Chapter 12: Structures & Properties of Ceramics

ISSUES TO ADDRESS...

• Bonding and structure of ceramic materials as compared with metals
Atomic Bonding in Ceramics

- Bonding:
  -- Can be ionic and/or covalent in character.
  -- % ionic character increases with difference in electronegativity of atoms.

- Degree of ionic character may be large or small (i.e., mostly covalent):

<table>
<thead>
<tr>
<th>IA</th>
<th>IIA</th>
<th>IIIA</th>
<th>IVA</th>
<th>VA</th>
<th>VIA</th>
<th>VIIA</th>
<th>He</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>2.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li</td>
<td>1.0</td>
<td>Be</td>
<td>1.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>0.9</td>
<td>Mg</td>
<td>1.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>0.8</td>
<td>Ca</td>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rb</td>
<td>0.8</td>
<td>Sr</td>
<td>1.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cs</td>
<td>0.7</td>
<td>Ba</td>
<td>0.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fr</td>
<td>0.7</td>
<td>Ra</td>
<td>0.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La</td>
<td>1.1</td>
<td>Lu</td>
<td>1.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hf</td>
<td>1.3</td>
<td>Ta</td>
<td>1.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>W</td>
<td>1.7</td>
<td>Re</td>
<td>1.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Os</td>
<td>2.2</td>
<td>Ir</td>
<td>2.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt</td>
<td>2.2</td>
<td>Au</td>
<td>2.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>1.9</td>
<td>Cd</td>
<td>1.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>In</td>
<td>1.7</td>
<td>Sn</td>
<td>1.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sb</td>
<td>1.9</td>
<td>Te</td>
<td>2.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>2.5</td>
<td>Xe</td>
<td>2.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>3.0</td>
<td>O</td>
<td>3.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>4.0</td>
<td>Ne</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>2.0</td>
<td>C</td>
<td>2.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>1.5</td>
<td>Si</td>
<td>1.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>2.1</td>
<td>S</td>
<td>2.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>3.0</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Br</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Adapted from Fig. 2.7, *Callister & Rethwisch 8e*. (Fig. 2.7 is adapted from Linus Pauling, *The Nature of the Chemical Bond*, 3rd edition, Copyright 1939 and 1940, 3rd edition. Copyright 1960 by Cornell University.)
Ceramic Crystal Structures

General considerations of structures for many (not all!) ceramics with ionic bonding

- Anions (e.g., O^{2-}, F^-, Cl^-) usually (but NOT always) larger than metal cations
  - Close packed anions in a lattice (usually FCC packing)
  - Cations fit into interstitial sites among anion
Factors that Determine Crystal Structure

1. Maximize the # of oppositely charged ion neighbors (or CN)
   - CN depends on **relative sizes of ions:**
     - unstable
     - stable
     - stable

2. **Maintenance of charge neutrality:**
   -- Net charge in a ceramics should be zero.
   -- Reflected in chemical formula:
   \[ \text{Am}^m \times \text{X}^p \]

Adapted from Fig. 12.1, Callister & Rethwisch 8e.
### Coordination # and Ionic Radii Ratio

To form a stable structure, how many anions would surround around a cation?

<table>
<thead>
<tr>
<th>( \frac{r_{\text{cation}}}{r_{\text{anion}}} )</th>
<th>CN</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>tetrahedral</td>
</tr>
<tr>
<td>0.414 - 0.732</td>
<td>6</td>
<td>octahedral</td>
</tr>
<tr>
<td>0.732 - 1.0</td>
<td>8</td>
<td>cubic</td>
</tr>
<tr>
<td>&gt; 1.0</td>
<td>12</td>
<td></td>
</tr>
</tbody>
</table>

- **ZnS**: (zinc blende)
- **NaCl**: (sodium chloride)
- **CsCl**: (cesium chloride)

Adapted from Table 12.2, Callister & Rethwisch 8e.

Adapted from Fig. 12.2, Callister & Rethwisch 8e.

Adapted from Fig. 12.3, Callister & Rethwisch 8e.

