Introduction to Engineering Materials
ENGR2000
Chapter 12: Structures and Properties of Ceramics
Dr. Coates
12.1 Introduction

- Ceramics
  - Compounds between metallic & non-metallic elements
  - Predominantly ionic bonds
  - Some have covalent bonds
  - Greek word *keramikos* which means ‘burnt stuff’
  - Traditional ceramics
    - china, porcelain, bricks, tiles, glasses, etc.
Learning Objectives

• Sketch/describe unit cells for the most common ceramic material

• Predict the crystal structure based on chemical formula and ionic radius

• Name and describe eight different ionic point defects that are found in ceramic material
Learning Objectives

• Explain why there is significant scatter in the fracture strength of identical ceramics

• Compute the flexural strength of a ceramic material based on three point loading tests

• On the basis of slip considerations explain why ceramic crystalline materials are normally brittle
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:

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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.)
12.2 Crystal Structures

- Crystals composed of electrically charged ions
- Cations
  - Positively charged
  - Metallic ions
- Anions
  - Negatively charged
  - Non-metallic ions
12.2 Crystal Structures

- Concepts influencing the crystal structure
  - Crystal must be electrically neutral
  - Cations & anions are of different sizes
  - Cations & anions may have different magnitudes of electrical charge
12.2 Crystal Structures

- Cations are usually smaller than anions

\[ \frac{r_C}{r_A} < 1 \]

- Each cation prefers to have as many nearest-neighbor anions as possible.
- Each anion prefers to have as many nearest-neighbor cations as possible.
Stable ceramic crystal structures

- Anions surrounding a cation are all in contact with that cation.

**Figure 12.1** Stable and unstable anion–cation coordination configurations. Open circles represent anions; colored circles denote cations.
Coordination number
– # of anion nearest neighbors for a cation

• The CN is related to

\[ r_c / r_A \]

• For a specific CN, there is a critical or minimum radius ratio for which this contact is established.
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<tr>
<th>Coordination Number</th>
<th>Cation-Anion Radius Ratio</th>
<th>Coordination Geometry</th>
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<td>2</td>
<td>&lt; 0.155</td>
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<td>3</td>
<td>0.155–0.225</td>
<td><img src="image" alt="Coordination 3 Geometry" /></td>
</tr>
<tr>
<td>4</td>
<td>0.225–0.414</td>
<td><img src="image" alt="Coordination 4 Geometry" /></td>
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</table>
6 0.414–0.732
8 0.732–1.0
<table>
<thead>
<tr>
<th>Cation</th>
<th>Ionic Radius (nm)</th>
<th>Anion</th>
<th>Ionic Radius (nm)</th>
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</thead>
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<tr>
<td>Al$^{3+}$</td>
<td>0.053</td>
<td>Br$^-$</td>
<td>0.196</td>
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<tr>
<td>Ba$^{2+}$</td>
<td>0.136</td>
<td>Cl$^-$</td>
<td>0.181</td>
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<td>F$^-$</td>
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<td>K$^+$</td>
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<td>Mg$^{2+}$</td>
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<td>Mn$^{2+}$</td>
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<td>Ni$^{2+}$</td>
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<td>Si$^{4+}$</td>
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<td>Ti$^{4+}$</td>
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Example 12.1

- Show that the minimum cation-to-anion radius ratio for the coordination number 3 is 0.155.
\( AP = r_A \)
\( AO = r_A + r_C \)
\[
\frac{AP}{AO} = \cos \alpha
\]

\[\Rightarrow \frac{r_A}{r_A + r_C} = \cos 30^0 = \frac{\sqrt{3}}{2}\]
\[\Rightarrow \frac{r_A / r_A}{r_A / r_A + r_C / r_A} = \frac{1}{1 + r_C / r_A} = 0.866\]
\[\Rightarrow \frac{r_C}{r_A} = \frac{1}{0.866} - 1 = 0.155\]
AX-Type Crystal Structures

- Equal number of cations & anions
- AX compounds
- A denotes the cation
- X denotes the anion
Rock salt (NaCl) structure

- Two interpenetrating FCC lattices – one composed of cations and the other of anions

\[
CN(Na^+) = CN(Cl^-) = 6 \\
0.414 \leq r_C / r_A \leq 0.732
\]

