Introduction into defect studies in ceramic materials (III)

Structure, Defects and Defect Chemistry

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January 18, 2002
1. Mass, Charge and Site Balance

The Schottky reactions for NaCl and MgO, respectively, can be written using Kröger-Vink notation as:

\[ \text{null} \rightarrow V'_{Na} + V^\bullet_{Cl} \]  \hspace{1cm} (2.10)
\[ \text{null} \rightarrow V''_{Mg} + V'^{\bullet\bullet}_{O} \]  \hspace{1cm} (2.11)

Where null (sometimes “nil”) indicates the creation of defects from a perfect lattice. The respective mass-action equilibrium constants are:

\[ K_s = \left[ V'_{Na} \right] \left[ V^\bullet_{Cl} \right] \]  \hspace{1cm} (2.12)
\[ K_s = \left[ V''_{Mg} \right] \left[ V'^{\bullet\bullet}_{O} \right] \]  \hspace{1cm} (2.13)

The brackets denote concentration, usually given in mole fraction (equivalent to \( n_v/N \)).
Defect Chemical Reaction

1. Mass, Charge and Site Balance

The free energy for each of these “quasichemical” reactions is simply the Schottky formation energy, and the equilibrium constant is given by:

\[ K_s = \exp\left(-\frac{\Delta g_s}{kT}\right) \] (2.14)

Notice that the equilibrium constant is a function of temperature only. This dictates that the product of the cation and anion vacancy concentrations (Eqs. 2.12 and 2.13) is a constant at fixed temperature. Furthermore, when only the intrinsic defects are present, the concentration of anion and cation vacancies must be equal for charge neutrality, and so we obtain

\[ [V'_{Na}] = [V^*_{Cl}] = \exp(-\frac{\Delta g_s}{2kT}) \] (2.15)

Which is the same result as in Table 2.1.
1. **Mass, Charge and Site Balance**

(1) Rules of defect chemical reactions—*mass, charge and site balance*.

- Mass balance simply means that a defect chemical reaction cannot create or lose mass.
- Site balance means that the ratio of cation and anion sites of the crystal must be preserved, although the total number of sites can be increased or decreased.
- Charge balance means the total effective charge is balanced in the Kröger-Vink notation system.

(2) As example of site balance

Consider the Schottky reactions for Al$_2$O$_3$ and BaTiO$_3$.

**Cation and anion vacancies must be formed in the stoichiometric ratios**, and if so, we find that the effective charges are automatically balanced:

\[ \text{null} = 2V''_{Al} + 3V''''_{O} \quad (Al_2O_3) \quad (2.16) \]

\[ \text{null} = V''_{Ba} + V''''_{Ti} + 3V''_{O} \quad 4 \quad (BaTiO_3) \quad (2.17) \]
Defect Chemical Reaction

1. Mass, Charge and Site Balance

The Frenkel reaction, written in Kröger-Vink notation for the system AgCl (in which this intrinsic mechanism is dominant) is

\[ Ag^x_{Ag} = Ag^+_i + V'_{Ag} \]  \hspace{1cm} (2.18)

Site balance is maintained here since the formation of interstitials does not create new crystal sites, but rather occupies pre-existing ones.

Discussion:

• “Correctness” of defect chemical reaction.
• Simultaneity of defect chemical reaction.
• It is the most probable reactions that are of greatest interest, and of which there are fortunately only a few that usually need to be considered.
• In addition to the formation of intrinsic defects, reactions of particular interest include the incorporation of solutes, formation of intrinsic electronic defects, oxidation and reduction, and defect association and precipitation.
2. Solute Incorporation.

(1) Iso-solutes incorporation
a substitutional solute of NiO in MgO.

\[ NiO = Ni^x_{Mg} + O^x_O \]  \hspace{1cm} (2.19)

and involves no charged species.

(2) Aliovalent solutes
we may presume that the aluminum will substitute for magnesium. The oxygen ion are likely to occupy additional oxygen lattice. We at this point have

\[ Al_2O_3 = 2Al^*_{Mg} + 3O^x_O \]

Which accounts for all of the mass involved. However, we have satisfied neither site nor charge balance.

