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Spinel structure and liquidus temperature relationships in nuclear waste glass

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The liquidus temperature of spinel (AB_2O_4) crystals frequently limits the waste loading of vitrified nuclear waste. In other studies, glass structure-spinel liquidus temperature relationships were discovered for the non-spinel forming cations in glass, but no such relationship was identified for the spinel-forming metal-ions. In this paper, coefficients from an empirical first order mixture model describing spinel liquidus temperature were correlated with the octahedral site preference energy (OSPE) of the spinel-forming metal ions. The OSPE was calculated using approximations of glass and spinel structure made by extrapolating from data on similar glasses and spinels. A literature review indicated that Cr(III), Ni(II), and Fe(II) are most likely to be in the octahedral sites in spinel, Mn(II) in the tetrahedral site, and that Fe(III) will be common in both sites. These assignments were used as starting assumptions to calculate the OPSE for each metal ion. A strong correlation between the OSPE and the liquidus temperature coefficients of spinel-forming metal ions was observed. Further correlations determined that the Crystal Field Stabilization Energy was the most important portion of the OSPE for these spinels. These results indicate that the thermodynamic properties of spinel could be predicted based on assumptions of spinel structure, underpinned by fundamental properties, when scaled empirically.

1. Introduction

The last few years have seen intense studies of Ni, Mn, Fe, and Cr containing spinels in nuclear waste glass. The liquidus temperature of spinel is commonly the most constraining glass property during the vitrification of high Fe, Ni, and Cr, containing nuclear waste [1]. The spinel concern is heightened at the Hanford site in the U.S.A. by Mn, which is amended to the waste in the pretreatment process [2]. Spinel crystallizes in the melter cold cap, dissolves into the melt, and then re-crystallizes if the temperature is below the liquidus [3]. Spinel rapidly crystallizes into a solid solution [4], and the spinel composition varies with temperature and glass composition [5]. There is limited thermodynamic data available to calculate the liquidus temperature for this complex spinel solid solution in the multi-component waste glass melt. Thermodynamic data, however, can often be estimated from structural data. Komatsu and Soga [6] found that the solubility of spinels in sodium silicate glass was correlated to the octahedral site preference energy (OSPE) of the metal-ions in spinel. Therefore, an attempt to correlate spinel liquidus temperature to the OSPE was undertaken here for nuclear waste glass.

2. Thermodynamics of spinel liquidus temperature

The liquidus temperature of spinel is a thermodynamic relation between the molten glass phase and the spinel solid; where the liquidus temperature is the highest temperature at which spinel can coexist in equilibrium with the melt. Here, the thermodynamics are reviewed in terms of ion activities rather than the more commonly used oxide activities because it makes some of the spinel structure-liquidus temperature relationships more self-evident.

In chemical thermodynamics, the equilibrium between solid and liquid phases is typically written [7]:

$$K_{\mathrm{sp}} = \frac{\mathrm{IAP}}{\text{Activity of Solid}} \tag{1}$$

The term K_{sp} = the equilibrium constant. The Ion Activity Product (IAP) is the product of the activities of the dissolved species that precipitate in Spinel, and takes the form:

$$\mathrm{IAP} = \mathrm{aFe(II)}^{v} * \mathrm{aFe(III)}^{w} * \mathrm{aNi}^{x} * \mathrm{aCr}^{y} * \mathrm{aMn}^{z} * \mathrm{aO}^{4} \tag{2}$$

Here, the superscripts represent the stoichiometry of the metal ions in spinel at equilibrium and $v + w + x + y + z = 3$. In order to maintain charge balance in spinel, $w + y$ must equal 2 because two out of every three cations must be trivalent. The "a" in front of each element's symbol denotes that the activity of that species in the melt is of interest rather than the concentration.