Adapted from Fig. 12.4, Callister & Rethwisch 8e.
Extra: Determination of Critical Cation to Anion Radius Ratio (Will NOT be examined)

Example for determining critical $r_{\text{cation}}/r_{\text{anion}}$ for an octahedral site with CN = 6

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

$$a = 2r_{\text{anion}}$$

$$2r_{\text{anion}} + 2r_{\text{cation}} = 2\sqrt{2}r_{\text{anior}}$$

$$r_{\text{anion}} + r_{\text{cation}} = \sqrt{2}r_{\text{anion}}$$

$$r_{\text{cation}} = (\sqrt{2} - 1)r_{\text{anior}}$$

$$\frac{r_{\text{cation}}}{r_{\text{anion}}} = \sqrt{2} - 1 = 0.414$$
Example Problem: Predicting the Crystal Structure of FeO

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

<table>
<thead>
<tr>
<th>Cation</th>
<th>Ionic radius (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$^{3+}$</td>
<td>0.053</td>
</tr>
<tr>
<td>Fe$^{2+}$</td>
<td>0.077</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>0.069</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>0.100</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Anion</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>O$^{2-}$</td>
<td>0.140</td>
</tr>
<tr>
<td>Cl$^{-}$</td>
<td>0.181</td>
</tr>
<tr>
<td>F$^{-}$</td>
<td>0.133</td>
</tr>
</tbody>
</table>

• Answer:

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

Based on this ratio,
-- coord # = 6 because \(0.414 < 0.550 < 0.732\)
-- crystal structure is NaCl (rocksalt) type

Data from Table 12.3, Callister & Rethwisch 8e.
Rock Salt (NaCl type) Structure

For NaCl (rock salt) structure

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

\[ \therefore \text{Since } 0.414 < 0.565 < 0.732 \]
\[ \text{octahedral (CN=6) sites preferred for } Na^+ \]

Q:
1) Does this CN number make sense based on the unit cell structure given?
2) Within one unit cell what are the averaged numbers of Na and Cl atoms?
   4 Na, 4 Cl
3) What is the chemical formula?
   NaCl

Adapted from Fig. 12.2, Callister & Rethwisch 8e.
MgO also has the NaCl structure

Adapted from Fig. 12.2, Callister & Rethwisch 8e.

- O\(^2-\) \(r_O = 0.140 \text{ nm}\)
- Mg\(^{2+}\) \(r_{Mg} = 0.072 \text{ nm}\)

\[ r_{Mg}/r_O = 0.514 \]

\[ \therefore \text{cations prefer octahedral sites} \]

\[ \therefore \text{Since } 0.414 < 0.514 < 0.732 \]
octahedral (CN=6) sites preferred

So each Mg\(^{2+}\) (or Fe\(^{2+}\)) has 6 neighbor oxygen atoms

Q:
1) Does this CN number make sense based on unit cell structure given?
2) Within one unit cell, what are the averaged numbers of Mg and O atoms?
   4Mg, 4O
3) What is the chemical formula?
   MgO
**CsCl Type Crystal Structures**

Cesium Chloride structure:

![CsCl structure diagram](image)

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

\[
\therefore \text{Since } 0.732 < 0.939 < 1.0, \text{ cubic sites preferred}
\]

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

Q:
1) Does this CN number make sense based on unit cell structure given?
2) Within one unit cell, what are the averaged numbers of Cs and Cl atoms?
   1 Cs, 1 Cl
3) What is the chemical formula?
   CsCl
Fluorite (CaF$_2$ type) Crystal Structures

- Calcium Fluorite (CaF$_2$ type)
- Cations in cubic sites
- UO$_2$, ThO$_2$, ZrO$_2$, CeO$_2$

Q:
1) Does this CN number make sense based on unit cell structure given?
2) Within one unit cell, what are the averaged numbers of Ca and F atoms?
4 Ca, 8 F
3) What is the chemical formula?
   CaF$_2$
Perovskite Crystal Structures

- **Perovskite structure**

Ex: complex oxide

Adapted from Fig. 12.6, Callister & Rethwisch 8e.

Q:

1) What is the CN number based on unit cell structure given for Ti$^{4+}$?

CN (Ti$^{4+}$) = 6

2) Within one unit cell, what are the averaged numbers of Ba, Ti, and O atoms?

1 Ba (hint: 8x1/8 = 1), 1 Ti (hint: one in unit cell center), 3 O (hint: 6 * ½ = 3),

3) What is the chemical formula?