By adding an additional vacant magnesium site, we can correct the situation:

\[ Al_2O_3 = 2Al^*_{Mg} + 3O^x_O + V^{''}_{Mg} \]  \hspace{1cm} (2.20)

and at the same time satisfy charge and site balance. Solutes greater or lesser in valence than the host must be charge-compensated in solid solution.
2. Solute Incorporation.

(3) As a third example, consider the incorporation of MgO into Al\(_2\)O\(_3\). In this instance, the Mg ions may enter the solid solution substitutionally or interstitially; it is not exactly clear which is the lower energy option. If it is substitutional, a possible reaction is

\[
2 \text{MgO} = 2 \text{Mg}_{\text{Al}}' + 2 \text{O}_O^x + V_O^{**}
\]  

(2.21)

and if it is interstitial, we can write:

\[
3 \text{MgO} = 3 \text{Mg}_i^{**} + 3 \text{O}_O^x + 2V_{\text{Al}}'''
\]

(2.22)

A third possibility is that magnesium is self-compensating and forms both the interstitial and substitutional defect:

\[
3 \text{MgO} = 2 \text{Mg}_{\text{Al}}' + \text{Mg}_i^{**} + 3 \text{O}_O^x
\]

(2.23)

We should confirm that mass, site, and charge balance is maintained in each of these instances.
2. Solute Incorporation.

Discussing:
- If the respective energies are similar, no one will be dominant in the three cases. These reactions are simultaneously in equilibrium.
- Experimental data and calculations of the relative energies for these incorporation mechanisms suggest that at high temperatures magnesium is self-compensated to a large extent, but that some minor compensation by cation vacancies or oxygen vacancies also exists. That is, the net incorporation can be considered to be mostly reaction 2.23, plus some fraction of reactions 2.21 or 2.22.
- We also emphasize that the free energy of solution for aliovalent solutes also includes the formation energy of the charge-compensating defects.

\[
\begin{align*}
2MgO &= 2Mg'_{Al} + 2O^x_O + V^\bullet\bullet_O \\
3MgO &= 3Mg''_{i} + 3O^x_O + 2V'''_{Al} \\
3MgO &= 2Mg'_{Al} + Mg^\bullet\bullet_i + 3O^x_O
\end{align*}
\]
Defect Chemical Reaction

3. Electrons, Holes, and Defect Ionization.

• “Intrinsic electronic” reaction:
  \[ \text{null} = e' + h^* \]  
  (2.24)

• The formation energy is the band gap.

• When electrons and holes are tightly bound to an ion, or otherwise localized at a lattice site, the whole is considered to be ionic defects.

• The valence state of defects can be vary.

• Changes in valence take place via ionization reactions such as:
  \[ V_o^{**} + e' = V_o^* \]  
  (2.25)
  \[ Zn_i^* + h^* = Zn_i^{**} \]  
  (2.26)

For which equilibrium constants can be written:

\[ K_{1(2)} = \left[ \frac{V_o^*}{V_o^{**}} \right] = \exp\left( -\frac{\Delta g_1}{kT} \right) \]  
(2.27)

\[ K_{1(2)} = \left[ \frac{Zn_i^{**}}{Zn_i^*} \right] = \exp\left( -\frac{\Delta g_2}{kT} \right) \]  
(2.28)
Defect Chemical Reaction

4. Oxidation and Reduction Reaction.

Reduction Reaction

- The reduction of an oxide can be written as the removal of oxygen to the gas phase leaving behind oxygen vacancies:

\[ O_\circ^x = \frac{1}{2}O_2(g) + V_O^{\bullet\bullet} + 2e' \]  \hspace{1cm} (2.29)

The two electrons that were associated with the \( O^{2+} \) ion are liberated within the solid.