**Figure 12.2** A unit cell for the rock salt, or sodium chloride (NaCl), crystal structure.
Rock salt (NaCl) structure

- Common ceramic materials with this crystal structure
  - NaCl, MgO, MnS, LiF, FeO
Cesium Chloride Structure

- Note that this is not a BCC crystal structure (different kinds of ions)

\[ CN(Cs^+) = CN(Cl^-) = 8 \]
Zinc Blende (ZnS) Structure

- Common ceramic materials with this crystal structure
  - ZnS, ZnTe, SiC

\[ CN(A) = CN(X) = 4 \]
A_mX_p-Type Crystal Structures

• Consider the AX_2- type CaF_2 (flourite) structure
  \[ r_C / r_A = 0.8 \]
  \[ \Rightarrow CN = 8 \text{ (from table)} \]

• Predicts a structure similar to the CsCl
• There are \( \frac{1}{2} \) as many Ca ions as there are F ions.
Flourite (CaF$_2$) Crystal Structure

- Only $\frac{1}{2}$ the center cube positions are occupied by Ca ions

**Figure 12.5** A unit cell for the fluorite (CaF$_2$) crystal structure.
Why are CN#’s different for cations and anions here

<table>
<thead>
<tr>
<th>Structure Name</th>
<th>Structure Type</th>
<th>Anion Packing</th>
<th>Coordination Numbers</th>
<th>Examples</th>
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<tr>
<td>Rock salt (sodium chloride)</td>
<td>AX</td>
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<td>NaCl, MgO, FeO</td>
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<td>CsCl</td>
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<td>Zinc blende (sphalerite)</td>
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<td>4(A) 6(B)</td>
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Example Problem: Predicting the Crystal Structure of FeO

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

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<th>Ionic radius (nm)</th>
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<td>Fe(^{2+})</td>
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<td>Fe(^{3+})</td>
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<td>Ca(^{2+})</td>
<td>0.100</td>
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<td>O(^{2-})</td>
<td>0.140</td>
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<tr>
<td>Cl(^{-})</td>
<td>0.181</td>
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<tr>
<td>F(^{-})</td>
<td>0.133</td>
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</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

Data from Table 12.3, Callister & Rethwisch 8e.
Example

• On the basis of ionic radii, what crystal structure would you predict for CaF$_2$?
CaF$_2$ is an AX$_2$ - type compound.

$$\frac{r_C}{r_{Ca^{2+}}} = \frac{0.100 \text{ nm}}{0.133 \text{ nm}} = 0.752$$

From Table 12.4:

$CN(Ca^{2+}) = 8$

\# of Ca$^{2+} = \frac{1}{2}$ \# of F$^-$

$$\frac{CN(Ca^{2+})}{CN(F^-)} = \frac{\# \text{ of } F^-}{\# \text{ of } Ca^{2+}} = 2$$

$CN(F^-) = 4$
Ceramic Density Computations

Theoretical density from unit cell data:

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

where \( n' \) is the number of formula units within the unit cell

\( \sum A_C \) is the sum of atomic wts of all cations in the formula unit

\( \sum A_A \) is the sum of atomic wts of all anions in the formula unit

\( V_C \) is the unit cell volume and

\( N_A \) is the Avogadro's number.
Formula unit

• All the ions that are included in the chemical formula.
  – A formula unit of BaTiO$_3$ consists of one barium ion, one titanium ion and three oxygen ions.
Example 12.3

- On the basis of crystal structure, compute the theoretical density for NaCl. How does this compare with its measured density?
Figure 12.2 A unit cell for the rock salt, or sodium chloride (NaCl), crystal structure.

\[ n' = \frac{1}{8} \times 8 + \frac{1}{2} \times 6 \]

\[ n' = 1 \times 1 + \frac{1}{4} \times 12 \]

\[ n' = 4 \]

\[ \sum A_C = A_{Na} = 22.99 \text{ g/mol} \]

\[ \sum A_A = A_{Cl} = 35.45 \text{ g/mol} \]
\[ V_C = a^3 \]
\[ a = 2(r_{Na^+} + r_{Cl^-}) \]

