Chapter 12: Structures & Properties of Ceramics

• **Structures of ceramic materials:**
  How do they differ from those of metals?

• **Point defects:**
  How are they different from those in metals?

• **Impurities:**
  How are they accommodated in the lattice and how do they affect properties?

• **Mechanical Properties:**
  What special provisions/tests are made for ceramic materials?
Ceramic Bonding

- Bonding:
  - Mostly ionic, some covalent.
  - % ionic character increases with difference in electronegativity.

- Large vs small ionic bond character:

<table>
<thead>
<tr>
<th>Period</th>
<th>IA</th>
<th>IIA</th>
<th>IIIA</th>
<th>IVA</th>
<th>VA</th>
<th>VIA</th>
<th>VIIA</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>H 2.1</td>
<td>Li 1.0</td>
<td>Be 1.5</td>
<td>Mg 1.2</td>
<td>Na 0.9</td>
<td>K 0.8</td>
<td>Ca 1.0</td>
<td>Sc 1.3</td>
<td>Ti 1.5</td>
</tr>
<tr>
<td></td>
<td>Sr 1.0</td>
<td>Y 1.2</td>
<td>Zr 1.4</td>
<td>Nb 1.6</td>
<td>Mo 1.8</td>
<td>Tc 1.9</td>
<td>Ru 2.2</td>
<td>Rh 2.2</td>
</tr>
<tr>
<td></td>
<td>Cs 0.7</td>
<td>Ba 0.9</td>
<td>La–Lu 1.1–1.2</td>
<td>Hf 1.3</td>
<td>Ta 1.5</td>
<td>W 1.7</td>
<td>Re 1.9</td>
<td>Os 2.2</td>
</tr>
<tr>
<td></td>
<td>Fr 0.7</td>
<td>Ra 0.9</td>
<td>Ac–No 1.1–1.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Adapted from Fig. 2.7, Callister 7e.
Ionic Crystals

Table 12.1  For Several Ceramic Materials, Percent Ionic Character of the Interatomic Bonds

<table>
<thead>
<tr>
<th>Material</th>
<th>Percent Ionic Character</th>
<th>Cation Radius (nm)</th>
<th>Anion Radius (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaF₂</td>
<td>89</td>
<td>0.100</td>
<td>0.133</td>
</tr>
<tr>
<td>MgO</td>
<td>73</td>
<td>0.072</td>
<td>0.14</td>
</tr>
<tr>
<td>NaCl</td>
<td>67</td>
<td>0.102</td>
<td>0.182</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>63</td>
<td>0.053</td>
<td>0.140</td>
</tr>
<tr>
<td>SiO₂</td>
<td>51</td>
<td>0.040</td>
<td>0.140</td>
</tr>
<tr>
<td>Si₃N₄</td>
<td>30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnS</td>
<td>18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiC</td>
<td>12</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: larger anion radius

Most ionic crystals can be considered as close-packed structure of anions with cations in the interstitial sites.

Cations: metallic ions, positively charged
Anions: nonmetallic ions, negatively charged
Ceramic Crystal Structures

Oxide structures

– oxygen anions much larger than metal cations
– close packed oxygen in a lattice (usually FCC)
– cations in the holes of the oxygen lattice
Site Selection

Which sites will cations occupy?

1. Size of sites
   - does the cation fit in the site

2. Stoichiometry
   - if all of one type of site is full, the remainder have to go into other types of sites.

3. Bond Hybridization
Ionic Bonding & Structure

1. Size - Stable structures:
   --maximize the # of nearest oppositely charged neighbors.

   ![Diagram showing stable and unstable configurations with ions and charge neutrality](Adapted from Fig. 12.1, Callister 7e.)

