LIQUIDUS TEMPERATURE AND PRIMARY CRYSTALLIZATION PHASES IN HIGH-ZIRCONIA HIGH-LEVEL WASTE BOROSILICATE GLASSES

TREVOR PLAISTED, PAVEL HRMA, JOHN VIENNA, AND ANTONIN JIRICKA
Pacific Northwest National Laboratory, Box 999, Richland, WA 99352

ABSTRACT

Liquidus temperature (T_L) studies of high-Zr high-level waste (HLW) borosilicate glasses have identified three primary phases: baddelyite (ZrO_2), zircon ($ZrSiO_4$), and alkali-zirconium silicates, such as parakeldyshite ($Na_2ZrSi_2O_7$). Using published T_L data for HLW glasses with these primary phases, we have computed partial specific T_Ls for major glass components. On the Na_2O-SiO_2-ZrO_2 submixture, we have determined approximate positions of the boundaries between the baddelyite, zircon, and parakeldyshite primary phase fields. The maximum that can dissolve at 1150°C in a borosilicate HLW glass subjected to common processability and acceptability constraints appears to be 16.5 mass% ZrO_2.

INTRODUCTION

Several published composition variation studies (CVS) [1-8] provide databases linking the liquidus temperature (T_L) associated with Zr-containing primary phases to high-level waste (HLW) glass composition. Three Zr-containing phases were identified. The zircon ($ZrSiO_4$) primary phase field occupied most of the region covered by the published data. The rest was divided between baddelyite (ZrO_2) and alkali zirconium silicates, mainly parakeldyshite ($Na_2ZrSi_2O_7$). Studies [2-5] express T_L as a function of glass composition by the equation

$$T_L = \sum_{i=1}^{N} T_{Li} g_i \tag{1}$$

where T_{Li} is the i-th component partial specific T_L (also called i-th component coefficient), g_i is the i-th component mass fraction in glass, and N is the number of components (usually limited to N-1 major components plus Others, the sum of all minor components; see the Table 1a footnote). Equation (1) represents a nearly planar liquidus surface. This is a satisfactory approximation of the real T_L surface on a constraint region within a multicomponent mixture. Such regions have narrow ranges of mass fractions of components. In this paper, we evaluated the following databases: Hanford CVS [1,2], simulated transuranic (TRU) waste CVS [3-5], and Idaho National Engineering Environmental Laboratory (INEEL) CVS [6-8]. To obtain T_{Li} values, we sorted the glasses into three groups according to the primary phase (zircon, baddeleyite, and parakeldyshite) and fitted Equation (1) to T_L versus g_i data for each group.

T_L VERSUS COMPOSITION DATA

This section summarizes the published T_L databases [1-8] that we used to compute the T_{Li} values. In all studies [1-8], the primary phases were identified by x-ray diffraction and scanning electron microscopy. T_L was measured by the gradient furnace method only in the earliest study, the Hanford CVS [1], that covers the glass-composition region envisaged for Hanford before 1995 [9]. A disadvantage of this method is that at T > 850°C, the surface-tension gradient induced by volatilization may generate melt convection that shifts the crystallization front. In later studies [3-8], this method was replaced by the uniform-temperature heat-treatment method.

Out of more than 100 glasses tested in Hanford CVS [1], 25 precipitated a Zr-containing primary phase: 18 precipitated zircon, 1 precipitated baddeleyite, and 6 formed an alkali-zirconium silicate, probably parakeldyshite. Although the Hanford CVS [1] did not focus solely on high-Zr glasses, it allowed the authors to determine a set of 10 component coefficients [2] for glasses with Zr-containing primary phases (all three phases taken together).

The TRU CVS [3-5] was designed for high-Zr Hanford HLW glasses. The initial study [3] tested 36 compositions and varied 9 components, one at a time. Zircon was the primary phase in 27 glasses, baddeleyite in 7 glasses, and 2 glasses precipitated CeO_2. T_{Li} values were determined only for glasses with a zircon primary phase. The following study [4] evaluated data from [1] and [3] and developed several sets of T_{Li} values. The final TRU CVS [5] added 10 compositions derived from the same baseline as in [3] except that two or three components were varied at a time. Several sets of T_{Li} values and second-order terms were developed.