- The equilibrium constant for this reaction is:

\[ K_R = n^2\left[V_O^{\bullet\bullet}\right]P_{O_2}^{1/2} = K_R^0 \exp\left(-\frac{\Delta g_R}{kT}\right) \]  \hspace{1cm} (2.30)

Where the oxygen partial pressure is equivalent to oxygen activity, \( K_R^0 \) is a constant, and \( \Delta g_R \) is the free energy of reduction. The concentration of oxygen ions on their proper sites, \( [O_O^x] \), is essentially unity (that is, the concentration of vacancies is assumed dilute).
Defect Chemical Reaction

4. Oxidation and Reduction Reaction.

Oxidation reaction

- Oxidation can be written as the consumption of oxygen vacancies:

\[
\frac{1}{2} O_2(g) + V_o^{\bullet\bullet} = O_o^x + 2 h^* \]  

(2.31)

- For which the equilibrium constant is:

\[
K_o = \frac{p^2}{[V_o^{\bullet\bullet}]P_{O_2}^{1/2}} = K_o^0 \exp\left( - \frac{\Delta g_o}{kT} \right) \]  

(2.32)

- It is important to note that since oxidation and reduction are the same thermodynamic process simply reversed, the reactions that we write to describe them are not independent.

- The equilibrium constants in Eqs.2.30 and 2.32 are also not unitless. Typically, the units will reflect whichever pressure and concentration units in use.
4. Oxidation and Reduction Reaction

There are a number of ways of writing the oxidation and reduction reactions, which we may choose for convenience in order to show the formation or removal of particular defects.

\[ \frac{1}{2} O_2(g) = O_x^O + V''_{Mg} + 2h^* \]  

(2.33)

Obtained by adding the Schottky reaction to Eq. 2.31. Another is

\[ \frac{1}{2} O_2(g) + 2e' = O_x^O + V''_{Mg} \]  

(2.34)

Obtained from the previous reaction by adding twice the intrinsic electronic reaction.

These schemes (Eqs. 2.29-2.34) are simply alternative representations of the chemical process of oxidation, written to include a particular defect type. It is usually convenient to choose just one representation that includes the prevailing defects in the system.

In some systems where the metal has significant vapor pressure it may be useful to write the oxidation/reduction reaction as the equilibration of the solid with the metal vapor rather than the anion vapor.
5. Intrinsic Ionic and Electronic Defect Concentrations in MgO and NaCl.

The lowest energy intrinsic defect in MgO is the Schottky pair, with an enthalpy estimated to be 7.7 eV.

The bandgap is rather close in value, being 7.65 eV at room temperature. At 1673 K the bandgap energy is $E_g \sim 6.28$ eV.

For absolutely pure and stoichiometric MgO, the Schottky defect concentration is given at a high temperature of 1400 °C by:

$$\left[V''_{Mg}\right] = \left[V_{\cdot\cdot}\right] = K_s^{1/2} \approx \exp\left(-\frac{\Delta h_s}{2kT}\right)$$

$$= 2.5 \times 10^{-12} \text{ mole fraction} \approx 1.4 \times 10^{11} \text{ cm}^{-3}$$

The electron and hole concentrations at 1673 K are given by:

$$n = p = K_i^{1/2} = (N_eN_v)^{1/2} \exp\left(-\frac{E_g}{2kT}\right) = 2\left(\frac{kT}{2\pi\hbar}\right)^{3/2}(m_e^*m_h^*)^{3/4} \exp\left(-\frac{E_g}{2kT}\right)$$

$$n = p = \left(1.3 \times 10^{20} \text{ cm}^{-3}\right)\exp(-6.28 eV / 2kT) = 4.6 \times 10^{10} \text{ cm}^{-3}$$
5. Intrinsic Ionic and Electronic Defect Concentrations in MgO and NaCl.

The effective masses $m_e^*$ and $m_h^*$ are, respectively, $0.38m_0$ and $0.77m_0$. We see that at this temperature, despite a considerably higher value of the Schottky defect concentration is still slightly greater than that of electrons and holes, due to the difference between the conduction band and valence band density of states($\sim10^{20}\text{ cm}^{-3}$) and the density of lattice sites($5.3\times10^{22}$).