• Charge Neutrality:
   --Net charge in the structure should be zero.

   \[ \text{CaF}_2: \quad \text{Ca}^{2+} \quad + \quad F^- \quad \text{anions} \]

   --General form: \[ A_m X_p \]

   \( m, p \) determined by charge neutrality
Coordination # and Ionic Radii

- Coordination # increases with $\frac{r_{\text{cation}}}{r_{\text{anion}}}$

**Issue:** How many anions can you arrange around a cation?

<table>
<thead>
<tr>
<th>$\frac{r_{\text{cation}}}{r_{\text{anion}}}$</th>
<th>Coord #</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 0.155</td>
<td>2</td>
<td>linear</td>
</tr>
<tr>
<td>0.155 - 0.225</td>
<td>3</td>
<td>triangular</td>
</tr>
<tr>
<td>0.225 - 0.414</td>
<td>4</td>
<td>$T_D$</td>
</tr>
<tr>
<td>0.414 - 0.732</td>
<td>6</td>
<td>$O_H$</td>
</tr>
<tr>
<td>0.732 - 1.0</td>
<td>8</td>
<td>cubic</td>
</tr>
</tbody>
</table>

Adapted from Table 12.2, *Callister 7e.*

Adapted from Fig. 12.2, *Callister 7e.*

Adapted from Fig. 12.3, *Callister 7e.*

Adapted from Fig. 12.4, *Callister 7e.*
**Cation-anion stable configuration**

![Diagram showing stable and unstable configurations](image)

**Figure 12.1** Stable and unstable anion–cation coordination configurations. Open circles represent anions; colored circles denote cations.

**Example:** 3-coordinate

When \( \cos \alpha = \frac{r_A}{r_A + r_C} \)

Rewrite as

\[
\frac{r_C}{r_A} = \frac{1}{\cos \alpha} - 1
\]

With \( \alpha = 30^\circ \)

\[
\frac{r_C}{r_A} = 0.155
\]
Cation Site Size

- Determine minimum $r_{\text{cation}}/r_{\text{anion}}$ for O$_H$ site (C.N. = 6)

\[ 2r_{\text{anion}} + 2r_{\text{cation}} = \sqrt{2}a \]

\[ a = 2r_{\text{anion}} \]

\[ 2r_{\text{anion}} + 2r_{\text{cation}} = 2\sqrt{2}r_{\text{anion}} \]

\[ r_{\text{anion}} + r_{\text{cation}} = \sqrt{2}r_{\text{anion}} \quad r_{\text{cation}} = (\sqrt{2} - 1)r_{\text{anion}} \]

\[ \frac{r_{\text{cation}}}{r_{\text{anion}}} = 0.414 \]
Site Selection II

2. Stoichiometry
   – If all of one type of site is full, the remainder have to go into other types of sites.

Ex: FCC unit cell has 4 $O_H$ and 8 $T_D$ sites.

   If for a specific ceramic each unit cell has 6 cations and the cations prefer $O_H$ sites
   4 in $O_H$
   2 in $T_D$
Intersttial sites in FCC

Octahedral ($O_h$) sites

1 at the center

Net 4 $O_h$ sites/unit cell

12 middle of the edge sites (each shared by 4 unit cells)

Tetrahedral ($T_d$) sites

Net 8 $T_d$ sites/unit cell
3. Bond Hybridization – significant covalent bonding
   – the hybrid orbitals can have impact if significant covalent bond character present
   – For example in SiC
     • $X_{\text{Si}} = 1.8$ and $X_{\text{C}} = 2.5$

   \[
   \% \text{ ionic character} = 100 \left\{ 1 - \exp\left[ -0.25 \left( X_{\text{Si}} - X_{\text{C}} \right)^2 \right] \right\} = 11.5\%
   \]

   • ca. 89% covalent bonding
   • both Si and C prefer $sp^3$ hybridization
   • Therefore in SiC get $T_D$ sites
Example: Predicting Structure of FeO

On the basis of ionic radii, what crystal structure would you predict for FeO?

