Chapter 12: Structures & Properties of Ceramics

ISSUES TO ADDRESS...

• 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></th>
<th>IA</th>
<th>IIA</th>
<th>IIIB</th>
<th>IIIV</th>
<th>IIIA</th>
<th>IVB</th>
<th>VIB</th>
<th>VIIB</th>
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<tr>
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<tr>
<td>Li</td>
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<td>Be</td>
<td>1.5</td>
<td></td>
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<tr>
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<td>Ba</td>
<td>0.9</td>
<td></td>
<td></td>
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<td></td>
<td></td>
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</tr>
<tr>
<td>Fr</td>
<td>0.7</td>
<td>Ra</td>
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<td></td>
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</tr>
</tbody>
</table>

\textbf{CaF}_2: large

\textbf{SiC}: small

Adapted from Fig. 2.7, Callister 7e. (Fig. 2.7 is adapted from Linus Pauling, \textit{The Nature of the Chemical Bond}, 3rd edition, Copyright 1939 and 1940, 3rd edition. Copyright 1960 by Cornell University.)
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.

   unstable

   stable

   stable

   Adapted from Fig. 12.1, Callister 7e.

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

     CaF$_2$: $\text{Ca}^{2+}$ cation + $\text{F}^-$ anions

     --General form: $A_mX_p$

     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>#</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 Site Size**

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

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

\[ a = 2r_{anion} \]

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

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

\[ \frac{r_{cation}}{r_{anion}} = 0.414 \]
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 $T_D$
Site Selection III

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 $X_{\text{C}} = 2.5$

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

• 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?

<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
--structure = NaCl

Data from Table 12.3, *Callister 7e.*
Rock Salt Structure

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

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

\[
\frac{r_{\text{Na}}}{r_{\text{Cl}}} = 0.564
\]

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

Adapted from Fig. 12.2, Callister 7e.
MgO and FeO also have the NaCl structure

\[ r_{\text{O}} = 0.140 \text{ nm} \]
\[ r_{\text{Mg}} = 0.072 \text{ nm} \]

\[ r_{\text{Mg}} / r_{\text{O}} = 0.514 \]

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

So each oxygen has 6 neighboring Mg\(^{2+}\)

Adapted from Fig. 12.2, Callister 7e.
AX Crystal Structures

AX–Type Crystal Structures include NaCl, CsCl, and zinc blende.

Cesium Chloride structure:

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

\[
\therefore \text{cubic sites preferred}
\]

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

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

Zinc Blende structure

Size arguments predict $\text{Zn}^{2+}$ in $O_H$ sites,

In observed structure $\text{Zn}^{2+}$ in $T_D$ sites

Why is $\text{Zn}^{2+}$ in $T_D$ sites?

- Bonding hybridization of zinc favors $T_D$ sites

So each $\text{Zn}^{2+}$ has 4 neighboring $O^{2-}$

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

Adapted from Fig. 12.4, Callister 7e.

Ex: ZnO, ZnS, SiC
AX$_2$ Crystal Structures

**Fluorite structure**

- Calcium Fluorite (CaF$_2$)
- Cations in cubic sites
- UO$_2$, ThO$_2$, ZrO$_2$, CeO$_2$
- Antifluorite structure – cations and anions reversed

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

- Perovskite

Ex: complex oxide

$\text{BaTiO}_3$

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

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

Number of formula units/unit cell

Volume of unit cell
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 (1710ºC)
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

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

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

- 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)
  - 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 $\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$
• 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 m²/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.

Adapted from Fig. 12.15, Callister 7e.
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 – 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.
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
  - \( \text{Ca}^{2+} \) impurity
  - Resulting geometry

- Substitutional anion impurity

  - Initial geometry
  - \( \text{O}^{2-} \) impurity
  - Resulting geometry
Ceramic Phase Diagrams

MgO-Al$_2$O$_3$ diagram:

Adapted from Fig. 12.25, Callister 7e.
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.

\[
E = \frac{F}{\delta} \quad \text{rect. cross section} = \frac{F}{\delta} \frac{L^3}{4bd^3}
\]

\[
E = \frac{F}{\delta} \quad \text{circ. cross section} = \frac{F}{\delta} \frac{L^3}{12 \pi R^4}
\]

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

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

![Diagram of 3-point bend test](image)

- Flexural strength:

$$\sigma_{fs} = \frac{1.5F_f L}{bd^2} \quad \text{rect.}$$

$$= \frac{F_f L}{\pi R^3}$$

- Typ. values:

<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>
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</table>

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

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

\[
\text{creep test} \quad \sigma \quad \varepsilon \quad \sigma \quad \text{time}
\]

slope = $\dot{\varepsilon}_{ss}$ = steady-state creep rate

Chapter 12 - 34
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).
ANNOUNCEMENTS

Reading:

Core Problems:

Self-help Problems: