2O, and Li_2O concentrations and low concentrations of ZrO_2 and Fe_2O_3 (all had Fe_2O_3 < 7 wt% and six of them only 2 wt% Fe_2O_3). Spinel crystallized in 2 glasses with higher Fe_2O_3 (6.7 and 4 wt%). Only these 2 glasses precipitated spinels during canister centerline cooling. Spinel crystallized in 1 glass that contained 2 wt% Fe_2O_3; its T_l = 800°C was the lowest liquidus temperature of spinel observed in this study. As mentioned earlier, the group of crystal free glasses includes 1 glass with 13 wt% ZrO_2.

CONCLUSIONS

The primary crystalline phase identified in the liquidus temperature samples was generally found also in canister centerline-cooled samples, but was suppressed in some glasses. In these glasses with suppressed primary phase, canister centerline cooling either produced different crystalline phases, or the glasses remained free of crystals.

The T_l of Zr-containing phases was usually higher (mostly above 900°C) than T_l of any other crystalline phase except spinel. Generally, the T_l of the Zr-containing phases increased as ZrO_2 concentration increased and alkali concentrations decreased. Crystallization of Zr-containing phases was suppressed in canister centerline-cooled high ZrO_2 glasses if T_l was $<$ 1100°C.

Magnesium and Fe were the major components in olivine, orthopyroxene, and most of the clinopyroxenes. High MgO glasses tended to form olivine, high Fe_2O_3 glasses tended to form orthopyroxene, and Mg- and Fe-containing clinopyroxenes were formed in the wide range of concentrations of MgO and Fe_2O_3. Because Fe in olivine, orthopyroxene, and most of the clinopyroxenes (except in those containing acmite) was in a reduced state (Fe^{2+}), the oxidation state of the glass would be an important factor affecting the precipitation of these crystals.

Spinel crystallization was affected mainly by the Fe_2O_3 concentration. The concentration of "Others," which contained spinel-forming elements Cr and Ni, becomes important in glasses with a low concentration of Fe_2O_3. Besides Fe_2O_3 and "Others," the concentration of alkali oxides and Al_2O_3 had a major effect on spinel crystallization. Among spinel crystals found in CPR glasses, magnetite ($Fe^{2+}Fe^{3+}{}_2O_4$) and chromite ($Fe^{2+}Cr_2O_4$) contain Fe^{2+}, which suggests that the glass oxidation state could also be an important factor in the crystallization of spinel.

The liquidus temperatures of spinel and clinopyroxene were increased most strongly by increased MgO concentration, which suggests caution in using MgO as a frit component. Glasses with high Al_2O_3 and Na_2O tended to crystallize nepheline. If high alkali oxide content is needed in high Al_2O_3 glasses to optimize viscosity and electrical conductivity, using Li_2O instead of Na_2O can prevent nepheline crystallization. However, this substitution should be balanced with concerns about possible liquid/liquid immiscibility problems.

Spinel and zirconium-containing phases have a potential to precipitate at $T >$ 1050°C, and thus it is desirable to estimate T_l for at least these phases. The first-order model for the T_l of spinel was presented in this study, but for zirconium-containing phases more experimental data are needed. First-order models, however, do not determine whether the crystalline phase is primary. An advanced thermodynamic model for liquidus temperature of CPR glasses is being developed. An important component of waste glass characterization is the knowledge of crystallinity in the canister. While a more complete model that would involve both phase equilibria and kinetics of crystallization is unavailable, crystallinity of the glass in the canister can be assessed with the help of the information presented in this paper.

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