From table 12.2:
\[ r_{Na^+} = 0.102 \text{ nm} \]
\[ r_{Cl^-} = 0.181 \text{ nm} \]

Theoretical density:
\[ \rho = \frac{n'(\sum A_C + \sum A_A)}{V_C N_A} = 2.14 \text{ g/cm}^3 \]

Measured density = 2.16 g/cm\(^3\)
12.3 Silicate Ceramics

- Silicates are materials composed primarily of Si and O, the two most abundant elements in the earth’s crust.
  - Soils, rocks, clay & sand
Silicate Ceramics

- Characterized by various arrangements of a $SiO_4^{4-}$ tetrahedron, the basic unit of all silicates

- Often not considered ionic because the Si-O bonds have significant covalent character

Adapted from Figs. 12.9-10, Callister & Rethwisch 8e
• Regardless of the character of the Si-O bond, there is a formal charge of -4 associated with every tetrahedron, why?

• Various silicates arise based on different ways in which the tetrahedron units can be combined into 1, 2, or 3 dimensional arrangements
Silica

- Chemically the simplest silicate, $\text{SiO}_2$ (silica)
- 3D network which occurs when the corner atoms of the tetrahedron are shared by adjacent tetrahedra
- **Polymorphic** forms are quartz, crystobalite, & tridymite
- The strong Si-O bonds lead to a high melting temperature (1710°C) for this material
- Not closely packed => relatively low densities
Simple Silicates

Bonding of adjacent $\text{SiO}_4^{4-}$ accomplished by the sharing with other tetrahedra

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

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

Presence of other 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

Adapted from Fig. 12.12, Callister & Rethwisch 8e.
Layered Silicates

- Layered silicates (e.g., clays, mica, talc)
  - A two-dimensional layered structure produced from the sharing of three oxygen ions in each tetrahedra
  - Repeating unit formula is $\text{Si}_2(\text{O}_5)^{2^-}$
  - Net negative charge is associated with unbonded oxygen atom
  - A second sheet having an excess of cations will bond to the unbonded oxygen atoms

Adapted from Fig. 12.13, *Callister & Rethwisch 8e.*
Silica Glasses

Glass is noncrystalline \textit{(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$^{3+}$

Adapted from Fig. 12.11, Callister & Rethwisch 8e.
12.4 Carbon

- Carbon exists in various polymorphic forms as well as in the amorphous form.
Polymorphic Forms of Carbon

Diamond

– tetrahedral bonding of carbon
  • 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.
Polymorphic Forms of Carbon (cont)

Graphite
- layered structure – parallel hexagonal arrays of carbon atoms

- weak van der Waal’s forces between layers
- planes slide easily over one another -- good lubricant
Polymorphic Forms of Carbon (cont)

Fullerenes and Nanotubes

- **Fullerenes** – spherical cluster of 60 carbon atoms, \( \text{C}_{60} \)
  - 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.
Carbon Nanotubes

• Tube diameters ~ 100 nm
• Each nanotube is a single molecule composed of millions of atoms
• Extremely strong & stiff as well as ductile
• Tensile strengths ~ 50 GPa to 200 GPa
• Elastic modulus ~ 1000 Gpa
• Low density
12.5 Imperfections in Ceramics
Atomic point defects

• Vacancies
  – Anion vacancy
  – Cation vacancy

• Interstitials
  – Anion interstitial
  – Cation interstitial
Point Defects in Ceramics (i)

• **Vacancies**
  -- vacancies exist in ceramics for both cations and anions

• **Interstitials**
  -- interstitials exist for cations
  -- interstitials are not normally observed for anions because anions are large relative to the interstitial sites

Adapted from Fig. 12.20, *Callister & Rethwisch 8e*. (Fig. 12.20 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.)
• **Frenkel Defect**
  -- a cation vacancy-cation interstitial pair.

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

• **Equilibrium concentration of defects**
  \[ \propto e^{-Q_D/kT} \]
Why are anion interstitials highly improbable?

• Anion is relatively larger
• Has to fit into a small interstitial position

Can defects in ceramics occur alone?

