Defect in ceramics

- A great many properties of crystals are determined by imperfections.

- Electrical conductivity
  - Diffusion transport
  - Optical properties
  - Rate of kinetic process

- Precipitation
  - Densification
  - Grain coarsening
  - High temperature creep deformation

- Kinetic processes

- Point defects: defined as deviations from the perfect atomic arrangement.
  - Missing ions
  - Substituted ions
  - Interstitial ions
    - Associated valence electrons

- Point defects occur in all crystalline materials
• Point defect: ionic defects, electric defects

• Ionic defects: vacancies, interstitial, substitutional, solutes

• Electric defects – formed when valence electrons are excited into higher orbital energy levels.

• Such an excitation may create an electron in the conduction band and/or an electron hole in the valence band of the crystal.

• Point defects in ceramic can be formed by thermal excitation, solutes (impurities), oxidation or reduction.

• In the solid-state analogy, the perfect crystal may be regarded as a neutral medium into which the charged defects are dissolved.

• Solid-state defect interaction (defect chemistry) similar solution-chemical interaction
• Point defect
  \[ \begin{aligned}
  \text{types} \\
  \text{concentration}
  \end{aligned} \]

• Depend on
  \[ \begin{aligned}
  \text{density} \\
  \text{melting point} \\
  \text{electrical conductivity} \\
  \text{diffusion} \\
  \text{optical absorb}
  \end{aligned} \]
  strong clues
defect behavior

• The formation of atomic defects requires the breaking of interatomic bonds

• The melting temperature \((T_m)\) of a compound scale with the strength of its interatomic bonding.

  scale to

• \(T/T_m\) (homologous temperature)
  \[ \begin{aligned}
  \text{defect properties} \\
  \text{diffusion}
  \end{aligned} \]
• Ex:
At equal temperature, the conc. of defects in MgO is many orders of magnitude lower than NaCl.

\[
\text{MgO } (T_m = 2825 \, ^\circ\text{C}), \quad \text{NaCl } (T_m < 1000 \, ^\circ\text{C})
\]

• At equal homologous temperature, the defect conc. are rather similar.

➢ Defect sties in the crystal structure

• A close–packed sublattice of ions does not easily accommodate interstitial defect.

Ex : rocksalt structure

\[
\begin{align*}
\text{Anion interstitials} & > \text{cation vacancies} \\
(\text{high energy}) & > \text{cation interstitials}
\end{align*}
\]

• The location of solutes and impurities in the lattice often depends on the compatibility in \{size, valence\} with host ions.

• Solutes that differ in valence from the host (aliovalent) must be compensated by additional charged defects in order to maintain overall electrical neutrality in the crystal.
• Nonstoichiometric compounds are those in which the metal/anion ratio deviates from the ideal value on which the structure is based, due to the existence of multiple ion valence state.

• Transition metal oxides (NiO, FeO, TiO$_2$ ...) are often highly defective.

Ex: Fe$_{1-x}$O
• Cation-deficient due to the presence of a significant fraction (at least 5%) of the iron being in the Fe$^{3+}$ state.
Intrinsic ionic disorder

- Crystalline defects in ionic materials
  - Frenkel defects
  - Schottky defects
- Intrinsic defects, they can be \textit{thermally generated} in perfect crystal.
- Extrinsic defects, which are formed only by the addition of impurities or solute.

![Frenkel disorder](image)

- A Frenkel defect is formed when an atom is displaced from its normal site onto an \textit{interstitial site} forming a defect pair
  - a vacancy
  - an interstitial
- In ionic materials, cation/anion can undergo this kind of displacement.

- In \{\textit{metals}, \textit{covalent compounds}\}, Frenkel defects can also form.

They differ from those in ionic compounds only in that the defect need not be electrically charged.
• The Schottky defect is unique to ionic compound and is represented by the simultaneous creation of both cation and anion vacancies.

• The vacancies must be formed in the stoichiometric ratio in order to preserve the electrical neutrality of the crystal.