If we compare these results to a similar calculation in NaCl, which has a Schottky energy of $2.2\sim2.4\text{ eV}$ and a bandgap of $7.3\text{ eV}$, it becomes apparent that anywhere below its melting point ($810\text{ °C}$) the intrinsic electronic carrier concentration in NaCl is truly infinitesimal.

At $T_m$, the intrinsic electron and holes concentration are only of order $10^4\text{ cm}^{-3}$ ($\sim10^{-19}$ mole fraction). The Schottky defect concentration is comparatively much higher, being $\sim1$ ppm ($\sim 10^{-6}$ mole fraction) near the melting point, due to the much smaller value of the Schottky energy. It is overwhelmingly dominated by ionic defects.
Another important complexity in the electrical behavior of solutes in ionic ceramics arises from the existence of simultaneous equilibria.

- In a covalent semiconductor such as silicon, the effectiveness of donor and acceptor solutes at a given temperature is solely determined by their ionization energies.

- In oxide semiconductors, the effectiveness of even shallow dopants also depends on the extent of oxidation and reduction.
  1. ionically compensated
  2. electronically compensated
  3. mixed compensated

- This effect is of particular interest in electronic ceramic systems, where large variations in electrical conductivity can result with changes in $\text{Po}_2$ and temperature at a constant doping level, due to changes in the compensation mechanism.

Let us now consider the incorporation of $\text{Nb}_2\text{O}_5$ as a solute in $\text{TiO}_2$, for which both ionic and electronic compensation can occur.
6. Electronic versus Ionic Compensation of Solutes

Incorporation of Nb$_2$O$_5$ as a solute in TiO$_2$:
The ionic compensation of niobium is given by:

$$2Nb_2O_5 = 4Nb_{Ti}^\bullet + 10O_{O}^x + V_{Ti}'''$$  \hspace{1cm} (2.36)

The alternative electronic compensation mechanism is:

$$2Nb_2O_5 = 4Nb_{Ti}^\bullet + 8O_{O}^x + O_2(g) + 4e'$$  \hspace{1cm} (2.37)

Where one molecule of oxygen gas has been liberated upon incorporation. Which of these reactions dominates, and under what conditions? Notice that Eq. 2.36 and 2.37 are interrelated by a third defect chemical reaction representing oxidation/reduction equilibrium, which upon subtracting Eq. 2.37 from Eq. 2.36 is:

$$O_2(g) + 4e' = 2O_{O}^x + V_{Ti}'''$$  \hspace{1cm} (2.38)

Examining Eqs. 2.36-2.38, one finds that the prevailing compensation mechanism will depend on solute concentration, oxygen pressure, and temperature.
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Defect Chemical Reaction

6. Electronic versus Ionic Compensation of Solutes

1. The oxidation reaction in Eq. 2.38 tends toward the right at higher oxygen pressure and lower temperature.
2. Thus niobium tends to be compensated by titanium vacancies when the niobium concentration is high, temperature low, and oxygen pressure high.
3. In the band gap scheme, ionic compensation is the condition where the niobium donor is completely compensated by the vacancy acceptor.

- At lower concentrations, higher temperature, and lower oxygen pressure, the compensating defect is the electron. This corresponds to the introduction of niobium donor levels in the energy gap without compensating ionic defects.

\[
2Nb_2O_5 = 4Nb^{\bullet}_{Ti} + 10O^x_O + V''''_{Ti} \tag{2.36}
\]

\[
2Nb_2O_5 = 4Nb^{\bullet}_{Ti} + 8O^x_O + O_2(g) + 4e' \tag{2.37}
\]

\[
O_2(g) + 4e' = 2O^x_O + V''''_{Ti} \tag{2.38}
\]
We have now discussed a wide variety of individual defect reactions that can occur in a solid. Let’s consider the net effect when all of these reactions take place simultaneously!

