8. Phase Equilibria
8.1 Introduction

- **Phase diagrams** are graphical representations of what equilibrium phases are present in a material system at various temperatures, compositions, and pressures.

→ A **phase** is defined as a region in a system in which the properties and compositions are spatially uniform.

→ The condition for equilibrium is one where the electrochemical gradient (i.e., for the charged species in ceramics) of all the components of a system vanish.

\[
\eta_i = \frac{\mu_i}{N_{AV}} + z_i e\phi
\]

\[
d\eta_i = 0
\]

where \(\mu_i\) is the chemical potential per mole, \(z_i\) is the net charge of a particle, and \(\phi\) is the electric potential.
A system is said to be at equilibrium when there are no observable changes in either properties or microstructure with the passing of time, provided, of course, that no changes occur in the external conditions during that time.

- Phase diagram is the roadmap without which it is very difficult to interpret and predict microstructure distribution and evolution, which in turn have a profound effect on the ultimate properties of a material.

→ In principle, phase diagrams provide the following information:

1. The phases represent at equilibrium
2. The composition of the phases represent at any time during the heating or cooling
3. The fraction of each phase represent
4. The range of solid solubility of one element or compound in another

→ Gibbs phase rule (Sec. 8.2)
→ Unary component system (Sec. 8.3)
→ Binary and ternary systems (Secs. 8.4 & 8.5)
→ Connection btw. free energy, temperature, and composition (i.e., construction of phase diagram)
8.2 Phase Rule

- As noted before, phase diagrams are equilibrium diagrams. J. W. Gibbs showed that the condition for equilibrium places constraints on the degree of freedom $F$ that a system may possess. This constraint is embodied in the phase rule which relates $F$ to the number of phases $P$ present and the number of components $C$

$$F = C + 2 - P$$

where the 2 on the right-hand side denotes that two external variables are being considered, usually taken to be the temperature and pressure of the system.

→ The number of phases $P$ is the number of physically distinct and, in principle, mechanically separable portions of the system.

One of the easiest and least ambiguous methods to identify a phase is by analyzing its X-ray diffraction pattern – every phase has a unique pattern with peaks that occur at very well defined angles (see Chap. 3).
In the liquid state, the number of phases is much more limited than in the solid state, since for the most part liquid solutions are single-phase (alcohol and water are a common example). However, in some systems, liquid-liquid immiscibility results in the presence of two or more phases (e.g., oil and water). The gaseous state is always considered one phase because gases are miscible in all proportions.

The number of components $C$ is the minimum number of constituents needed to fully describe the compositions of all the phase present.

When one is dealing with binary systems, then perforce the number of components is identical to the number of elements present. Similarly, in ternary systems, one would expect $C$ to be 3. There are situations, however, when $C$ is only 2. For example, for any binary join in a ternary phase diagram the number of components is 2, since one element is common.

The number of degrees of freedom $F$ represents the number of variables, which include temperature, pressure, and composition, that have to be specified to completely define a system at equilibrium.
8.3 One-Component Systems

- For a one-component system $C = 1$ (if $P = 1$), and the degrees of freedom $F = 2$. In other words, to completely define the system, both temperature and pressure must be specified.

- If two phases are present ($P = 2$), $F = 1$, and either pressure or temperature needs to be specified, but not both. For example, at 1 atm pressure, water and ice can coexist at only one temperature ($0\, ^\circ C$). At the triple point, three phases coexist ($P = 3$), and there are no degrees of freedom left ($F = 0$) – the three phases must coexist at a unique temperature and pressure.

Fig: water’s phase diagram

A: Normal freezing point
B: Normal boiling point
Above the critical point, supercritical fluid exists.
As single-phase substances are heated or cooled, they can undergo a number of **polymorphic transformations**. Polymorphs (다형체, 동질이상) are different crystalline modifications of the same chemical substance. These transformations are quite common and include crystallization of glasses, melting, and many solid-solid phase transformations, some of which are described next.

In general, there are two types of polymorphic transformations, displacive and reconstructive.

- **Reconstructive Transformations**
  
  As shown schematically in Fig. 8.1a, reconstructive transformations involve the breaking and rearrangement of bonds. Such transformations usually occur by nucleation and growth, which in turn usually depend on the rate at which atoms diffuse and consequently are relatively sluggish (.Ordinal이 같은) and easily suppressed.

→ The constructive transformations that occur in quartz, specifically the $\alpha$-$\beta$ transformation, are good example.

→ Melting and crystallization are also examples (needs bond breaking).
Figure 8.1 Schematic of (a) reconstructive and (b) displacive transformations.

Figure 1.1 (a) Long-range order; (b) short-range order.
Displacive Transformations

In contrast to reconstructive transformations, displacive transformations do not involve the breaking of bonds, but rather occur by the displacement of atomic planes relative to one another, as illustrated in Fig. 8.1b.