Ex: NaCl $\rightarrow V'_\text{Na} + V'_\text{Cl}$ a Schottky pair

MgO $\rightarrow V''_\text{Mg} + V''_\text{O}$

TiO$_2$ the Schottky defect consist $\begin{cases} 2V''_\text{O} \\ + \\ 1V'''_\text{Ti} \end{cases}$

Al$_2$O$_3$ the Schottky defect consist $\begin{cases} 2V'''_\text{Al} \\ + \\ 3V''_\text{O} \end{cases}$
Concentration of Intrinsic Defects
Consider the change in free energy of a perfect crystal with initial free energy $G_0$, upon forming $n$ Frenkel defect pairs at an energy expense of $\Delta g_f$ per pair. The free energy of the crystal becomes:

$$G = G_0 + n\Delta g_f - T\Delta S_c$$  \hspace{1cm} (\Delta S_c : the increase in configurational entropy of the crystal)

The change in free energy

$$\Delta G = G - G_0 = n\Delta g_f - T\Delta S_c$$  \hspace{1cm} ($\Omega$ is the number of distinct ways in which the defect can be arranged)

$$\Delta S_c = k\ell n\Omega$$

(1) If these are arranged on a total of $N$ lattice site, the vacancies can be arranged in $\Omega_v$ ways.

$$\Omega_v = \frac{N!}{(N - n_v)!n_v!}$$  \hspace{1cm} ( $n_v$ : number of vacancies $n_i$ : number of interstitial)

(2) If these are arranged on a total of $N$ lattice site, the interstitial can be arranged in $\Omega_i$ ways.

$$\Omega_i = \frac{N!}{(N - n_i)!n_i!}$$
The total number of configuration:

\[ \Omega = \Omega_i \Omega_v \]

\[ \therefore n_v = n_i = n \]

\[ \Delta S_c = k \ln \left[ \frac{N!}{(N-n_v)! n_v!} \right] \left[ \frac{N!}{(N-n_i)! n_i!} \right] \]

\[ = 2k \ln \left[ \frac{N!}{(N-n)! n!} \right] \]

\[ \approx 2k [N \ln N - (N-n) \ln(N-n) - n \ln n] \]

(stirling’s approximation \( \ln N! = N \ln N - N \))

The total free energy change:

\[ \Delta G = n \Delta g - 2kT \left[ N \ln \left( \frac{N}{N-n} \right) + n \ln \left( \frac{N-n}{n} \right) \right] \]

• To find the equilibrium conc. of defects.

\[ \left( \frac{\partial \Delta G}{\partial n} \right)_{T,P} = 0 \quad \text{(for dilute conc. of defect \( (N-n) \approx N \))} \]

For the conc. of defects:

\[ \frac{n}{N} = \exp \left( -\frac{\Delta g}{2kT} \right) = \exp \left( \frac{\Delta S}{2k} \right) \exp \left( -\frac{\Delta h}{2kT} \right) \]

\( \Delta S \): non — configuration entropy

\( \Delta h \): energy of formation
\[ \Delta S \ll \text{Configuration entropy} \]

\[ \exp \left( \frac{\Delta s}{2k} \right) \text{ ranging from } 10^{-4} \sim 10^4 \text{ (from experimental data)} \]

- In table 2.1, defect conc. are shown as a function of \( \Delta h \) and temperature, assuming that \( \exp(\Delta S/2k) \sim 1 \).