Studies [6-8] extended the high-Zr composition region to incorporate INEEL high-Zr HLW. The first of these studies [6] developed a glass (marked B1-2 in Table Ia) with as high Zr content as possible while maintaining acceptable processing properties. This glass formed parakeldyshite as a primary phase. The following study [7] covered a broad composition region for INEEL wastes. Out of 44 glasses, 5 precipitated lithium, sodium, and sodium-lithium-zirconium-silicates as primary phases. The final study [8] generated 30 glasses with the same calculated viscosity value (6 Pa· s) at 1150°C. The primary phases were zircon in 17 glasses, baddeleyite in 6 glasses, and parakeldyshite in 7 glasses.

Space limitations do not allow us to list all T_L and g_i data. Table Ia shows only data that are not readily available and Table Ib lists the reference glasses.

Table Ia. Compositions (in Mass Fractions) and T_L Values for HLW High-Zr Glasses that Precipitate Alkali-Zirconium-Silicate as the Primary Phase ([6] and [7] data only)

ID	Al_2O_3	B_2O_3	Bi_2O_3	CaO	CeO_2	Fe_2O_3	Li_2O	MgO	Na_2O	P_2O_5	SiO_2	ZrO_2	Others*	T_L °C
IG1-10	.0000	.0653	.0000	.0000	.0000	.0005	.0900	.0000	.1560	.0000	.5439	.1400	.0043	981
IG1-12	.0317	.1500	.0000	.0000	.0000	.0005	.0000	.0000	.1530	.0000	.4205	.1400	.1043	1075
IG1-25	.0750	.0750	.0000	.0000	.0000	.0005	.0510	.0000	.1273	.0362	.4744	.1050	.0556	991
IG1-33	.0000	.0500	.0000	.0000	.0000	.0000	.0116	.0000	.2000	.0000	.4936	.1400	.1048	1310
IG1-39	.0751	.1250	.0000	.0000	.0000	.0000	.0675	.0000	.0883	.0125	.4469	.1049	.0798	855
Bl-2	.0169	.0500	.0000	.0009	.0000	.0005	.0700	.0000	.1687	.0056	.5220	.1503	.0151	1077

* Others contain 7 minor components: BaO, Cs_2O, CuO, Gd_2O_3, K_2O, PbO, and SrO.

Table Ib. Compositions (in Mass Fractions) and T_L Values for Reference Glasses

ID	Phase	Ref.	Al_2O_3	B_2O_3	Bi_2O_3	CaO	CeO_2	Fe_2O_3	Li_2O	MgO	Na_2O	P_2O_5	SiO_2	ZrO_2	Others	T_L °C
Zr-1	ZS	[3]	.0450	.1000	.0000	.0009	.0002	.0000	.0750	.0000	.1100	.0021	.5114	.1500	.0054	1064
IG1-25	PK	[7]	.0750	.0750	.0000	.0000	.0000	.0005	.0510	.0000	.1273	.0362	.4744	.1050	.0556	991
CVS2-88	Z	[1]	.1050	.0600	.0000	.0400	.0000	.0250	.0700	.0050	.1403	.0000	.4597	.0750	.0200	982

Primary phases: ZS zircon, Z baddeleyite, PK parakeldyshite

Partial Specific Liquidus Temperatures

Table II summarizes the T_{Li} values computed by fitting Equation (1) to the T_L values of glasses within the three primary phase fields using data from studies [1–8]. The effect of the i-th component on T_L can be judged from the difference between T_{Li} and the computed T_L value of a reference glass ($T_{L,ref}$). Table III shows the effect (S_i) of adding 1 mass% of the i-th component to a reference glass shown in Table Ib for each primary phase. The S_i values were calculated by the formula $S_i = 0.01(T_{Li} - T_{L.ref})/(1 - g_{i,ref})$, where subscript *ref* stands for the reference glass. The $T_{L.ref}$ values were obtained from Equation (1) and the T_{Li} values listed in Table II.

Zircon (ZS), the most common primary phase, occurs in n = 70 out of 103 compositions in the combined database (n is the number of data points within a primary phase field). We

computed several sets of T_{Li} coefficients for ZS. The largest set (N = 13) is composed of 12 major oxides (Al_2O_3, B_2O_3, Bi_2O_3, CaO, CeO_2, Fe_2O_3, Li_2O, MgO, Na_2O, P_2O_5, SiO_2, and ZrO_2) plus Others. Note that the number and kind of components in Others may change from set to set and varies from study to study. Interestingly, moving three components, Bi_2O_3, CaO, and CeO_2, that are absent or minor in most glasses to Others (reducing the number of coefficients to N = 10), reduced S_i for Others from 5.3 to 3.3°C/mass%. Adding Fe_2O_3, a component with the smallest effect (S_i = 0.6°C/mass%), to Others decreased the number of coefficients to N = 9. We also reduced the component set to N = 8 by removing from the database 4 glasses in which P_2O_5 was the single component varied in the TRU CVS [3]. To compare the coefficients for ZS with those for baddeleyite (Z) and alkali-zirconium-silicates (labeled as PK), we moved MgO to Others (N = 7). However, we do not recommend this set for estimating T_L because the effect of MgO on T_L is one of the largest (approximately 30°C/mass%).

