



The effect of high-level waste glass composition on spinel liquidus temperature

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ABSTRACT

Spinel crystals precipitate in high-level waste glasses containing Fe, Cr, Ni, Mn, Zn, and Ru. The liquidus temperature (T_L) of spinel as the primary crystallization phase is a function of glass composition, and the spinel solubility (c_0) is a function of both glass composition and temperature (T). Previously reported models of T_L as a function of composition are based on T_L measured directly, which requires laborious experimental procedures. Viewing the curve of c_0 versus T as the liquidus line allows a significant broadening of the composition region for model fitting. This paper estimates T_L as a function of composition based on c_0 data obtained with the X-ray diffraction technique.

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1. Introduction

High-level nuclear waste (HLW¹) contains 40 to 60 chemical elements. Borosilicate glass is a chemically durable waste form capable of dissolving HLW oxides and halides and keeping them immobilized as long as the radioactive components do not decay. Because of the large number of components and a large compositional variability, where several hundreds of batches of different compositions are anticipated for Hanford (Washington, USA) alone, mathematical models are indispensable for relating key properties to HLW glass compositions such as viscosity, electrical conductivity, and chemical durability. The liquidus temperature (T_L) of the primary crystalline phase is one of such properties, and upon vitrification spinel is the primary crystalline phase of most US wastes from Pu production. Spinel crystals easily form during waste glass melting and exist in the melt at relatively high temperatures, at which they can interfere with the melter operation [1–24]. Several studies were performed to obtain the liquidus temperature (T_L) of spinel as a function of glass composition [1,2,4,8,10,12,22].

The experimental determination of T_L is based on the identification of the highest temperature at which spinel can exist in glass at equilibrium. Spinel crystals are detected in quenched melts optically or with X-ray diffraction (XRD) [18,25,26]. Both techniques require multiple melts and laborious sample preparation. Moreover, measuring T_L poses

numerous experimental difficulties including the control of redox reactions, glass homogeneity, and sample volatility [4]. The method based on differential scanning calorimetry is ruled out by the very low fraction of spinel precipitated (several mass%) and the low thermal effect of the diffusion-controlled process of spinel crystallization.

In contrast with the time-consuming and laborious direct methods for measuring T_L , the experimental determination of the spinel solubility (c_0) is relatively easy. Determining c_0 as a function of glass composition and temperature only requires quantitative XRD on specimens heat treated at various temperatures below T_L that are doped with a known standard. While the direct method determines T_L via extrapolation of the c_0 versus temperature (T) function to $c_0=0$, this study estimates the T_L of glasses from each $c_0(T)$ data point. It is based on the simple idea that the temperature at which the c_0 was obtained is the liquidus temperature of the matrix glass [27]. Since the matrix glass composition changes as spinel precipitates, the composition region for model fitting significantly broadens without the necessity of making the corresponding glasses and the separate laborious determination of T_L for each. Moreover, having a c_0 data set per glass provides an opportunity to detect sample alterations caused by volatility, redox, and/or crystallization upon cooling. These effects are not easily observed when a single value is determined by optical measurements.

Although the idea of using c_0 data for T_L determination appears simple, it faces its own challenge when applied to spinel. Spinel that precipitate in HLW glasses are solid solutions in the form $A^{2+}B^{3+}_2O_4$, containing Cr^{3+} , $Fe^{2+/3+}$, Ni^{2+} , $Mn^{2+/3+}$, and Zn^{2+} plus minor components, such as Al^{3+} , Ru^{4+} , and Rh^{3+} . Oxides of these elements can be combined to make various spinel types. Thus, oxides of Fe, Cr, and Ni can be combined into four spinel end members: trevorite ($NiFe_2O_4$), nichromite ($NiCr_2O_4$), chromite ($FeCr_2O_4$), and magnetite (Fe_3O_4) with complete solid solutions existing between all. Various

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¹ High-level waste is the highly radioactive waste material resulting from the reprocessing of spent nuclear fuel including liquid waste produced directly in reprocessing and any solid material derived from such liquid waste that contains fission products in sufficient concentrations and other highly radioactive materials that are determined consistent with existing law, to require permanent isolation.

reports show that spinel composition changes with both glass composition and temperature [4,28,29] and may not be uniform within the crystals because of changes in melt composition and redox [12]. The authors are not aware of any systematic study relating spinel composition to the conditions of crystal formation.

Because the composition of the matrix glass at equilibrium with spinel depends on spinel composition, the lack of precise knowledge of spinel composition complicates our task of obtaining T_L as a function of glass composition. We circumvent this obstacle by either (1) assuming that spinel composition does not change with experimental variables (this approximation is good for small composition regions) or (2) by constructing simple rules for estimating spinel composition based on the content of spinel oxides in glass.

Several studies investigated spinel solubility in HLW glasses [5,9,22,30–33]. Here we use two data sets, one by Schweiger et al. [22] and the other by Matyas et al. [33]. In both studies, glass samples were heat treated at various temperatures until the phase equilibrium was established. The mass fraction of spinel in the samples was measured with XRD. Both studies increased the precision of c_0 values with advanced XRD equipment and analysis software.

2. Theory

At phase equilibrium between the melt and the primary crystalline phase, the crystals are surrounded with the matrix glass of a uniform composition. The content and composition of both the matrix glass and the crystalline phase are related to the composition of the original glass (before the crystals were formed) via the i -th component mass balance equation, also known as the lever rule:

$$g_i^0 = (1 - c_0)g_i + c_0s_i \quad (1)$$

where g_i is the i -th component mass fraction in the matrix glass at equilibrium with spinel, g_i^0 is the i -th component mass fraction in the original glass with no spinel, c_0 is the equilibrium mass fraction of spinel phase in the mixture (of spinel and matrix glass), and s_i is the i -th component mass fraction in spinel.