Traditionally, the activity of the solid phase has been assigned a value of one [7]. Thus, Equation 1 can be rearranged to:

$$1 = \frac{\mathrm{IAP}}{K_{\mathrm{sp}}} \tag{3}$$

Chemical thermodynamics describes K_{sp} as a function of temperature using the following equation [7]:

$$K_{\mathrm{sp}} = \exp\left(\frac{\Delta G^f}{-RT}\right) \tag{4}$$

where ΔG^f is the Free Energy of Formation of the Spinel phase at equilibrium, R is the universal gas constant, and T is temperature. From Equation 4, the K_{sp} can be calculated for any temperature. Equation 4 can be substituted into Equation 3:

$$1 = \frac{\mathrm{IAP}}{\exp\left(\frac{\Delta G^f}{-RT}\right)} \tag{5}$$

Which can be solved for T.

$$T = -\frac{\Delta G^f}{R^* \ln(\mathrm{IAP})} \tag{6}$$

Not just any equilibrium temperature is of interest for preventing crystallization in a melter. Specifically, the Liquidus Temperate (T_L) is of concern. Therefore, of interest is the IAP at liquidus temperature (IAP_L) and the Free Energy of Formation of spinel at Liquidus Temperature (ΔG_L^f). Hence,

$$T_L = -\frac{\Delta G_L^f}{R^* \ln(\mathrm{IAP_L})} \tag{7}$$

In the case of spinel, the quantities IAP_L and ΔG_L^f are functions of melt and spinel composition because both the liquid and solid are mixtures. Furthermore, these two quantities interrelate because the IAP drives the composition of the solid mixture [8]. The IAP_L and $\Delta \mathrm{G}_L^f$ are not known for any spinel or melt composition in the range expected for high-level nuclear waste glass. Therefore, the right side of Equation 7 has traditionally been modeled as a function of melt composition with a combination of empirical fitting parameters, with or without additional theoretical mechanistic hypotheses. Any glass property-composition model equating an empirical formula to liquidus temperature must also be equates that formula to the right side of Equation 7.

Equation 7 gives some understanding to the affects of glass composition on spinel liquidus temperature and to the coefficients obtained by empirical models. For instance, the numerator is a function only of the spinel composition at equilibrium. Thus, only spinel-forming elements (Fe, Ni, Cr, Mn, O) directly affect the numerator. Non-spinel forming elements that have a large effect on spinel liquidus, such as Zr and Na, do so solely through their modification of the species and activities of the spinel-forming ions in the melt. Nonetheless, all elements that bond with oxygen (essentially all of the waste glass constituents) will determine the species and activity of oxygen anion in the melt. Consequently, the non-spinel forming elements would be expected to affect spinel equilibrium through the oxygen anion, which is raised to the fourth power within the IAP term (Equation 2), more than through their effects on the activities of the other spinel forming ions.

3. Introduction to spinel liquidus temperature models

Empirical models of spinel T_L versus glass composition have been developed so that glasses can be formulated with acceptable T_L [9–12]. Kim and Hrma [13] developed an empirical mixture model of the general form shown in Equation 8.

$$T_L = -\frac{\Delta G_{\mathrm{L}}^f}{R^* \ln(\mathrm{IAP}_L)} = \sum_{i=1}^{N} T_i * X_i \tag{8}$$

Here, X_i = the mass fraction of metal ‘i’ in the melt and T_i is a coefficient. The model coefficients were recently updated to reflect additional data [10, 11]. Hrma *et al.* [12] amended this model with a Fe(II) coefficients for glasses with mixed oxidation states. Vienna *et al.* [10, 11] found that the T_i coefficients could be correlated to their ionic potential (charge divided by ionic radius) for the non-spinel forming cations and ferric iron. For Mn, Ni, and Cr, however, the T_i coefficients do not correlate to their ionic potential. Table I contains the T_i values compiled by these authors [10–12] for the spinel forming metal-ions, along with the crystal field stabilization energy (CFSE) for the ions in spinel compiled by Burns [14]. The CFSE is the energy gained by metals with d electrons by forming undistorted octahedrons.

It has been long known that the structure and CFSE determine the thermodynamic properties of spinel [14–16]. Fig. 1 shows a correlation between the T_i coefficients and CFSE for the spinel forming metal-ions. The CFSE of these metal-ions is likely a contributing factor to the low solubility of spinel in nuclear waste glass. As described later, the CFSE is a significant component of the Octahedral Site Preference Energy (OSPE).