These reactions occur quite rapidly, and the resulting microstructures are usually heavily twinned.

In these transformations, the role of thermal entropy is important since the enthalpies of the phases on either side of the transformation temperature are quite comparable. It follows that the transformation usually results in the formation of more open (less dense) structures at higher temperature, for reasons that the more open structures have higher thermal entropies.

Martensitic transformations in steel are probably the most studied of these transformations.

Examples in ceramic systems of technological importance include the tetragonal-to-monoclinic transformation in ZrO$_2$, the cubic-to-tetragonal transformation in BaTiO$_3$, and numerous transformation in silica.
Zirconia

- Upon heating under 1 atm pressure, zirconia goes through the following transformations:

  \[ \text{Monoclinic} \xrightarrow{1170^\circ C} \text{tetragonal} \xrightarrow{2370^\circ C} \text{cubic} \xrightarrow{2680^\circ C} \text{liquid} \]

  It exhibits three well-defined polymorphs: a monoclinic phase, a tetragonal phase, and a cubic phase. The low-temperature phase is monoclinic, stable to 1170°C at which temperature it changes reversibly to the tetragonal phase, which in turn is stable to 2370°C. Above that temperature the cubic phase becomes stable up to the melting point of 2680°C.

- The tetragonal-to-monoclinic (\( t \Rightarrow m \)) transformation is believed to occur by a diffusionless shear process that is similar to the formation of martensite in steels. This transformation is associated with a large volume change and undergoes extensive shear which is the basis for transformation toughening of zirconia.
Transformation toughening

→ The tetragonal phase can often be retained to room temperature where it is metastable. (in lightly doped ZrO$_2$)

→ The transformation to the monoclinic phase involves not only a change in symmetry but also a volume expansion of about 4.7%.

→ When this phase change is stimulated by the local stress field at the end of a sharp crack, the associated energy absorption and volume expansion can be used to impede the propagation of the crack, leading to toughening and strengthening of an otherwise brittle ceramic body.

→ the crystal symmetry differs, as do the detailed interatomic spacings, but the numerical coordination of ions does not.
Barium titanate

- Barium titanate goes through the following phase transitions upon heating:

\[
\text{Rhombohedral} \xrightarrow{-90^\circ\text{C}} \text{orthorhombic} \xrightarrow{0^\circ\text{C}} \text{tetragonal} \xrightarrow{130^\circ\text{C}} \text{cubic}
\]

Above \(130^\circ\text{C}\), the unit cell is cubic, and the Ti ions are centered in the unit cell. Between \(130^\circ\text{C}\) and \(0^\circ\text{C}\), however, \(\text{BaTiO}_3\) has a distorted perovskite structure with an eccentricity of the Ti ions.

- It is this eccentricity that is believed to be the origin of the main technological application of \(\text{BaTiO}_3\) as a capacitor material with a high dielectric constant.
8.4 Binary Systems

- A binary system consists of two components and is influenced by three variables: temperature, pressure, and composition.

- When two components are mixed together and allowed to equilibrate, three outcomes are possible:

  1. Mutual solubility and solid solution formation over the entire composition range, also known as **complete solid solubility**.

  2. Partial solid solubility without the formation of an intermediate phase

  3. Partial solid solubility with the formation of intermediate phases

- One objective of this section is to qualitatively describe the relationship between these various outcomes and the resulting phase diagrams. First, however, it is important to appreciate what is meant by a solid solution in a ceramic system and the types of solid solutions that occur.

- The two main types of solid solutions, described next, are substitutional and interstitial.
Substitutional solid solutions

- In a substitutional solid solution, the solute ion directly substitutes for the host ion nearest to it in electronegativity, which implies that cations will substitute for cations and anions for anions.

→ Needless to say, the rules for defect incorporation reactions have to be satisfied at all times. For instance, the incorporation reaction of NiO in MgO would be written as

\[ \text{NiO}_{\text{MgO}} \rightarrow O_{O}^{X} + \text{Ni}_{Mg}^{X} \]

where the Ni\(^{2+}\) ions substitute for Mg\(^{2+}\) ions.

The resulting substitutional solid solution is denoted by \((\text{Ni}_{1-x}\text{Mg}_{x})\text{O}\).