• Since any one defect can participate in a number of defect reactions, in a real system multiple defect equilibria will occur.
• In order to determine the defect concentrations, we must simultaneously solve a number of defect reactions.
• In principle, the number of defect reactions that can be written for any system is nearly limitless; to account for all of them would appear to be a daunting task.
• Fortunately, the number of defects that must be included for an adequate description of defect-related properties in a system is usually small.
• Which defects are important? The majority defects are always important; but in addition, certain minority defects may have direct relevance to a property of interest, such as the electrical conductivity. Conversely, in a small band gap compound where electronic defects dominate, minority ionic defects remain important for diffusional processes.
Most often we are interested in the variation of defect concentration with temperature, solute concentration, and ambient gas activity (usually $P_{O_2}$). The defect formation reactions of interest will generally include those for:

1. Predominant intrinsic ionic defects (Schottky or Frenkel).
2. Intrinsic electronic defects.
3. Oxidation and reduction.
4. Incorporation of any significant solutes or impurities.

These reactions will involve a total of $N$ defects, the concentrations of which are $N$ variables to be solved for. If we are careful to write only independent reactions, one finds that the equilibrium constants for the above reactions always result in $(N-1)$ independent equations.
Simultaneous Defect Equilibria: The Brouwer Diagram

For MgO, there are four defects of interest, for which the relevant defect-forming reactions are:

\[ \text{null} \rightarrow V''_{\text{Mg}} + V''_{\text{O}} \quad (2.11) \]
\[ \text{null} = e' + h^* \quad (2.24) \]
\[ O^x_O = \frac{1}{2} O_2(g) + V''_{\text{O}} + 2e' \quad (2.29) \]

With the respective equilibrium constants:

\[ K_s = [V''_{\text{Mg}}][V''_{\text{O}}] \quad (2.13) \]
\[ K_i = np \quad (2.39) \]
\[ K_R = n^2[V''_{\text{O}}]P_{O_2}^{1/2} \quad (2.30) \]

One additional equation is always necessary. This is provided by the requirement of bulk electrical neutrality:

\[ 2[V''_{\text{Mg}}] + n = 2[V''_{\text{O}}] + P_{21} \quad (2.40) \]
Simultaneous Defect Equilibria: The Brouwer Diagram

In order to solve for all defect concentrations, one additional equation is always necessary. This provided by the requirement of bulk electrical neutrality. In the electroneutrality condition each defect contributes a charge equal to its concentration times the effective charge per defect. In the current example this is:

\[ 2[V''_{Mg}] + n = 2[V''_{O}] + P \]  

(2.40)

This system of equations can now be solved to give the concentration of each defect at any temperature and \( P_{O_2} \) of interest, provided that the equilibrium constants. Note that neutral defects are not included in the electroneutrality condition. Their concentration can nonetheless vary with temperature, solute concentration, and oxygen pressure through ionization and association reactions involving charged defects.

Solving this set of simultaneous equations using the electroneutrality condition (Eq. 2.39) is usually a fairly straightforward procedure of solving a polynomial.
Brouwer approximation

• There is just one positive defect and one negative defect.
• This assumption is valid when a single defect of each sign has a concentration much higher than others of the same sign.
• This condition is often satisfied due to the strong (exponential) dependence of defect concentration on T and formation energy.
• For pure MgO, four Brouwer approximations are in principal possible:

1. \( n = 2[V_O^{**}] \)
2. \( 2[V_{Mg}^{''}] = p \)
3. \( [V_{Mg}^{''}] = [V_O^{**}] \)
4. \( n = p \)

Only one of the last two of these will be important, depending on the relative values of the Schottky energy and the band gap.
Simultaneous Defect Equilibria

Brouwer approximation

In MgO, we found earlier:

1. The Schottky concentration (3) is higher than the electronic carrier concentration (4) at high temperature.

2. For simplicity, consider (3) to be dominant, in which case there are only three Brouwer regimes to be considered, those defined by (1), (2), and (3).

3. Each of these regimes will be represented by a different range of oxygen activity.

   • Since reduction raises the concentration of oxygen vacancies and electrons (Eq.2.29), Brouwer approximation (1) is likely to be important at the lowest range of oxygen pressure.