Table II. T_{Li} (in °C) for Glasses with Zircon (ZS), Baddeleyite (Z), and Parakeldyshite (PK) as Primary Phases

	ZS					Z	PK
N	13	10	9	8	7	7	7
Al_2O_3	1570	1535	1570	1593	1494	5372	1688
B_2O_3	554	527	568	550	707	-686	168
Bi_2O_3	1274						
CaO	855						
CeO_2	1843						
Fe_2O_3	1353	1119					
Li_2O	-1448	-1275	-1300	-1257	-436	-4463	-1085
MgO	3973	4083	3974	3914			
Na_2O	-2130	-1935	-1907	-1884	-1423	-1523	2612
P_2O_5	2062	2256	2166				
SiO_2	1154	1116	1078	1052	1143	974	568
ZrO_2	4510	4470	4561	4602	3463	6244	2346
Others	1593	1395	1355	1404	1376	1701	970
n	70	70	70	66	66	14	19
R^2	0.857	0.842	0.840	0.837	0.752	0.548	0.736
s [°C]	32	32	32	34	41	93	85

Table III. Predicted Change in T_L (in °C/mass%) from Adding 1 Mass% of a Component to a Reference Glass

	ZS					Z	PK
N	13	10	9	8	7	7	7
Al_2O_3	5.3	4.9	5.3	5.6	4.5	49.4	7.6
B_2O_3	-5.7	-6.0	-5.5	-5.7	-3.9	-17.4	-8.8
Bi_2O_3	2.1						
CaO	-2.1						
CeO_2	7.8						
Fe_2O_3	2.9	0.5					
Li_2O	-27.2	-25.3	-25.6	-25.1	-16.2	-58.2	-21.8
MgO	29.1	30.2	29.1	28.5			
Na_2O	-35.9	-33.7	-33.4	-33.1	-27.9	-28.7	18.6
P_2O_5	10.0	11.9	11.0				
SiO_2	1.8	1.0	0.2	-0.2	1.7	0.5	-8.0
ZrO_2	40.5	40.0	41.1	41.7	28.3	57.3	15.2
Others	5.3	3.3	2.9	3.4	3.2	7.7	-0.2

In Table II, R^2 is the fraction of the variation in T_L database values accounted for by Equation (1), and the quantity s is the root mean square error that estimates the experimental error standard deviation if Equation (1) does not have a significant lack of fit. For ZS with N = 8

to 10, R^2 = 0.84 suggests that Equation (1) provides a reasonable approximation to the relationships between glass composition and T_L. The *s* value of approximately 32°C for N > 8 includes the measurement error of 10 to 15°C and the model lack of fit. Removing MgO from the set of major components resulted in a lower R^2 and higher *s*. Generally, the R^2 and *s* values are such that the models have some lack of fit, and thus the S_i values in Table III should be considered to have moderate uncertainties. The measured versus calculated T_L values, shown for the N = 13 (SZ) set in Figure 1, indicate that Equation (1) fits the data without a significant bias.

The baddeleyite (Z) and PK primary phase fields were supported by smaller numbers of data points than that of ZS (n = 14 for Z and 19 for PK). This limited the number of T_{Li} values to N = 7 (i = Al_2O_3, B_2O_3, Li_2O, Na_2O, SiO_2, ZrO_2, and Others). Both sets have large values of *s* (85°C for PK and 93°C for Z) and low R^2 values, though the R^2 value for PK is comparable to the N = 7 set for ZS (Table II). The very low R^2 value for Z indicates that the corresponding T_{Li} values provide a rather rough estimate of T_L. This is also evident from extremely large positive and negative values of coefficients and a large T_{Li} value for Others. Clearly, the T_L database for baddeleyite is insufficient to support the model.