4. Metal-ion sites in spinel

In this section the results of a literature review on the site preference for metals ions in spinel is presented. In a later section the OSPE is calculated, which could

TABLE I Crystal field stabilization energy (CFSE) and T_i coefficients for spinel forming metal-ions

Metal-ion	CFSE (KJ/mol)	T_i coefficients	Source of T_i
Cr	−224.7	33271	Vienna *et al.* [11]
Ni	−122	13675	Vienna *et al.* [11]
Fe(II)	−49.8	5674	Hrma *et al.* [12]
Fe(III)	0	3688	Vienna *et al.* [10]
Mn(II)	0	1316	Vienna *et al.* [11]

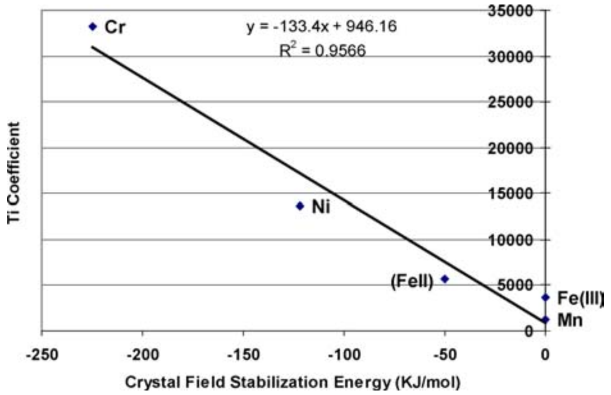

Figure 1 The T_i coefficients and crystal field stabilization energy of the spinel forming metal ions.

TABLE II Bond-lengths and site occupancy for metal ions in spinel

Metal-ion	Assumed site occupancy	Tetrahedral metal–oxygen bond length (angstroms)	Octahedral metal–oxygen bond length (angstroms)
Cr	Octahedral	N/A	1.995
Ni	Octahedral	1.94	2.06
Fe(II)	Octahedral	2.000	2.150
Fe(III)	Both	1.875	2.025
Mn	Tetrahedral	2.036	2.191

be used to determine exactly what site the metal-ions occupy. The dominant components in the octahedral site, however, are needed as a starting assumption for this calculation. While there is no structural data on multi-component spinels exactly like the spinels in nuclear waste glass, data exists for slightly simpler spinels containing three or more transition metals.

A spinel cubic lattice has eight formula units [17]. Each cubic cell has 32 oxygen atoms and 24 cations. There are 64 tetrahedral interstices, of which only eight are occupied by cations with the remainder being vacant. Sixteen of the 32 octahedral interstices are occupied by cations. The tetrahedral sites are isolated from each other and bound by each corner oxygen to a separate octahedron. Hence, there is no edge sharing between the tetrahedrons with either another tetrahedron or an octahedron [17]. The occupied octahedrons, however, share half of their edges with neighboring occupied octahedrons, while the other half of their edges are shared with unoccupied octahedrons. For a more detailed description of the spinel lattice, the reader is referred to Sickafus *et al.* [17]. Numerous metal-ions can occupy the octahedral and tetrahedral sites in spinel, including most transition metals, magnesium, and aluminum. The spinel in nuclear waste glass, however, is a solid solution of Fe, Cr, Ni, and Mn [5].

The preference for Cr(III) for the octahedral site in spinel is so strong that Cr(III) has generally been assumed to always reside in the octahedral site [14]. During this literature review, no cases of Cr(III) in a tetrahedral site were found for spinel. Therefore, it is reasonable to assume that Cr(III) will always be in the octahedral site in spinel.

Ferric iron can simultaneously occur in both the octahedral and tetrahedral sites, as has been observed in multi-component spinels [18–20]. Ferric iron has little preference for either the octahedral or tetrahedral sites [21].

Nickel primarily occurs in the octahedral site, but will go into the tetrahedral site in the presence of large amounts of Cr(III). Lenglet *et al.* [20] found that nickel is always in the octahedral site in Ni-Fe-Cr spinels as long as chromium occupies less than half of the octahedral sites, which means that Cr accounts for less than 1/3 of all the metal-ions in spinel. In spinels precipitated from nuclear waste-glass, Cr generally occupies less than 1/3 of all the metal sites. Thus, it is assumed here that Ni will predominantly occupy the octahedral site in these spinels. Wei *et al.* [18] found that small quantities of Ni are pulled into the tetrahedral site in the presence of large quantities of Mn(II). Mn(II) was predominantly in the tetrahedral site in these spinels [18].