Cation | Ionic radius (nm) |
-------|------------------|
Al^{3+} | 0.053 |
Fe^{2+} | 0.077 |
Fe^{3+} | 0.069 |
Ca^{2+} | 0.100 |

Anion |
-------|
O^{2-} | 0.140 |
Cl^{-} | 0.181 |
F^{-} | 0.133 |

Data from Table 12.3, Callister 7e.

Answer:

\[
\frac{r_{\text{cation}}}{r_{\text{anion}}} = \frac{0.077}{0.140} = 0.550
\]

based on this ratio,
--coord # = 6
--structure = NaCl
Rock Salt Structure

Same concepts can be applied to ionic solids in general. Example: NaCl (rock salt) structure

\[ r_{Na} = 0.102 \text{ nm} \]
\[ r_{Cl} = 0.181 \text{ nm} \]
\[ r_{Na}/r_{Cl} = 0.564 \]

∴ cations prefer \( O_H \) sites

Adapted from Fig. 12.2, Callister 7e.
MgO and FeO

MgO and FeO also have the NaCl structure

So each oxygen has 6 neighboring Mg$^{2+}$

Adapted from Fig. 12.2, Callister 7e.
AX–Type Crystal Structures include NaCl, CsCl, and zinc blende

Cesium Chloride structure:

\[
\frac{r_{\text{Cs}^+}}{r_{\text{Cl}^-}} = \frac{0.170}{0.181} = 0.939
\]

\[\therefore\] cubic sites preferred

So each Cs\(^+\) has 8 neighboring Cl\(^-\)

Adapted from Fig. 12.3, Callister 7e.
AX Crystal Structures

Zinc Blende structure

\[ \frac{r_{\text{Zn}^{2+}}}{r_{\text{O}^{2-}}} = \frac{0.074}{0.140} = 0.529 \Rightarrow O_H?? \]

- Size arguments predict Zn\(^{2+}\) in \(O_H\) sites,
- In observed structure Zn\(^{2+}\) in \(T_D\) sites
- Why is Zn\(^{2+}\) in \(T_D\) sites?
  - bonding hybridization of zinc favors \(T_D\) sites

So each Zn\(^{2+}\) has 4 neighboring O\(^{2-}\)

Ex: ZnO, ZnS, SiC

Adapted from Fig. 12.4, *Callister 7e.*
AX₂ Crystal Structures

Fluorite structure

- Calcium Fluorite (CaF₂)
- Cations in cubic sites
- UO₂, ThO₂, ZrO₂, CeO₂
- Antifluorite structure – cations and anions reversed

Adapted from Fig. 12.5, Callister 7e.
ABX₃ Crystal Structures

- Perovskite

Ex: complex oxide

BaTiO₃

Adapted from Fig. 12.6, Callister 7e.
Mechanical Properties

We know that ceramics are more brittle than metals. Why?

- Consider method of deformation
  - slippage along slip planes
    - in ionic solids this slippage is very difficult
    - too much energy needed to move one anion past another anion
Ceramic Density Computation

\[ \rho = \frac{n'(\Sigma A_C + \Sigma A_A)}{V_C N_A} \]

- \( n' \) = number of cations in unit cell
- \( A_C \) = atomic weight of cation
- \( n_A \) = number of anions in unit cell
- \( A_A \) = atomic weight of anion
- \( V_C \) = volume of unit cell
- \( N_A \) = Avogadro’s number
Theoretical Density Calculation of NaCl

\[ \rho = \frac{n'(\Sigma A_C + \Sigma A_A)}{V_C N_A} \]

\[ A_{Na} = 22.99 \text{ g/mol} \]
\[ A_{Cl} = 35.45 \text{ g/mol} \]

\[ a = 2(r_{Na^+} + r_{Cl^-}) = 2(0.102 + 0.181) \text{ nm} \]

Thus, \( V_C = a^3 = (2r_{Na^+} + 2r_{Cl^-})^3 \)