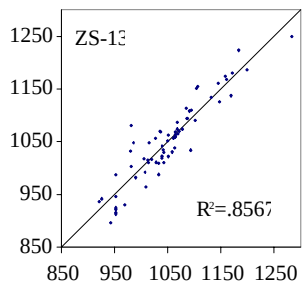

Figure 1. Measured Versus Calculated T_L (ZS-13 indicates zircon as the primary phase with N = 13)

Not unexpectedly, ZrO_2 has the strongest effect on T_L (approximately 41°C/mass% for ZS). Within the ZS and Z fields, alkali oxides decrease T_L (Na_2O by 34°C/mass% and Li_2O by 25°C/mass% for ZS). Not surprisingly, Na_2O increases T_L for glasses with PK as the primary phase, but the strong negative effect of Li_2O is unexpected, considering that Li_2O is also found in alkali-zirconium-silicates. Interestingly, P_2O_5 increases T_L for ZS by 11°C/mass%. Zirconium phosphate was not detected as a crystalline phase in the databases analyzed. Al_2O_3 somewhat increases (by 5°C/mass%) and B_2O_3 decreases (by 6°C/mass%) T_L for glasses with the ZS primary phase, but the T_L for Z is predicted to be strongly increased by Al_2O_3. SiO_2 has virtually no effect except for glasses with PK as the primary phase.

PRIMARY PHASE FIELDS: GRAPHICAL REPRESENTATION

For a graphical representation of the primary phase fields, we calculated component coefficients on the Na_2O-SiO_2-ZrO_2 submixture, a composition subspace, on which mass fractions are defined as $g_i' = g_i/(1-g_{others})$, (i = Na_2O, SiO_2, ZrO_2), where the subscript *others* stands for all remaining glass components. Ternary submixtures have previously been used to illustrate phase behavior of HLW glasses. For example, the $(Na,Li)_2O$-B_2O_3-SiO_2 submixture displays phase separation [10], and the Na_2O-Al_2O_3-SiO_2 submixture indicates formation of nepheline [11]. Crum et al. [3] used the Na_2O-ZrO_2-SiO_2 submixture to delineate boundaries between primary phase fields for Zr-containing HLW glasses. They observed that baddeleyite was likely to form if $g'_{ZrO_2} > 0.22$ zircon was likely to form if $0.08 < g'_{ZrO_2} < 0.22$ and $g'_{Na_2O} < 0.22$, and alkali-zirconium-silicates and rare-earth-zirconates were likely to form if $0.08 < g'_{ZrO_2} < 0.22$ and $g'_{Na_2O} > 0.22$. Other than Zr-containing primary phases were likely to precipitate if $g'_{ZrO_2} < 0.08$.

We applied the Na_2O-ZrO_2-SiO_2 submixture approach to our database. In addition to drawing boundaries between primary phase fields, we also depicted T_L-isotherms using a modified form of Equation (1), i.e., $T_L^p = T_{L0}^p + T_{Lz}^p g_z' + T_{Ln}^p g_n'$, where the superscript *p* indicates the primary phase field, and the subscripts *z* and *n* stand for ZrO_2 and Na_2O. On the boundary

between p and r primary phase fields, $T_L^p = T_L^r$, and thus $T_{L0}^p + T_{Lz}^p g_z' + T_{Ln}^p g_n' = T_{L0}^r + T_{Lz}^r g_z' + T_{Ln}^r g_n'$, or, after rearrangement

$$g_n' = k_{pr} + l_{pr} g_z' \tag{2}$$

where $k_{pr} = \dfrac{T_{L0}^r - T_{L0}^p}{T_{Ln}^p - T_{Ln}^r}$ and $l_{pr} = \dfrac{T_{Lz}^r - T_{Lz}^p}{T_{Ln}^p - T_{Ln}^r}$. Equation (2) represents the phase field boundary and the k_{pr} and l_{pr} coefficients relate the boundary slopes and intercepts to those of isotherms.

Attempts to compute the isotherms from the T_L database were successful only for ZS as the primary phase. We estimated the boundaries between primary phase fields by drawing lines that separate the data points for individual phases (Figure 2). Thus we obtained six values for k_{pr} and l_{pr} coefficients (two for each boundary). These values are shown in Table IV. Then we forced the isotherms for PK to intersect with the isotherms for SZ on the ZS-PK boundary. Finally, we obtained T_{Li} coefficients for Z by connecting intersects of ZS and PK isotherms with Z-ZS and Z-PK boundaries. The T_{Li} values are listed in Table V.