<table>
<thead>
<tr>
<th>\text{Defect Concentration}</th>
<th>\text{( n / N \text{ at } 100^\circ C )}</th>
<th>\text{( n / N \text{ at } 500^\circ C )}</th>
<th>\text{( n / N \text{ at } 800^\circ C )}</th>
<th>\text{( n / N \text{ at } 1000^\circ C )}</th>
<th>\text{( n / N \text{ at } 1200^\circ C )}</th>
<th>\text{( n / N \text{ at } 1500^\circ C )}</th>
<th>\text{( n / N \text{ at } 1800^\circ C )}</th>
<th>\text{( n / N \text{ at } 2000^\circ C )}</th>
</tr>
</thead>
<tbody>
<tr>
<td>\text{( N )}</td>
<td>\text{1eV}</td>
<td>\text{2eV}</td>
<td>\text{4eV}</td>
<td>\text{6eV}</td>
<td>\text{8eV}</td>
<td>\text{10eV}</td>
<td>\text{15eV}</td>
<td>\text{20eV}</td>
</tr>
</tbody>
</table>
| \text{1eV} \( = 23.05 \text{ kcal/mole} \) | \begin{align*} 2 \times 10^{-7} & \quad 3 \times 10^{-14} & \quad 1 \times 10^{-27} & \quad 3 \times 10^{-41} & \quad 1 \times 10^{-54} \\
6 \times 10^{-4} & \quad 3 \times 10^{-7} & \quad 1 \times 10^{-12} & \quad 3 \times 10^{-20} & \quad 8 \times 10^{-27} \\
4 \times 10^{-3} & \quad 2 \times 10^{-5} & \quad 4 \times 10^{-10} & \quad 8 \times 10^{-15} & \quad 2 \times 10^{-19} \\
1 \times 10^{-2} & \quad 1 \times 10^{-4} & \quad 1 \times 10^{-8} & \quad 1 \times 10^{-12} & \quad 1 \times 10^{-16} \\
2 \times 10^{-2} & \quad 4 \times 10^{-4} & \quad 1 \times 10^{-7} & \quad 5 \times 10^{-11} & \quad 2 \times 10^{-19} \\
4 \times 10^{-2} & \quad 1 \times 10^{-4} & \quad 2 \times 10^{-6} & \quad 3 \times 10^{-9} & \quad 4 \times 10^{-12} \\
6 \times 10^{-2} & \quad 4 \times 10^{-3} & \quad 1 \times 10^{-5} & \quad 5 \times 10^{-8} & \quad 2 \times 10^{-10} \\
8 \times 10^{-2} & \quad 6 \times 10^{-3} & \quad 4 \times 10^{-5} & \quad 2 \times 10^{-7} & \quad 1 \times 10^{-9} \\
\end{align*} |

- For system with large \( \Delta h \), Table 2.1 shows that concentration change by many orders of magnitude as \( T \) varies.
Intrinsic V.S. Extrinsic Behavior

• The concentration of intrinsic defect can be small in highly refractory ceramics of large defect formation energy.

➢ Intrinsic defect – Temp.
➢ Extrinsic defect – solute (especially aliovalent solutes)
  oxidation process
  reduction process

• Intrinsic defect concentrations increase with temperature.

• Extrinsic defects, with the exception of nonstoichiometry, remain constant in concentration with various temperature.

Ex. Rocksalt structure type – NaCl and MgO

• In both, the dominant intrinsic defect is the Schottky defect.

• The concentration of defects

\[
\frac{n}{N} = \exp \left( \frac{\Delta S}{2k} \right) \exp \left( -\frac{\Delta h}{2kT} \right)
\]

\[
= \exp \left( -\frac{\Delta g}{2kT} \right)
\]

\[
\Delta h (\text{NaCl}) = 2.2\sim2.4\,\text{eV}, \quad T_m = 801^\circ\text{C}
\]

\[
\Delta h (\text{MgO}) = 7.74\,\text{eV}, \quad T_m = 2825^\circ\text{C}
\]

• High \(\Delta h\), with the stronger bonding and higher \(T_m\).
• At 700°C, $n_v/N$ (MgO) has many orders of magnitude fewer than $n_v/N$ (NaCl).

• But at $\frac{T}{T_m}=1$,

\[
\frac{n_v}{N} (\text{NaCl}) \approx 2 \times 10^{-6} \text{ (2ppm)}
\]
\[
\frac{n_v}{N} (\text{MgO}) \approx 4 \times 10^{-7} \text{ (0.4ppm)}
\]

• There is a great difference in the purity level with zone-refining procedures.

\[\text{NaCl} \sim 1\text{ppm(impurities)} \quad \text{MgO} \sim 50\text{ppm(impurities)} \quad \text{aliovalent cations.} \]

( Because of the much higher processing temperatures necessary, contamination from crucibles is harder to avoid.)

