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Liquidus temperature in the spinel primary phase field: A comparison between optical and crystal fraction methods

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ABSTRACT

Liquidus temperature (T_L) was measured for 38 simulated high-level waste borosilicate glasses covering a Hanford composition region, using optical microscopy and crystal-fraction extrapolation methods to analyze isothermally heat-treated specimens. The glasses encompassed a one-component-at-a-time variation of 16 components from a representative Hanford HLW simulant baseline composition. The T_L values ranged from 1006 °C to 1603 °C. First-order models were fit to data to obtain component effects on T_L (per 1 mass% additions) and then the components were grouped into three categories: T_L-increasing components [i.e., Cr_2O_3 (264 °C), "Others" (minor components, 163 °C), oxides of noble metals (137 °C), NiO (91 °C), as well as Al_2O_3 and Fe_2O_3 (~19–21 °C)]; T_L-decreasing components [i.e., K_2O (−26 °C), Na_2O (−41 °C), and Li_2O (−68 °C)]; and those of little effect [i.e., MnO, P_2O_5, ZrO_2, F, Bi_2O_3, SiO_2, B_2O_3, and CaO (9 to −12 °C)]. Also presented are temperatures at which 1 vol% of spinel is at equilibrium with the melt ($T_{1\%}$) as these values are considered relevant to the Hanford Tank Waste Treatment and Immobilization Plant. The measured and estimated values are compared and contrasted and the effect of T_L and $T_{1\%}$ on glass formulation is discussed. The different methods for measuring T_L are compared and contrasted.

1. Introduction

The high-level waste (HLW) at the Hanford Site will be vitrified at the Hanford Tank Waste Treatment and Immobilization Plant. The HLW streams contain a large variety of constituents. Composition-property models are used to estimate the properties and formulate glasses for each particular batch of waste. One property that is frequenty modeled is the liquidus temperature (T_L), defined as the lowest temperature (T) at which the melt and the crystalline phases are in equilibrium [1]. Thus, crystals can precipitate at $T < T_L$. If crystal density is high compared to the melt and crystal size is large enough, crystals can settle to the melter bottom or even clog the melter pour spout [2–5]. Although T_L does not directly correlate to the risk of melter operating problems [6–10], it is still a primary thermodynamic property of the melt and is often used as a rough indicator of risk for crystal accumulation [5,11–23]. Recently, the temperature at 1% crystal ($T_{1\%}$) has been used as an ad hoc indication of risk for crystal accumulation [19,20].

Many different methods can be used to measure T_L of waste glasses [1] and each of these methods have advantages and disadvantages. This study evaluates the impacts of different measurement methods on both the measured T_L and the compositional effect on T_L and $T_{1\%}$. A one-component-at-a-time variation study was performed for 38 glasses with 16 component variables where the glasses were characterized with a variety of techniques. The tests include chemical analysis of glass composition, viscosity, electrical conductivity, T_L, canister centerline cooling, the product consistency test, and the toxicity characteristic leaching procedure. The methods and results for all testing performed are presented elsewhere in more detail [24]. In this paper, solely T_L and $T_{1\%}$ results are reported, analyzed, and discussed. Also, the data obtained using the different T_L methods as well as the methods are compared and contrasted.

2. Methods

2.1. Glass fabrication

The 38 unique glass compositions were designed around the baseline (BL) glass, EM07-BL-1 (made in duplicate; i.e., EM07-BL-2), with variations in 16 components on a one-at-a-time basis by mass: Al_2O_3 (6–20%), B_2O_3 (5–20%), Bi_2O_3 (0–5%), CaO (0–7%), Cr_2O_3 (0.1–2%), F (0.088–2%), Fe_2O_3 (5–20%), K_2O (0–6%), Li_2O (1.5–4%), MnO

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Table 1
Target compositions of all glasses in mass% [24]. The "Others" column includes BaO, CdO, MgO, PbO, PdO, Rh_2O_3, RuO_2, SO_3, SrO, TiO_2, ZnO, Ce_2O_3, La_2O_3, and Nd_2O_3 (see Table 2 for a breakdown of "Others" components with compositional ranges). *EM07-BL-2, not listed in the table, had the same targeted composition as EM07-BL-1.