The factors that determine the extent of solid solubility are discussed shortly.
### Binary Ionic Compounds

<table>
<thead>
<tr>
<th>Structure name</th>
<th>Anion packing</th>
<th>Coordination no. of M and X</th>
<th>Sites occupied by cations</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rock salt</td>
<td>Cubic close-packed</td>
<td>6:6 MX</td>
<td>All oct.</td>
<td>NaCl, KCl, LiF, KBr, MgO, CaO, SrO, BaO, CdO, VO, MnO, FeO, CoO, NiO</td>
</tr>
<tr>
<td>Rutile</td>
<td>Distorted cubic close-packed</td>
<td>6:3 MX&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1/2 oct.</td>
<td>TiO&lt;sub&gt;2&lt;/sub&gt;, GeO&lt;sub&gt;2&lt;/sub&gt;, SnO&lt;sub&gt;2&lt;/sub&gt;, PbO&lt;sub&gt;2&lt;/sub&gt;, VO&lt;sub&gt;2&lt;/sub&gt;, NbO&lt;sub&gt;2&lt;/sub&gt;, TeO&lt;sub&gt;2&lt;/sub&gt;, MnO&lt;sub&gt;2&lt;/sub&gt;, RuO&lt;sub&gt;2&lt;/sub&gt;, OsO&lt;sub&gt;2&lt;/sub&gt;, IrO&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>Zinc blende</td>
<td>Cubic close-packed</td>
<td>4:4 MX</td>
<td>1/2 tet.</td>
<td>ZnS, BeO, SiC</td>
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<tr>
<td>Antifluorite</td>
<td>Cubic close-packed</td>
<td>4:8 M&lt;sub&gt;2&lt;/sub&gt;X</td>
<td>All tet.</td>
<td>Li&lt;sub&gt;2&lt;/sub&gt;O, Na&lt;sub&gt;2&lt;/sub&gt;O, K&lt;sub&gt;2&lt;/sub&gt;O, Rb&lt;sub&gt;2&lt;/sub&gt;O, sulfides</td>
</tr>
<tr>
<td>Wurtzite</td>
<td>Hexagonal close-packed</td>
<td>4:4 MX</td>
<td>1/2 tet.</td>
<td>ZnS, ZnO, SiC, ZnTe</td>
</tr>
<tr>
<td>Nickel arsenide</td>
<td>Hexagonal close-packed</td>
<td>6:6 MX</td>
<td>All oct.</td>
<td>NiAs, FeS, FeSe, CoSe</td>
</tr>
<tr>
<td>Cadmium iodide</td>
<td>Hexagonal close-packed</td>
<td>6:3 MX&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1/2 oct.</td>
<td>CdI&lt;sub&gt;2&lt;/sub&gt;, TiS&lt;sub&gt;2&lt;/sub&gt;, ZrS&lt;sub&gt;2&lt;/sub&gt;, MgI&lt;sub&gt;2&lt;/sub&gt;, VBr&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>Corundum</td>
<td>Hexagonal close-packed</td>
<td>6:4 M&lt;sub&gt;2&lt;/sub&gt;X&lt;sub&gt;3&lt;/sub&gt;</td>
<td>2/3 oct.</td>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;, Fe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;, Cr&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;, Ti&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;, V&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;, Ga&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;, Rh&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
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<tr>
<td>CsCl</td>
<td>Simple cubic</td>
<td>8:8 MX</td>
<td>All cubic</td>
<td>CsCl, CsBr, CsI</td>
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<tr>
<td>Fluorite</td>
<td>Simple cubic</td>
<td>8:4 M&lt;sub&gt;2&lt;/sub&gt;X</td>
<td>1/2 cubic</td>
<td>ThO&lt;sub&gt;2&lt;/sub&gt;, CeO&lt;sub&gt;2&lt;/sub&gt;, UO&lt;sub&gt;2&lt;/sub&gt;, ZrO&lt;sub&gt;2&lt;/sub&gt;, HfO&lt;sub&gt;2&lt;/sub&gt;, NbO&lt;sub&gt;2&lt;/sub&gt;, PuO&lt;sub&gt;2&lt;/sub&gt;, AmO&lt;sub&gt;2&lt;/sub&gt;, PrO&lt;sub&gt;2&lt;/sub&gt;, MgO&lt;sub&gt;2&lt;/sub&gt;, FeO&lt;sub&gt;2&lt;/sub&gt;</td>
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<tr>
<td>Silica types</td>
<td>Connected tetrahedra</td>
<td>4:2 MO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>—</td>
<td>SiO&lt;sub&gt;2&lt;/sub&gt;, GeO&lt;sub&gt;2&lt;/sub&gt;</td>
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</table>