• MgO, the impurity concentration is much greater than the intrinsic defect concentration.

• NaCl, intrinsic defect can in practice be achieved rather easily.
• Units for defect concentration

\( \frac{n_v}{N} \) : mole fraction, # of defect \( n \) relative to # of possible site \( N \).

\( n \) : number per unit volume (no./cm\(^3\) or cm\(^{-3}\))

\( N \) : density of atoms in solid (~10\(^{23}\) cm\(^{-3}\))

factor: \( \frac{\text{Na}(\text{no./mole}) \rho(\text{g/cm}^3)}{\text{MW}(\text{g/mole})} \)

mole fraction \( \rightarrow \text{cm}^{-3} \) \( \frac{N_a}{13} \)

Na (Avogadro’s no.)

\( = 6.02 \times 10^{23}/\text{mole} \)
**Kröger - Vink Notation**

缺陷總類

- (ˈ) : negative charge
- (⋅) : positive charge

\[ V_M', V_X' \text{ (vacancies)} \quad (V_{\text{Mg}''}, V_{\text{O}''}) \]
\[ M_i', X_i' \text{ (interstitials)} \quad (Mg_{i''}, O_{i''}) \]
\[ M_X', X_M \text{ (misplaced atoms)} \]
\[ e' \text{ (electrons)} \]
\[ h^- \text{ (electron holes)} \]

Solute: \( Fe_{\text{Mg}}^X (Fe^{2+}), Fe_{\text{Mg}}^- (Fe^{3+}) \)

- Cluster defects or defect associates

\[ (V_{\text{Mg}''} - V_{\text{O}'}) \text{ – dimer} \]
\[ (Al_{\text{Mg}}' - V_{\text{Mg}''} - Al_{\text{Mg}}^-) \text{ – trimer} \]

The concentration of defects is denoted by [_______]

ex:

\[ [V_{\text{Mg}}''], [Al_{\text{Mg}}'], [ (V_{\text{Na}}' - V_{\text{Cl}})^x ] \]
Kroger-Vink Notation
Defect chemical reactions

- From a statistical thermodynamic viewpoint, defect concentration depend on 
  \[ \text{formation energy (\(\Delta h\)) } \]
  \[ \text{temperature (T)} \]

- An equivalent way to view the formation of defects is as a chemical reaction, for which there is an equilibrium constant which is governed by the law of mass action.

Ex. Schottky reaction for NaCl and MgO

\[
\text{null} \xrightarrow{NaCl} V_{Na}' + V_{Cl}'
\]

\[
\text{null} \xrightarrow{MgO} V_{Mg}'' + V_{O}''
\]

(indicates the creation of defects from a perfect lattice.)

mass-action equilibrium constant

\[
k_S = \left[ V_{Na}' \right] \left[ V_{Cl} \right]
\]

\[
k_S = \left[ V_{Mg}'' \right] \left[ V_{O}'' \right]
\]

\[
k_s = \exp\left[ -\frac{\Delta g_s}{kT} \right]
\]

\[
k_S = f(T)
\]

- When only the intrinsic defects are present,

\[
[V_{Na}'] = [V_{Cl}] = \exp\left[ -\frac{\Delta g_s}{2kT} \right]
\]
Defect chemical reaction must obey

\[
\begin{align*}
\text{(quasichemical reaction)} \quad & \quad \text{(chemical reaction)} \\
\text{mass} \quad & \quad \text{mass} \\
\text{site} \quad & \quad \text{charge} \\
\text{charge} \quad & \quad \text{balance} \\
\end{align*}
\]

- **Mass balance**: a chemical reaction cannot create or lose mass.

- **Site balance**: the ratio of cation to anion site of the crystal must be preserved, although the total no. of sites can be increased or decreased.