Glass ID	Al_2O_3	B_2O_3	Bi_2O_3	CaO	Cr_2O_3	F	Fe_2O_3	K_2O	Li_2O	MnO	Na_2O	NiO	P_2O_5	SiO_2	ZrO_2	Others
EM07-BL-1*	10.00	10.00	0.00	0.00	0.50	0.10	10.00	0.00	2.75	2.00	15.00	1.00	1.25	43.33	2.50	1.57
EM07-Al-06	**6.00**	10.44	0.00	0.00	0.52	0.10	10.44	0.00	2.87	2.09	15.67	1.04	1.31	45.26	2.61	1.64
EM07-Al-15	**15.00**	9.44	0.00	0.00	0.47	0.09	9.44	0.00	2.60	1.89	14.17	0.94	1.18	40.92	2.36	1.48
EM07-Al-20	**20.00**	8.89	0.00	0.00	0.44	0.09	8.89	0.00	2.44	1.78	13.33	0.89	1.11	38.52	2.22	1.39
EM07-B-05	10.56	**5.00**	0.00	0.00	0.53	0.11	10.56	0.00	2.90	2.11	15.83	1.06	1.32	45.74	2.64	1.66
EM07-B-15	9.44	**15.00**	0.00	0.00	0.47	0.09	9.44	0.00	2.60	1.89	14.17	0.94	1.18	40.92	2.36	1.48
EM07-B-20	8.89	**20.00**	0.00	0.00	0.44	0.09	8.89	0.00	2.44	1.78	13.33	0.89	1.11	38.52	2.22	1.39
EM07-Bi-025	9.75	9.75	**2.50**	0.00	0.49	0.10	9.75	0.00	2.68	1.95	14.63	0.98	1.22	42.24	2.44	1.53
EM07-Bi-05	9.50	9.50	**5.00**	0.00	0.48	0.10	9.50	0.00	2.61	1.90	14.25	0.95	1.19	41.16	2.38	1.50
EM07-Ca-035	9.65	9.65	0.00	**3.50**	0.48	0.10	9.65	0.00	2.65	1.93	14.48	0.97	1.21	41.81	2.41	1.52
EM07-Ca-07	9.30	9.30	0.00	**7.00**	0.47	0.09	9.30	0.00	2.56	1.86	13.95	0.93	1.16	40.30	2.33	1.46
EM07-Cr-001	10.04	10.04	0.00	0.00	**0.10**	0.10	10.04	0.00	2.76	2.01	15.06	1.00	1.26	43.51	2.51	1.58
EM07-Cr-012	9.93	9.93	0.00	0.00	**1.20**	0.10	9.93	0.00	2.73	1.99	14.89	0.99	1.24	43.02	2.48	1.56
EM07-Cr-02	9.85	9.85	0.00	0.00	**2.00**	0.10	9.85	0.00	2.71	1.97	14.77	0.99	1.23	42.68	2.46	1.55
EM07-F-02	9.81	9.81	0.00	0.00	0.49	**2.00**	9.81	0.00	2.70	1.96	14.72	0.98	1.23	42.51	2.45	1.54
EM07-Fe-05	10.56	10.56	0.00	0.00	0.53	0.11	**5.00**	0.00	2.90	2.11	15.83	1.06	1.32	45.74	2.64	1.66
EM07-Fe-15	9.44	9.44	0.00	0.00	0.47	0.09	**15.00**	0.00	2.60	1.89	14.17	0.94	1.18	40.92	2.36	1.48
EM07-Fe-20	8.89	8.89	0.00	0.00	0.44	0.09	**20.00**	0.00	2.44	1.78	13.33	0.89	1.11	38.52	2.22	1.39
EM07-K-03	9.70	9.70	0.00	0.00	0.49	0.10	9.70	**3.00**	2.67	1.94	14.55	0.97	1.21	42.03	2.43	1.53
EM07-K-06	9.40	9.40	0.00	0.00	0.47	0.09	9.40	**6.00**	2.59	1.88	14.10	0.94	1.18	40.73	2.35	1.48
EM07-Li-015	10.13	10.13	0.00	0.00	0.51	0.10	10.13	0.00	**1.50**	2.03	15.19	1.01	1.27	43.88	2.53	1.59
EM07-Li-04	9.87	9.87	0.00	0.00	0.49	0.10	9.87	0.00	**4.00**	1.97	14.81	0.99	1.23	42.78	2.47	1.55
EM07-Mn-01	10.19	10.19	0.00	0.00	0.51	0.10	10.19	0.00	2.80	**0.10**	15.29	1.02	1.27	44.17	2.55	1.60
EM07-Mn-04	9.80	9.80	0.00	0.00	0.49	0.10	9.80	0.00	2.69	**4.00**	14.69	0.98	1.22	42.44	2.45	1.54
EM07-Na-05	11.18	11.18	0.00	0.00	0.56	0.11	11.18	0.00	3.07	2.24	**5.00**	1.12	1.40	48.43	2.79	1.75
EM07-Na-10	10.59	10.59	0.00	0.00	0.53	0.11	10.59	0.00	2.91	2.12	**10.00**	1.06	1.32	45.88	2.65	1.66
EM07-Na-20	9.41	9.41	0.00	0.00	0.47	0.09	9.41	0.00	2.59	1.88	**20.00**	0.94	1.18	40.78	2.35	1.48
EM07-Ni-001	10.09	10.09	0.00	0.00	0.51	0.10	10.09	0.00	2.78	2.02	15.14	**0.10**	1.26	43.73	2.52	1.58
EM07-Ni-02	9.90	9.90	0.00	0.00	0.50	0.10	9.90	0.00	2.72	1.98	14.85	**2.00**	1.24	42.89	2.48	1.55
EM07-P-0	10.13	10.13	0.00	0.00	0.51	0.10	10.13	0.00	2.79	2.03	15.19	1.01	**0.00**	43.88	2.53	1.59
EM07-P-025	9.87	9.87	0.00	0.00	0.49	0.10	9.87	0.00	2.72	1.98	14.81	0.99	**2.50**	42.79	2.47	1.55
EM07-Si-30	12.35	12.35	0.00	0.00	0.62	0.12	12.35	0.00	3.40	2.47	18.53	1.24	1.54	**30.00**	3.09	1.94
EM07-Si-37	11.12	11.12	0.00	0.00	0.56	0.11	11.12	0.00	3.06	2.22	16.67	1.11	1.39	**37.00**	2.78	1.75
EM07-Si-50	8.82	8.82	0.00	0.00	0.44	0.09	8.82	0.00	2.43	1.77	13.23	0.88	1.10	**50.00**	2.21	1.39
EM07-Zr-001	10.25	10.25	0.00	0.00	0.51	0.10	10.25	0.00	2.82	2.05	15.37	1.03	1.28	44.40	**0.10**	1.61
EM07-Zr-05	9.74	9.74	0.00	0.00	0.49	0.10	9.74	0.00	2.68	1.95	14.62	0.97	1.22	42.22	**5.00**	1.53
EM07-NM-0025	9.98	9.98	0.00	0.00	0.50	0.10	9.98	0.00	2.74	2.00	14.97	1.00	1.25	43.24	2.50	1.78