**Complex structures**

<p>| | | | | |</p>
<table>
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</thead>
<tbody>
<tr>
<td>Perovskite</td>
<td>Cubic close-packed</td>
<td>12:6:6 ABO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>1/4 oct. (B)</td>
<td>CaTiO&lt;sub&gt;3&lt;/sub&gt;, SrTiO&lt;sub&gt;3&lt;/sub&gt;, SrSnO&lt;sub&gt;3&lt;/sub&gt;, SrZrO&lt;sub&gt;3&lt;/sub&gt;, SrHfO&lt;sub&gt;3&lt;/sub&gt;, SrTaO&lt;sub&gt;3&lt;/sub&gt;, BaTiO&lt;sub&gt;3&lt;/sub&gt;</td>
</tr>
<tr>
<td>Spinel (normal)</td>
<td>Cubic close-packed</td>
<td>4:6:4 AB&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;</td>
<td>1/8 tet. (A)</td>
<td>FeAl&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;, ZnAl&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;, MgAl&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;</td>
</tr>
<tr>
<td>Spinel (inverse)</td>
<td>Cubic close-packed</td>
<td>4:6:4 BiAB&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;</td>
<td>1/2 oct. (B)</td>
<td>FeMgFeO&lt;sub&gt;4&lt;/sub&gt;, MgTiMgO&lt;sub&gt;4&lt;/sub&gt;</td>
</tr>
<tr>
<td>Olivine</td>
<td>Hexagonal close-packed</td>
<td>6:4:4 AB&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;</td>
<td>1/2 oct. (A)</td>
<td>Mg&lt;sub&gt;2&lt;/sub&gt;SiO&lt;sub&gt;4&lt;/sub&gt;, Fe&lt;sub&gt;2&lt;/sub&gt;SiO&lt;sub&gt;4&lt;/sub&gt;</td>
</tr>
</tbody>
</table>

Binary Ionic Compounds (FCC-based)

- Three-dimensional arrangements of interstitial sites in FCC

  # of octahedral sites
  → one at the cube center, and one halfway along each edge
  → \(1 + \frac{1}{4} \times 12 = 4\)
  → the ratio of octahedral sites to atoms = 1:1
    (\(\because\) fcc unit cell contains 4 atoms)

  # of tetrahedral sites
  → one inside each corner, coordinated by the corner atom and the three closest face atoms
  → 8 of these sites
  → the ratio of tetrahedral sites to atoms = 2:1

---

Fig. 1.8 (a) Octahedral sites (O) in FCC. The body-centered site and one edge site are outlined. (b) Tetrahedral sites (T) in FCC. There is one within each corner, and together they form a simple cubic array.
• Rocksalt structure

→ FCC anion lattice in which all octahedral sites are filled with cations

→ $r_c/r_a = 0.414 \sim 0.732$

→ Coordination # of MX = 6:6

→ NaCl, KCl, LiF, MgO, …
Fluorite & antifluorite structures

Antifluorite
- FCC anion lattice in which all tetrahedral sites are filled with cations
- Coordination # of $M_2X = 4:8$
- $Li_2O$, $Na_2O$, $K_2O$

Fluorite
- FCC cation lattice in which all tetrahedral sites are filled with anions
- Coordination # of $MX_2 = 8:4$
  - [CN = 8 (simple cubic arrangement of anions) for $M \cdot r_c/r_a \rightarrow 1$]
- $CaF_2$, $ZrO_2$, $UO_2$, $CeO_2$
- Rutile structure (mineral name of TiO$_2$)

- HCP anion lattice in which one-half of octahedral sites are filled with cations (\(\therefore\) MX$_2$ stoichiometry)

- Fig. 1.25; by completely filling alternating diagonal rows, any horizontal row then obviously has one-half of octahedral sites filled. dotted rectangle = one side of the unit cell (\(\therefore\) tetragonal unit cell)

- consisting of TiO$_6$ octahedra that share edges and corners in such a way that each oxygen is shared by three octahedra \(\therefore\) Coordination # of MX$_2$ = 6:3

- TiO$_2$, SnO$_2$
• If the solute atoms are small, they may dissolve interstitially in the host crystal.

The ease with which interstitial solid solutions form depends on the size of the interstitial sites in the host lattice relative to that of the solute ions. For example, in a close-packed structures such as rocksalt, the only available interstitial sites are small tetrahedral sites, and the interstitial solid solubility is not very likely.

In contrast, in ThO₂ with its fluorite structure and TiO₂ where the interstitial sites are quite large (i.e., large octahedral sites), interstitial solid solutions form more easily. For example, it has been established that when YF₃ is dissolved in CaF₂, the appropriate incorporation reaction is

\[
YF_3 \overset{CaF_2}{\longrightarrow} Y^{\bullet}_{Ca} + 2F^{X}_F + F_i'
\]

In other words, to maintain charge neutrality, the F ion reside on interstitial sites (see Fig. 8.3b).
Another example involves the dissolution of ZrO$_2$ (fluorite structure) in Y$_2$O$_3$ (cubic bixbyite, the derivative of the fluorite structure, one out of every four oxygen ions is missing) where it has been established that the appropriate defect reaction is

$$2ZrO_2 \xrightarrow{Y_2O_3} 2Zr^\bullet_Y + 3O^X_O + O''_i$$

H.W. Worked Example 8.1

→ After this brief introduction to solid solutions, it is instructive to consider the type of phase diagrams expected for each of the three possible outcomes outlined before.