• No, they occur in pairs
• Electro neutrality must be maintained
Stoichiometry

• A state for ionic compounds wherein there is the exact ratio of cations to anions as predicted by the chemical formula.

• NaCl is stoichiometric if the ratio of Na+ ions to Cl- ions is exactly 1:1
The ratio of cations to anions is not altered by the formation of a Frenkel or Schottky defect. - Material is stoichiometric.
Non stoichiometric materials

- FeO – iron is present as Fe\(^{2+}\) or Fe\(^{3+}\)
Impurities in Ceramics

• Substitutional solid solution
  – Substitutional impurity will substitute for the host ion to which it is most similar in an electrical sense
Impurities in Ceramics

- Interstitial solid solution
  - impurity must be relatively small
12.7 Ceramic Phase Diagrams
The Al$_2$O$_3$ – Cr$_2$O$_3$ system

• Substitutional solid solution
  – Al$^{3+}$ substitutes for Cr$^{3+}$
  – Similarly charged ions
  – Similar ionic radii (0.053 nm and 0.062 nm)
  – Al$_2$O$_3$ and Cr$_2$O$_3$ have similar crystal structures
The equilibrium numbers of Frenkel or Schottky defects depend on temperature similar to the number of vacancies in metals (4.1)

For Frenkel defects, the number of cation vacancy/cation interstitial pairs,

$$N_{fr} = Ne^\left(\frac{Q_{fr}}{2kT}\right)$$

where $N$ is the total number of lattice sites, $Q_{fr}$ is the energy required for formation of each Frenkel defect.

For Shottky defects in an AX type compound

$$N_S = Ne^\left(\frac{Q_s}{2kT}\right)$$

where $Q_s$ is the Shottky defect energy of formation.
Isomorphous system

Figure 12.24 The aluminum oxide–chromium oxide phase diagram. (Adapted from E. N. Bunting, “Phase Equilibria in the System Cr$_2$O$_3$–Al$_2$O$_3$,” Bur. Standards J. Research, 6, 1931, p. 948.)
The MgO – Al\textsubscript{2}O\textsubscript{3} system

- Limited solubility
  - Differences in charge in Mg\textsuperscript{2+} and Al\textsuperscript{3+}
  - Differences in radii (0.072 nm and 0.053 nm)
Eutectic points

Intermediate phase

Mechanical Properties

**Figure 12.30** Typical stress–strain behavior to fracture for aluminum oxide and glass.

Brittle fracture - before any plastic deformation

Slope = elastic modulus
Brittle Fracture

• Ceramics are subject to static fatigue or delayed fracture below the $K_{IC}$ value: combination of moisture and applied stress causes ionic bonds to rupture

• Higher probability of flaws (fabrication technique, heat treatment) $\Rightarrow$ excessive scatter of tensile strength values
Elastic modulus of metals, ceramics & polymers

• Ceramics
  – high elastic modulus
  – diamond, graphite (covalent bonds)

• Metals
  – high elastic modulus

• Polymers
  – low elastic modulus
  – weak secondary bonds between chains
Plastic deformation in metals, ceramics & polymers

- Polymers
  - strain hardening due to chain alignment
- Metals
  - strain hardening
- Ceramics
  - almost no plastic deformation

Increasing tendency for plastic deformation
Resistance to environmental failure of metals, ceramics & polymers

- Ceramics
  - high resistance to environmental attack
- Metals
- Polymers
  - moisture effects

Increasing resistance
12.9 Stress-Strain Behavior
# Mechanical properties of metals & ceramics