In a study of Fe(II), Fe(III) and Ni containing spinels, Saito *et al.* [19] found that Fe(II) was only in the octahedral site. Therefore, it is assumed that Fe(II) is predominantly in the octahedral site in spinels precipitated from nuclear waste glass.

The typical lengths of metal-oxygen bonds in spinel provided by Lavina *et al.* [22] are shown in Table II, along with the site occupancy assumed from the discussion above.

5. Octahedral site preference energy and spinel liquidus temperature

Spinel solubility in sodium silicate glass has previously been correlated to the OSPE of the spinel forming metal-ions [6], and it is shown here that this relationship also holds true for spinels precipitated from high-level nuclear waste glass melts. O'Neill and Navrotsky [23] have shown that the OSPE of a cation is dependent on the CFSE, the size mismatch between the cations, and the electronic exchange energy. The CFSE for each metal-ion was listed in Table I. As shown earlier, there is a strong relationship between the CFSE of the metal-ion and the T_i coefficients even without including the rest of the OSPE contributors. Given that spinel contains both Fe(II) and Fe(III), the electronic exchange energy would be expected to have a notable effect on the OSPE for the iron ions. However, there is no basis available for assigning the electronic exchange energy for this complex spinel, so it will be neglected here. Later, it will be shown that the OSPE is well correlated to the T_i values despite neglecting the electronic exchange energy (probably because the effect of both Fe ions is small).

From [23], the size mismatch energy is:

$$E_{\mathrm{sm}} = 239.3(\Delta R) + 0.3 \qquad (9)$$

where ΔR is the is the difference in the metal-oxygen radius between the cubes of the target metal-ion and the dominant metal-ion. This term is mathematically defined as

$$\Delta R = (R_2 - R_1)/0.5(R_2 + R_1) \qquad (10)$$

where R_1 and R_2 are the cubes of the metal-ion-oxygen bond lengths of the target and dominant octahedral

TABLE III OSPE of spinel metal-ions calculated for differing dominant octahedral metal-ions

Element Element	Cr dominant (KJ/mol)	Fe(III) dominant (KJ/mol)	Ni dominant (KJ/mol)
Cr	−224.7	−235.43	−247.7
Ni	−98.70	−109.4	−121.7
Fe(II)	4.792	−5.810	−18.04
Fe(III)	11.01	0.300	−12.00
Mn	67.14	56.60	44.43

cations, respectively. The size mismatch energy and the CFSE are then summed to give the OSPE. The OSPE was calculated using the CFSE in Table I and the size mismatch energy for Cr, Fe(III), and Ni each as the dominant octahedral cation. The results are tabulated in Table III.

Figs 2 through 4 plot the T_i coefficients against the OSPE reported in Table III, and demonstrate that there is approximately a linear relationship between these two parameters for the spinel forming metal-ions. The r^2 values for the linear regression of the data have little dependence on the dominant octahedral cation (Cr, Fe(III), or Ni) even though the size of the OSPE does. Likewise, the correlation coefficient (−0.981) is the same regardless of the dominant octahedral metal ion. These results reveal a relationship between the thermodynamic and structural properties of spinel precipitated from nuclear waste glass. In the future, it is likely that improved property-composition models for spinel liquidus temperature can be generated by understanding the spinel structure.

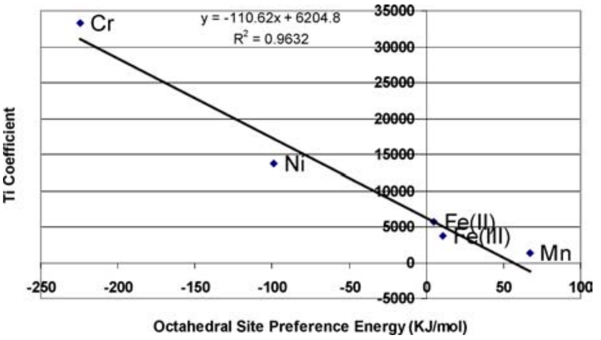

Figure 2 OSPE versus T_i coefficient with Cr as the dominant octahedral site cation.

