Chapter 12: Structures & Properties of Ceramics

Review: 12.1-12.4
Read: 12.6-12.7 and 12.11
Study: 12.8-12.10

• 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?
Bonding in ceramics

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

• Large vs small ionic bond character:

Adapted from Fig. 2.7, *Callister 7e*. (*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.*)
 Ionic Bonding & Structure

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

   ![Diagram of ionic bonding and structure]

   unstable
   stable
   stable

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

   --General form: $A_mX_p$
   m, p determined by charge neutrality

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Adapted from Fig. 12.1, Callister 7e.
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>Coordination #</th>
<th>Coordination #</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>&lt; 0.155</td>
</tr>
<tr>
<td>3</td>
<td>0.155 - 0.225</td>
</tr>
<tr>
<td>4</td>
<td>0.225 - 0.414</td>
</tr>
<tr>
<td>6</td>
<td>0.414 - 0.732</td>
</tr>
<tr>
<td>8</td>
<td>0.732 - 1.0</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.
Rock Salt Structure

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

Adapted from Fig. 12.2, Callister 7e.

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

r_{\text{Na}}/r_{\text{Cl}} = 0.564

\therefore \text{ cations prefer } O_H \text{ sites}
 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.
ABX$_3$ Crystal Structures

- Perovskite

Ex: complex oxide

BaTiO$_3$

Adapted from Fig. 12.6, *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
  \[ \sim e^{-\frac{Q_D}{2kT}} \]

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
  - Ca\(^{2+}\) impurity
  - Resulting geometry
- Substitutional anion impurity
  - Initial geometry
  - O\(^{2-}\) impurity
  - Resulting geometry
Stress-strain behavior

• Flectural testing replaces tensile testing
• Reasons not to perform a standard tension test
  – difficult to prepare and test specimens having a required geometry
  – difficult to grip brittle materials without fracturing them
  – ceramics fail after only about 0.1% strain and samples are difficult to align without experiencing bending stress
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.

\[
E = \frac{F}{\delta} \quad \text{slope} = \frac{F}{\delta} \quad \text{linear-elastic behavior}
\]

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

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

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

• Flexural strength:

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

• 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>
</tbody>
</table>

Data from Table 12.5, *Callister 7e.*
Elastic behavior

• Typical stress-strain behavior to fracture for aluminum oxide and glass
Mechanisms of plastic deformation

- **Crystalline ceramics are brittle**
  - Covalent bonds are relatively strong
  - There are limited numbers of slip systems
  - Dislocation structures are complex

- **Noncrystalline ceramics**
  - Plastic deformation does not occur by dislocation motion for noncrystalline ceramics
  - Viscosity is a measure of resistance to deformation
# Hardness

**Table 13.6** Approximate Knoop Hardness (100 g load) for Seven Ceramic Materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Approximate Knoop Hardness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamond (carbon)</td>
<td>7000</td>
</tr>
<tr>
<td>Boron carbide (B₄C)</td>
<td>2800</td>
</tr>
<tr>
<td>Silicon carbide (SiC)</td>
<td>2500</td>
</tr>
<tr>
<td>Tungsten carbide (WC)</td>
<td>2100</td>
</tr>
<tr>
<td>Aluminum oxide (Al₂O₃)</td>
<td>2100</td>
</tr>
<tr>
<td>Quartz (SiO₂)</td>
<td>800</td>
</tr>
<tr>
<td>Glass</td>
<td>550</td>
</tr>
</tbody>
</table>
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 with $T$.
- Room $T$ mechanical response is elastic, but fracture is brittle, with negligible deformation.