<table>
<thead>
<tr>
<th>Metals</th>
<th>Ceramics</th>
</tr>
</thead>
<tbody>
<tr>
<td>• high elastic modulus</td>
<td>• higher elastic modulus</td>
</tr>
<tr>
<td>• significant plastic deformation</td>
<td>• no significant plastic deformation</td>
</tr>
<tr>
<td>• high fracture stress</td>
<td>• higher fracture stress</td>
</tr>
<tr>
<td>• stress-strain curves for tension &amp; compression are nearly identical</td>
<td>• stress-strain curves depend on the load (tension or compression)</td>
</tr>
<tr>
<td>Material</td>
<td>Flexural Strength</td>
</tr>
<tr>
<td>--------------------------------</td>
<td>-------------------</td>
</tr>
<tr>
<td></td>
<td>MPa</td>
</tr>
<tr>
<td>Silicon nitride ($\text{Si}_3\text{N}_4$)</td>
<td>250–1000</td>
</tr>
<tr>
<td>Zirconia ($\text{ZrO}_2$)</td>
<td>800–1500</td>
</tr>
<tr>
<td>Silicon carbide ($\text{SiC}$)</td>
<td>100–820</td>
</tr>
<tr>
<td>Aluminum oxide ($\text{Al}_2\text{O}_3$)</td>
<td>275–700</td>
</tr>
<tr>
<td>Glass-ceramic (Pyroceram)</td>
<td>247</td>
</tr>
<tr>
<td>Mullite ($3\text{Al}_2\text{O}_3•2\text{SiO}_2$)</td>
<td>185</td>
</tr>
<tr>
<td>Spinel ($\text{MgAl}_2\text{O}_4$)</td>
<td>110–245</td>
</tr>
<tr>
<td>Magnesium oxide ($\text{MgO}$)</td>
<td>105$^b$</td>
</tr>
<tr>
<td>Fused silica ($\text{SiO}_2$)</td>
<td>110</td>
</tr>
<tr>
<td>Soda-lime glass</td>
<td>69</td>
</tr>
</tbody>
</table>

$^a$ Partially stabilized with 3 mol% $\text{Y}_2\text{O}_3$.

$^b$ Sintered and containing approximately 5% porosity.
Mechanical Properties

Ceramic materials are more brittle than metals. Consider mechanism of deformation

- In crystalline, by dislocation motion
- In highly ionic solids, dislocation motion is difficult
  - few slip systems
  - resistance to motion of ions of like charge (e.g., anions) past one another
Flexural Tests – Measurement of Flexural Strength

- 3-point bend test to measure room flexural strength.

- Flexural strength:
  
  \[
  \sigma_{fs} = \frac{3F_fL}{2bd^2} \quad \text{(rect. cross section)}
  \]
  
  \[
  \sigma_{fs} = \frac{F_fL}{\pi R^3} \quad \text{(circ. cross section)}
  \]

- Typical 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-lime)</td>
<td>69</td>
<td>69</td>
</tr>
</tbody>
</table>

Data from Table 12.5, *Callister & Rethwisch 8e.*
12.11 Miscellaneous Mechanical Considerations

• Porosity
  – Initial material is in the form of a powder for some ceramic fabrication techniques
  – Residual pores or void spaces remain after the fabrication process
• Pores reduce cross sectional area that carries the load
• Act as stress raisers
• for some ceramic materials, elastic modulus and flexural strength may be determined by:

\[ E = E_0 \left( 1 - 1.9P + 0.9P^2 \right) \]

\[ P \text{ is the volume fraction porosity} \]
\[ E_0 \text{ is the elastic modulus of the nonporous material.} \]

\[ \sigma_{fs} = \sigma_0 e^{-nP} \]

\( n, \sigma_0 \) experimental constants
\( \sigma_{fs} \) flexural strength
Hardness

- Ceramics are the hardest known materials
  - utilized when an abrasive or grinding action is required

<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 (B$_4$C)</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 (Al$_2$O$_3$)</td>
<td>2100</td>
</tr>
<tr>
<td>Quartz (SiO$_2$)</td>
<td>800</td>
</tr>
<tr>
<td>Glass</td>
<td>550</td>
</tr>
</tbody>
</table>
SUMMARY

• Interatomic bonding in ceramics is ionic and/or covalent.

• Ceramic crystal structures are based on:
  -- maintaining charge neutrality
  -- cation-anion radii ratios.

• Imperfections
  -- Atomic point: vacancy, interstitial (cation), Frenkel, Schottky
  -- Impurities: substitutional, interstitial
  -- Maintenance of charge neutrality

• Room-temperature mechanical behavior – flexural tests
  -- linear-elastic; measurement of elastic modulus
  -- brittle fracture; measurement of flexural modulus
Recommended problems

12.2, 12.5, 12.12, 12.15, 12.20, 12.29, 12.41, 12.45, 12.48, 12.50