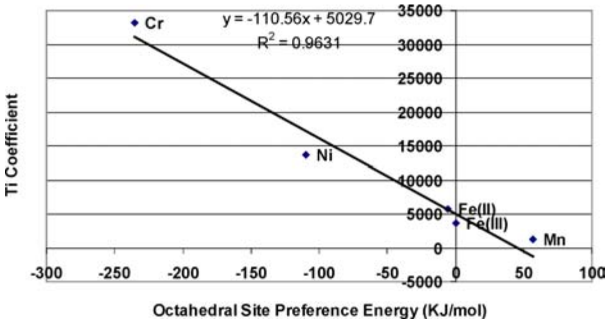

Figure 3 OSPE versus T_i coefficient with Fe(III) as the dominant octahedral site cation.

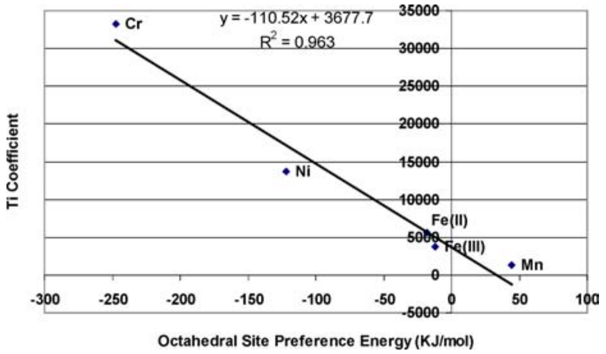

Figure 4 OSPE versus T_i coefficient with Ni as the dominant octahedral site cation.

6. Spinel forming metal-ions in glass

The reason that OSPE is so well correlated to the T_i coefficients may be the result of coordination changes by the spinel-forming metal-ions. The coordination numbers of spinel-forming metal-ions have been recorded in nuclear waste glasses or complex multi-component glasses of similar composition. The cations that reside in the tetrahedral site in spinel (Fe(III), and Mn) are also primarily in tetrahedral coordination in glass [24–26]. Thus, the tetrahedral cations would not change coordination upon entering spinel. In contrast, the cations that are likely to reside in the octahedral site in spinel have coordination numbers less than six in glass [24, 27, 28]. The exception is chromium, which occupies a highly distorted octahedron in glass [29], but nonetheless, occupies a more ordered octahedron in spinel (C_{3v} symmetry) [17]. Therefore, all of the metal-ions will have to change their coordination environment upon entering the octahedral sites in spinel. The following is an example (for ferric iron) of a reaction with a coordination change:

$$\mathrm{FeO_4^{5-}} + 2\mathrm{O^{2-}} \Leftrightarrow \mathrm{FeO_6^{9-}} \tag{11}$$

$$K = \frac{\left(\mathrm{FeO_5^{2-}}\right)(\mathrm{O^{2-}})^2}{\mathrm{FeO_6^{9-}}} \tag{12}$$

This expression (Equation 12) indicates that the equilibrium between four and six coordinate ferric iron depends more on the activity of oxygen anion than on the activity of ferric iron. The activity of the oxygen anion is dependent on the melt bascisity [30]. The coordination numbers for ferric iron and the other spinel-forming metal-ions are dependent on melt bascisity as well [31]. Per Equation 2, the activity of the oxygen anion ion will exert a large influence on the liquidus temperature of spinel. Per Equations 11 and 12, the coordination environment of the spinel forming metal ions is dependent on the oxygen anion activity. Lastly, per Figs 2 through 4, the liquidus temperature of spinel is correlated to the coordination environment of the spinel forming metal ions. Hence, the oxygen anion activity, the site occupancy in spinel, the coordination environment of metal ions in glass, and spinel liquidus temperature are all interrelated.

7. Conclusion

The results in this report indicate a strong relationship between the spinel liquidus temperature and two structural parameters, the CFSE and the OSPE. These relationships are in part from changes in the coordination number of the spinel-forming metal-ions upon entering spinel from the melt. From mass balance relationships found in the equilibrium expression, it was shown that non-spinel forming ions are likely to have a large impact on spinel liquidus temperature when they change the species and activity of the oxygen anions in the melt. This observation is consistent with the results of others [10], who established that spinel liquidus temperature depends on the ionic potential of the non-spinel forming species in the melt. These relationships could be utilized in developing the next generation of liquidus temperature models.

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