Table 2
Compositional range of constituents for "Others" column in Table 1 (in mass%). Molar volume, (V_i) coefficients are provided from Vienna et al. [6].

Additive	EM07-BL-1	Min	Max	V_i
BaO	5.00E–02	4.40E–02	6.20E–02	18.866
CdO	1.40E–01	1.24E–01	1.73E–01	17.600
MgO	1.50E–01	1.32E–01	1.85E–01	13.028
PbO	3.70E–01	3.26E–01	4.57E–01	22.250
PdO	9.00E–03	8.00E–03	7.20E–02	15.069
Rh_2O_3	3.00E–03	3.00E–03	2.40E–02	38.855
RuO_2	1.80E–02	1.60E–02	1.44E–01	25.070
SO_3	3.00E–01	2.65E–01	3.71E–01	35.526
SrO	2.40E–01	2.12E–01	2.96E–01	17.611
TiO_2	4.00E–02	3.50E–02	4.90E–02	17.964
ZnO	6.00E–02	5.30E–02	7.40E–02	15.069
Ce_2O_3	5.00E–02	4.40E–02	6.20E–02	45.341
La_2O_3	7.00E–02	6.20E–02	8.60E–02	40.000
Nd_2O_3	7.00E–02	6.20E–02	8.60E–02	48.117

(0.1–4%), Na_2O (5–20%), NiO (0.1–2%), P_2O_5 (0–2.5%), SiO_2 (30–50%), ZrO_2 (0.1–5%), NM (oxides of noble metals PdO, Rh_2O_3, and RuO_2; 0.03–0.25%) and "Others" (combining minor oxides BaO, CdO, MgO, PbO, SO_3, SrO, TiO_2, ZnO, Ce_2O_3, La_2O_3, and Nd_2O_3; 1.36–1.90%). The compositions are listed in Table 1 with the breakdown of distribution for the "Others" components listed in Table 2 (for more precise compositional values see Schweiger et al. [24]).

Batches to make 400 g of each glass were prepared from H_3BO_3, NaF, $NaPO_3$, Na_2SO_4, carbonates of Li, Na, K, Ca, Sr, and Ba, nitrates of Pd and Ru, and oxides of all other elements; all of analytical grade. For Pd and Ru, nitrosyl nitrate solutions were added, drop-by-drop, to 100 g of SiO_2 dispersed on a glass dish to absorb the liquid, kept in an oven at 105 °C for 1 h, and then incorporated into the rest of the batch.

The batches were homogenized for 4 min in a tungsten carbide milling chamber using an Angstrom® vibratory mill. Each glass was melted twice in a Pt/10%Rh crucible covered with a flat Pt/10%Rh lid. In the first melt, the batch was added at 1200 °C in doses small enough, and at a time interval long enough, to minimize foaming. Then, the complete batch was heat treated for 1 h and the melt was poured onto an Inconel® quench plate. The glass was ground in a tungsten carbide milling chamber using the Angstrom mill for 6 min and remelted at 1150 to 1300 °C for 45–60 min. For glasses containing crystalline material after the first melt, successively higher melting temperatures were used until there were no visible signs of crystals.

2.2. T_L heat treatments and characterization

For T_L heat treatments, 1.2 cm^3 Pt-alloy (Pt/10%Rh) crucibles were filled to ~75 vol% with glass chunks prepared following the procedure defined in ASTM C1720-11 [25]. Crucibles were covered with tight-fitting lids to reduce losses of volatile components and heated at a set of soak temperatures (T_s) in Deltech® furnaces (Denver, CO) with readouts calibrated using SRM-773 standard glass [26]. In order to allow for equilibrium to be achieved, soak times were 48 ± 2 h for T_s < 850 °C, 24 ± 2 h for T_s = 850–1300 °C, and ~4 h for T_s > 1300 °C, according to ASTM C1720-11 [25]. It was common to find condensed volatilized species on inner crucible walls upon the heat treatment of glasses with $T_L \geq 1250$ °C, and EM07-Si-30 exhibited