- **Charge balance**: total effective charge is balanced. 
  (cation and anion vacancies must be formed in the stoichiometric ratios, the effective charges are automatically balanced.)

Ex: Schottky reaction for \( \text{Al}_2\text{O}_3 \) and \( \text{BaTiO}_3 \)

\[
\begin{align*}
\text{null} \quad & \quad \text{null} \\
\text{Al}_2\text{O}_3 \quad & \quad \text{BaTiO}_3 \\
\rightarrow 2V_{\text{Al}}^{	ext{''''}} + 3V_{\text{0}}^{	ext{''}} \\
\rightarrow V_{\text{Ba}}^{	ext{''}} + V_{\text{Ti}}^{	ext{''''}} + 3V_{\text{0}}^{	ext{''}}
\end{align*}
\]

Ex: Frenkel reaction for \( \text{AgCl} \)

\[
\begin{align*}
\text{Ag}_{\text{Ag}}^x \quad & \quad \text{Ag}_{\text{Ag}}^x \\
\rightarrow & \quad \text{Ag}_{\text{i}}^1 + V_{\text{Ag}}^1 \\
+ (V_{\text{i}}) \\
\end{align*}
\]

(site balance is maintained here since the formation of interstitials does not create new crystal sites.)
In addition to the formation of intrinsic defect, reaction of particular interest include:

- The incorporation of solutes
- Formation of intrinsic electron defects
- Oxidation/reduction
- Defect association and precipitation

**Solute Incorporation**

- Solute may enter solid solution in crystal as either *substitutional* or *interstitial* species.

- Isovalent substitution, NiO in MgO

\[
\text{(MgO)} \quad \text{NiO} = \text{Ni}^\times_{\text{Mg}} + \text{O}_\text{O}^\times \rightarrow \text{no charged species}
\]

Aliovalent substitution, greater or lesser in valence than the host, must be *charge compensated* in solid solution.

- (1) formation of additional ionic defect \( \rightarrow \) ionic compensation
- (2) liberating electrons and holes \( \rightarrow \) electronic compensation
Ionic compensation mechanisms:

Ex1: The dissolution of $\text{Al}_2\text{O}_3$ in MgO
- Based on $\Gamma_{\text{Al}^{3+}} \approx \Gamma_{\text{Mg}^{2+}}$, we may presume that $\text{Al}^{3+}$ will substitute for $\text{Mg}^{2+}$, the O ions are likely to occupy additional O lattice sites.

\[
\text{Al}_2\text{O}_3 + \text{MgO} \rightleftharpoons 2\text{Al}^{3+}_{\text{Mg}} + 3\text{O}^\times_{\text{O}} + \text{V}''_{\text{Mg}}
\]

Ex2: The incorporation of MgO into $\text{Al}_2\text{O}_3$
- Mg ion may enter the solid solution substitutionally or interstitially.

1. If it is substitutional:

\[
2\text{MgO} + \text{Al}_2\text{O}_3 \rightleftharpoons 2\text{Mg}^{3+}_{\text{Al}} + 2\text{O}^\times_{\text{O}} + \text{V}^\times_{\text{O}} \quad \Delta h_1
\]

2. If it is interstitial:

\[
3\text{MgO} + \text{Al}_2\text{O}_3 \rightleftharpoons 3\text{Mg}^\times_{\text{i}} + 3\text{O}^\times_{\text{O}} + 2\text{V}^\times_{\text{Al}} \quad \Delta h_2
\]

3. Self-compensating (from both interstitial/substitutional defect)

\[
3\text{MgO} + \text{Al}_2\text{O}_3 \rightleftharpoons 2\text{Mg}^{3+}_{\text{Al}} + \text{Mg}^\times_{\text{i}} + 3\text{O}^\times_{\text{O}} \quad \Delta h_3
\]

If $\Delta h_1 \approx \Delta h_2 \approx \Delta h_3$, no single one will be the dominant mechanism of incorporation. (simultaneously in equilibrium)