   • Conversely, at high oxygen pressures the electron concentration is suppressed and the hole concentration $p$ increases ($K_i=np$). Brouwer approximation (2) may the apply.
The Brouwer diagram (also referred to as a Kröger-Vink diagram) is a convenient way to represent the variation in defect concentrations with changes in the activity of a component of the compound, usually oxygen pressure.

It is a plot of log [concentration] against log $P_{O_2}$ showing variations in defect concentrations at constant temperature in different Brouwer regimes.

The Brouwer diagram for a binary metal oxide such as MgO is shown in Fig. 2.10. Consider the regime defined by the Brouwer approximation $\left[ V^*_{Mg} \right] = \left[ V^{**}_O \right] = K_s^{1/2}$.

Note that $K_i^{1/2}$ lies below $K_s^{1/2}$ since electronic defects are in the minority.

Rearranging Equation 2.30, we obtain the $P_{O_2}$ dependence of the electron concentration:

$$n = K_R^{1/2} K_s^{-1/4} P_{O_2}^{-1/4}$$  (2.41)
Fig. 2.10 Schematic representation of defect concentration as a function of oxygen pressure for a pure oxide that forms predominantly stoichiometric crystallites.
Simultaneous Defect Equilibria:

Brouwer Diagram

And upon taking the logarithm of both sides, we have

$$\log n \propto -\frac{1}{4} \log P_{O_2}$$

- In the central region of Fig. 2.10, the line representing $n$ therefore has a slope of $-1/4$. Since $np=K_i$ and is constant at fixed temperature, the hole concentration follows a $P_{O_2}$ dependence opposite to that of the electron concentration:

$$p = \frac{K_i}{n} = K_i K_R^{-1/2} K_s^{1/4} P_{O_2}^{1/4}$$

And show a $+1/4$ slope on the Kröger-Vink diagram.

- With sufficient reduction, the Brouwer approximation $n=2[V_{O}^{\bullet\bullet}]$ may come into play; this is the leftmost region of Fig. 2.10. By substituting the Brouwer approximation into Eq. 2.30 and rearranging, one obtains

$$n = 2[V_{O}^{\bullet\bullet}] = (2K_R)^{1/3} P_{O_2}^{-1/6}$$

and both $n$ and $[V_{O}^{\bullet\bullet}]$ show a $-1/6$ slope, displaced from one another by a factor of log 2. Lines for $p$ and $[V_{Mg}^{\bullet\bullet}]$ show the opposite slope, being coupled to $n$ and $[V_{O}^{\bullet\bullet}]$ through the intrinsic electronic and Schottky equilibria (Eq.2.13).
Simultaneous Defect Equilibria: The Brouwer Diagram

- With increasing $P_{O_2}$ the hole concentration $p$ increases, until the Brouwer approximation $2\left[\nu_{Mg}''\right] = p$ comes into play. In this regime, substitution of the Brouwer approximation into the set of Eqs. 2.13, 2.39, 2.30 results in the $+1/6$ slopes in Fig. 2.10.

$$p = 3\sqrt{2} K_i^{2/3} K_R^{-1/3} K_s^{1/3} P_{O_2}^{1/6}$$

- Notice that at all times $[\nu_o''']$ and $[\nu_{Mg}''']$ are symmetric about the horizontal line given by $K_s^{1/2}$, and $n$ and $p$ about $K_i^{1/2}$. This is required by the Schottky and intrinsic electronic equilibria.

Discussion:
1. Not all of these may be relevant to real defect behavior.
2. The experimentally accessible range of $P_{O_2}$ may only cover one or two Brouwer regimes.
Simultaneous Defect Equilibria: The Brouwer Diagram

Fig. 2.11 Kröger–Vink diagram for an oxide in which oxygen Frenkel defects dominate the intrinsic defect structure.

Fig. 2.12 Kröger-Vink diagram for oxide similar to Fig. 2.11 except that electronic defects dominate ($K_i > K_p$).
The Brouwer Diagram

Fig. 2.13 shows a more complex diatam which represents the binary metal oxide in Fig. 2.10 when it is \( [F_M^*] > K_s^{1/2} \) dominated by trivalent impurities. Defect associates are included in this diagram, but the minority...