The glass composition region in the composition space has as many dimensions as the number of components that are considered influential. Because the fractions of all components sum to 1, the large number of “crowded” components results in relatively narrow ranges of individual components. This situation favors approximating property-composition relationship with simple functions, such as first- or second-order polynomials. Hence, in spite of the general complexity of phase diagrams, the liquidus hypersurface for spinel is nearly flat within the composition region of HLW glasses [4,19]. This “simplicity of complexity” allows us to postulate the relationship

$$T_L^0 = \sum_{i=1}^N T_i g_i^0 \quad (2)$$

where T_L^0 is the liquidus temperature and T_i is the i -th component liquidus temperature coefficient. Similar relationships have been applied to the liquidus for sufficiently small composition regions of waste glasses and commercial glasses with various primary crystalline phases [34–36].

When the glass is allowed to reach phase equilibrium at $T < T_L$ and spinel is the only crystalline phase present in the melt, the temperature becomes a liquidus temperature for the matrix glass from which the spinel precipitated. This follows from the definition of T_L as the maximum temperature at which the glass is at equilibrium with the primary crystalline phase. Suppose we remove spinel from the matrix melt, for example, by allowing it to settle, thus separating it from the matrix glass. From the spinel-free matrix melt, we can precipitate more spinel by decreasing the temperature. This spinel will dissolve completely by

Table 1

Baseline glass composition in mass fractions [22].

Al ₂ O ₃	0.1000	MgO	0.0015	PdO	0.00009
B ₂ O ₃	0.1000	MnO	0.0200	Rh ₂ O ₃	0.00003
BaO	0.0005	Na ₂ O	0.1500	RuO ₂	0.00018
Bi ₂ O ₃	0.0000	Nd ₂ O ₃	0.0007		
CaO	0.0000	NiO	0.0100		
CdO	0.0014	P ₂ O ₅	0.0125		
Ce ₂ O ₃	0.0005	PbO	0.0037		
Cr ₂ O ₃	0.0050	SiO ₂	0.4333		
F	0.0010	SO ₃	0.0030		
Fe ₂ O ₃	0.1000	SrO	0.0024		
K ₂ O	0.0000	TiO ₂	0.0004		
La ₂ O ₃	0.0007	ZnO	0.0006		
Li ₂ O	0.0275	ZrO ₂	0.0250		

returning to the original heat-treatment temperature. Consequently, the T_L of the matrix glass will be given by the formula

$$T_L = \sum_{i=1}^N T_i g_i \quad (3)$$

with the same component coefficients as in Eq. (1) and T_L being identical to the heat-treatment temperature. Substituting for g_i from Eq. (1) into (3), we obtain

$$T_L = \frac{\sum_{i=1}^N T_i g_i^0 - c_0 \sum_{i=1}^N T_i s_i}{1 - c_0} \quad (4)$$

Provided that both c_0 versus T data and the spinel composition data are available, the T_i values can be computed by fitting Eq. (4) to these data. The needed c_0 versus T data can be obtained with XRD. Crystal composition is obtainable with scanning electron microscopy and energy dispersive spectroscopy (SEM-EDS) or by chemical analysis of clean crystals isolated from the glass phase that can be dissolved in acid. If the spinel composition data are not available, as is the case in our study, we can still estimate the T_i values by either treating s_i as a set of fitting coefficients or approximating s_i with simple rules specified below (Section 4).

3. Experimental data

The test glasses in the Schweiger et al. study [22] were designed as one-component-at-a-time variations of a baseline glass, whose composition is in Table 1. The components marked bold in the table were varied while all other components were kept at the same proportions as in the baseline glass. The composition variations for glasses with spinel primary phase are shown in Table 2. The measured c_0 values for the

Table 2

List of test glasses with component varied [22].

ID	Oxide	Mass fraction	ID	Oxide	Mass fraction	ID	Oxide	Mass fraction
Al-06	Al ₂ O ₃	0.0600	Cr-02	Cr ₂ O ₃	0.0200	Na-20	Na ₂ O	0.2000
Al-15	Al ₂ O ₃	0.1500	F-02	F	0.0200	Ni-001	NiO	0.0010
Al-20	Al ₂ O ₃	0.2000	Fe-05	Fe ₂ O ₃	0.0500	Ni-02	NiO	0.0200
B-05	B ₂ O ₃	0.0500	Fe-15	Fe ₂ O ₃	0.1500	P-0	P ₂ O ₅	0.0000
B-15	B ₂ O ₃	0.1500	Fe-20	Fe ₂ O ₃	0.2000	P-025	P ₂ O ₅	0.0250
B-20	B ₂ O ₃	0.2000	K-03	K ₂ O	0.0300	Si-30	SiO ₂	0.3000
Bi-025	Bi ₂ O ₃	0.0250	K-06	K ₂ O	0.0600	Si-37	SiO ₂	0.3700
Bi-05	Bi ₂ O ₃	0.0500	Li-015	Li ₂ O	0.0150	Si-50	SiO ₂	0.5000
Ca-035	CaO	0.0350	Li-04	Li ₂ O	0.0400	Zr-001	ZrO ₂	0.0010
Ca-07	CaO	0.0700	Mn-01	MnO	0.0010	Zr-05	ZrO ₂	0.0500
Cr-001	Cr ₂ O ₃	0.0010	Mn-04	MnO	0.0400	NM-0025	NM ^a	0.0024
Cr-012	Cr ₂ O ₃	0.0120	Na-10	Na ₂ O	0.1000			

^a Noble metals: PdO 0.00072, Rh₂O₃ 0.00024, and RuO₂ 0.00144.

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