And \( n' \) is 4 pair of Na and Cl in one unit cell finally,

\[ \rho = \frac{n'(A_{Na} + A_{Cl})}{(2r_{Na^+} + 2r_{Cl^-})^3 N_A} = 2.14 \text{ g/cm}^3 \]
Silicate Ceramics

Most common elements on earth are Si & O

- SiO$_2$ (silica) structures are quartz, crystobalite, & tridymite
- The strong Si-O bond leads to a strong, high melting material (1710$^\circ$C)
Amorphous Silica

- Silica gels - amorphous SiO$_2$
  - Si$^{4+}$ and O$^{2-}$ not in well-ordered lattice
  - Charge balanced by H$^+$ (to form OH$^-$) at “dangling” bonds
    - very high surface area > 200 m$^2$/g
  - SiO$_2$ is quite stable, therefore unreactive
    - makes good catalyst support

Adapted from Fig. 12.11, Callister
Silica Glass

• Dense form of amorphous silica
  – Charge imbalance corrected with “counter cations” such as Na⁺
  – Borosilicate glass is the pyrex glass used in labs
    • better temperature stability & less brittle than sodium glass
Silicates

– Combine $\text{SiO}_4^{4-}$ tetrahedra by having them share corners, edges, or faces

$\text{Mg}_2\text{SiO}_4 \quad \text{Ca}_2\text{MgSi}_2\text{O}_7$

– Cations such as $\text{Ca}^{2+}$, $\text{Mg}^{2+}$, & $\text{Al}^{3+}$ act to neutralize & provide ionic bonding

Adapted from Fig. 12.12, *Callister 7e.*
Layered Silicates

- Layered silicates (clay silicates)
  - $\text{SiO}_4$ tetrahedra connected together to form 2-D plane

- $(\text{Si}_2\text{O}_5)^{2-}$
- So need cations to balance charge

Adapted from Fig. 12.13, *Callister 7e.*
Layered Silicates

- Kaolinite clay alternates \((\text{Si}_2\text{O}_5)^{2-}\) layer with \(\text{Al}_2(\text{OH})_4^{2+}\) layer

Note: these sheets loosely bound by van der Waal’s forces

Adapted from Fig. 12.14, *Callister 7e.*
Layered Silicates

• Can change the counterions
  – this changes layer spacing
  – the layers also allow absorption of water

• Micas $\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$
  – smooth surface for AFM sample holder

• Bentonite
  – used to seal wells
  – packaged dry
  – swells 2-3 fold in $\text{H}_2\text{O}$
  – pump in to seal up well so no polluted ground water seeps in to contaminate the water supply.
Carbon Forms

- Carbon black – amorphous – surface area ca. 1000 m$^2$/g
- Diamond
  - tetrahedral carbon
    - hard – no good slip planes
    - brittle – can cut it
  - large diamonds – jewelry
  - small diamonds
    - often man made - used for cutting tools and polishing
  - diamond films
    - hard surface coat – tools, medical devices, etc.
Carbon Forms - Graphite

- layer structure – aromatic layers
  
  - weak van der Waal’s forces between layers
  - planes slide easily, good lubricant

Adapted from Fig. 12.17, Callister 7e.
Carbon Forms - Graphite
Carbon Forms –
Fullerenes and Nanotubes

• Fullerenes or carbon nanotubes
  – wrap the graphite sheet by curving into ball or tube
  – Buckminster fullerenes
    • Like a soccer ball $C_{60}$ - also $C_{70}$ + others

Adapted from Figs. 12.18 & 12.19, Callister 7e.
Diamond-like Carbon Film

- Ultralow friction surface
Defects in Ceramic Structures

- **Frenkel Defect**
  --a cation is out of place.

- **Shottky Defect**
  --a paired set of cation and anion vacancies.