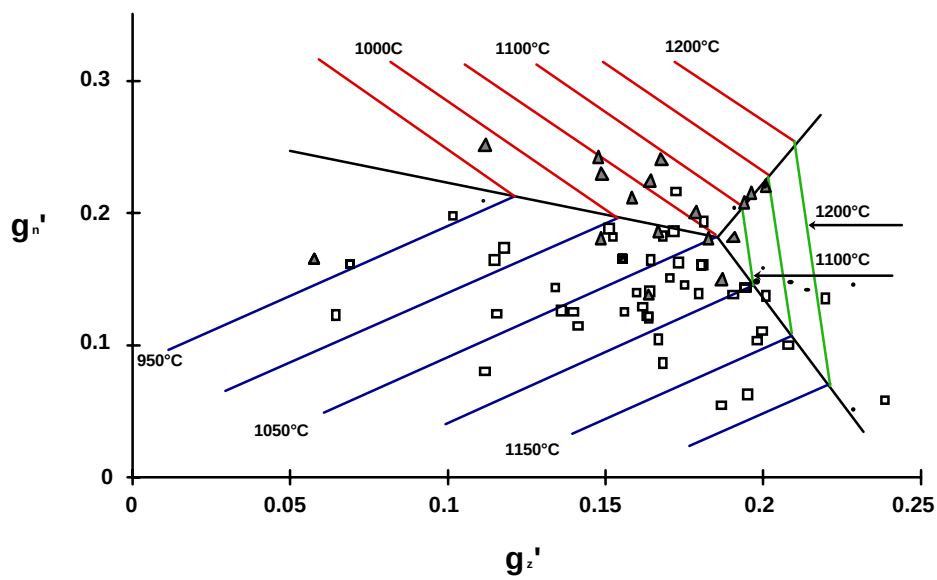

Figure 2. Na_2O-SiO_2-ZrO_2 Ternary Submixture Phase Diagram
(□—zircon, ▲—parakeldyshite, •—baddeleyite)

Figure 2 clearly indicates the opposite effect of Na_2O on T_L for ZS and PK fields whereas Z is little affected by Na_2O. It also shows that while T_L increases with ZrO_2 content in all fields, the slope is much steeper in the baddeleyite field. The primary-phase boundaries reasonably agree with those previously estimated by Crum et al. [3].

As the low R^2 values in Table V indicate, the ternary-phase diagram is a useful aid for rough orientation when formulating high-Zr HLW glasses, but cannot be used for estimating T_L. For example, we can estimate glass composition with a maximum ZrO_2 content that meets the constraint $T_L \leq 1050°C$ (needed to restrict solid phase settling in Joule-heated melters [1]). The 1050°C isotherm passes through the common intersection of the field boundaries, corresponding to 18.6 mass% ZrO_2 in the submixture. Since the submixture is only a fraction of the overall composition, the actual ZrO_2 content in a HLW glass with $T_L \leq 1050°C$ will be lower. The

maximum ZrO_2 content experimentally verified in a glass with $T_L \leq 1050°C$ was 16.5 mass% [6-8].

Table IV. Coefficients for Boundaries between the Primary Phase Fields for Na_2O-SiO_2-ZrO_2 Ternary Submixture

	k_{pr}	l_{pr}
ZS-PK	0.270	-0.482
ZS-Z	0.758	-3.109
Z-PK	-0.356	2.891

Table V. T_L Component Coefficients (in °C) for Na_2O-SiO_2-ZrO_2 Ternary Submixture

	T_{L0}^{p}	T_{Lz}^{p}	T_{Ln}^{p}	R^2
ZS	1033	1070	-1006	0.598
Z	25	5202	324	0.104
PK	393	2210	1358	0.630

CONCLUSIONS

Available data on T_L for HLW glasses with Zr-containing primary crystallization phases provide T_{Li} values for all major HLW glass components. These values are reasonably accurate for HLW glasses that precipitate zircon as their primary phase and should be used with caution for HLW glasses with alkali-zirconium silicates as their primary phase. The current T_L database for HLW glasses with baddeleyite as the primary phase is insufficient to provide dependable T_{Li} values. Because T_L changes strongly with the ZrO_2 content in the baddeleyite field, we do not recommend formulating HLW glasses that form baddelyite as the primary phase.

ACKNOWLEDGMENTS

The authors thank Greg Piepel, Linda Davis, and Wayne Cosby for helpful suggestions. Trevor Plaisted is grateful to Associated Western Universities for his fellowship at Pacific Northwest National Laboratory (PNNL). Funding for this task was provided by the U.S. Department of Energy Office of Science and Technology. PNNL is operated for the U.S. Department of Energy by Battelle under Contract DE-AC06-76RLO 1830.

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