BaTiO$_3$
This module allows you to observe and rotate (using mouse click-and-drag) unit cells for the seven common ceramic crystal structures listed in the left bar window. For each of these crystal structures, atomic/ionic packing arrangements for several crystallographic planes may be generated, which planes may also be rotated. Spinel and inverse spinel crystal structures may be displayed in terms of close-packed planes of oxygen ions and...
Density Computations for Ceramics

Number of formula units/unit cell

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

- \( n' \) = Avogadro’s number
- \( \sum A_C \) = sum of atomic weights of all cations in formula unit
- \( \sum A_A \) = sum of atomic weights of all anions in formula unit
- \( V_C \) = Volume of unit cell
- \( N_A \) = Avogadro’s number
Silicate Ceramics

Most common elements on earth are Si & O

SiO$_2$ (silica) **polymorphic** forms are quartz, crystobalite, & tridymite

- The strong Si-O bonds lead to a high melting temperature ($1710^\circ$C) for this material
Silicates

Bonding of adjacent $\text{SiO}_4^{4-}$ accomplished by the sharing of common corners, edges, or faces

Basic building block

$\text{SiO}_4^{4-}$  $\text{Si}_2\text{O}_7^{6-}$  $\text{Si}_3\text{O}_9^{6-}$

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

Presence of cations such as $\text{Ca}^{2+}$, $\text{Mg}^{2+}$, & $\text{Al}^{3+}$
1. maintain charge neutrality, and
2. ionically bond $\text{SiO}_4^{4-}$ to one another
Glass Structure

• Basic Unit:
  \[ \text{SiO}_4^{4-} \text{ tetrahedron} \]
  
  \[ \text{Si}^{4+} \]
  \[ \text{O}^{2-} \]

Glass is noncrystalline (amorphous)
• Fused silica is SiO\(_2\) to which no impurities have been added
• Other common glasses contain impurity ions such as Na\(^+\), Ca\(^{2+}\), Al\(^{3+}\), and B\(^{3+}\)

• Quartz is crystalline SiO\(_2\):

Adapted from Fig. 12.11, Callister & Rethwisch 8e.
Layered Silicates

• Layered silicates (e.g., clays, mica, talc)
  – SiO$_4$ tetrahedra connected together to form 2-D plane

• A net negative charge is associated with each (Si$_2$O$_5$)$_2^-$ unit
  – Each hexagon has 6 Si corner, but each Si can be counted only as 1/3
    therefore, 6 x 1/3 = 2 Si
  – Two types of oxygen:
    • 6 O, one on each side of the hexagon, counted as ½, therefore 6 x ½ = 3
    • 6 O, each along the three-cell edge, counted as 1/3, therefore, 6x1/3 = 2
    • Totally: 3+2 = 5 per unit (hexagonal) cell

• Negative charge balanced by adjacent plane rich in positively charged cations

Adapted from Fig. 12.13, Callister & Rethwisch 8e.
Layered Silicates (cont.)

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

Note: Adjacent sheets of this type are loosely bound to one another by van der Waal’s forces.

Adapted from Fig. 12.14, *Callister & Rethwisch 8e.*
Polymorphic Forms of Carbon

(1) **Diamond**
- Tetrahedral bonding of carbon atoms
  - Hardest material known
  - Very high thermal conductivity
- Large single crystals – gem stones
- Small crystals – used to grind/cut other materials
- Diamond thin films
  - Hard surface coatings – used for cutting tools, medical devices, etc.

Adapted from Fig. 12.15, *Callister & Rethwisch 8e.*
Polymorphic Forms of Carbon (cont)

(2) **Graphite**

- Layered structure – parallel hexagonal arrays of carbon atoms

  - Weak secondary bonding (van der Waal’s forces) between layers → planes slide easily over one another – as good lubricant

Adapted from Fig. 12.17, *Callister & Rethwisch 8e.*
Polymorphic Forms of Carbon (cont)

Fullerenes and Nanotubes

Others

• **Fullerenes** – spherical cluster of 60 carbon atoms, $C_{60}$
  – Like a soccer ball

• **Carbon nanotubes** – sheet of graphite rolled into a tube
  – Ends capped with fullerene hemispheres

Adapted from Figs. 12.18 & 12.19, *Callister & Rethwisch 8e.*
Boron Nitride: Cubic vs. Hexagonal

Cubic BN (cBN)
All covalent bonding

Hexagonal BN (hBN):
secondary bonding between layers

CBN is extremely hard (second only to diamond) and useful for machining cast iron, while hBN is extremely soft and useful as a lubricant.