- Equilibrium concentration of defects $\sim e^{-Q_D / kT}$

Adapted from Fig. 12.21, *Callister 7e*. (Fig. 12.21 is from W.G. Moffatt, G.W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. 1, *Structure*, John Wiley and Sons, Inc., p. 78.)
Impurities

- Impurities must also satisfy charge balance = Electroneutrality
- Ex: NaCl  \( \text{Na}^+ \bullet \text{Cl}^- \)

**Substitutional cation impurity**

- Initial geometry
- \( \text{Ca}^{2+} \text{ impurity} \)
- Resulting geometry

**Substitutional anion impurity**

- Initial geometry
- \( \text{O}^{2-} \text{ impurity} \)
- Resulting geometry
For the MgO/Al₂O₃ phase diagram, what are the:

a) Composition of the MgO (ss) phase for a 40 wt% Al₂O₃ alloy at 1800°C?

b) Chemical formula of the interceramic compound?

c) Composition of the eutectic alloy with the lowest MgO composition?

d) Primary phase for a 30 wt% Al₂O₃ alloy cooled from the liquid phase to room temperature?

e) Solubility of Al₂O₃ in MgO at 1900°C?
a) Composition of the MgO(ss) phase:
   MgO: 92-93 wt% , Al2O3: 7-8 wt%

b) Chemical formula of the interceramic compound:
   MgAl2O4

c) Composition of the eutectic alloy with the lowest MgO composition:
   MgO: 6-7 wt% , Al2O3: 93-94 wt%

d) Primary phase for a 30 wt% Al2O3 alloy cooled from the liquid phase to room temperature:
   MgO(ss)

e) Solubility of Al2O3 in MgO at 1900 °C:
   12-13 wt%
Measuring Elastic Modulus

- Room $T$ behavior is usually elastic, with brittle failure.
- 3-Point Bend Testing often used.
  -- tensile tests are difficult for brittle materials ($\varepsilon<0.1\%$).

\[ E = \frac{F}{\delta} \left( \frac{L^3}{4bd^3} \right) \text{ or } \frac{F}{\delta} \left( \frac{L^3}{12\pi R^4} \right) \]

\[ \text{rect. cross section} \]
\[ \text{circ. cross section} \]

---

Adapted from Fig. 12.32, *Callister 7e.*
Measuring Strength

• 3-point bend test to measure room $T$ strength.

\[ \sigma_{fs} = \frac{1.5 F_f L}{bd^2} \text{ rect.} = \frac{F_f L}{\pi R^3} \]

• Flexural strength:

<table>
<thead>
<tr>
<th>Material</th>
<th>$\sigma_{fs}$ (MPa)</th>
<th>$E$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si nitride</td>
<td>250-1000</td>
<td>304</td>
</tr>
<tr>
<td>Si carbide</td>
<td>100-820</td>
<td>345</td>
</tr>
<tr>
<td>Al oxide</td>
<td>275-700</td>
<td>393</td>
</tr>
<tr>
<td>glass (soda)</td>
<td>69</td>
<td>69</td>
</tr>
</tbody>
</table>

Data from Table 12.5, *Callister 7e.*
Measuring Elevated $T$ Response

• Elevated Temperature Tensile Test ($T > 0.4 \ T_m$).

\begin{figure}
\centering
\includegraphics[width=\textwidth]{creep_test_diagram.png}
\caption{Creep test diagram showing the steady-state creep rate $\dot{\varepsilon}_{ss}$.}
\end{figure}
Summary

• Ceramic materials have covalent & ionic bonding.
• Structures are based on:
  -- charge neutrality
  -- maximizing # of nearest oppositely charged neighbors.
• Structures may be predicted based on:
  -- ratio of the cation and anion radii.
• Defects
  -- must preserve charge neutrality
  -- have a concentration that varies exponentially w/ \( T \).
• Room \( T \) mechanical response is elastic, but fracture is brittle, with negligible deformation.
• Elevated \( T \) creep properties are generally superior to those of metals (and polymers).