Objectives/outcomes: You will learn the following:
- Ceramic crystal structures.
- Diamond and graphite.
- Structure of AX compounds:
  - Structure of AX$_2$ compounds,
  - The Perovskite (BaTiO$_3$) structure.
- Silicate structures. The SiO$_4$ tetrahedron.
Ceramic articles


http://www.mse.ncsu.edu/zhu/  Department of Materials Sci. & Eng.
Introduction on Ceramics

- **Bounding:** ionic or covalent
- **Physical properties:**
  - electrical and heat insulation
  - Magnetic, piezoelectric (special ceramics)
- **Mechanical Properties:** Brittle
- **Chemical properties:** stable and high melting temperature.
- **Traditional Ceramics:** Basic components (Clay and Silica).
- **Engineering Ceramics:** Pure compounds (Al$_2$O$_3$, SiC, etc).
Ionic and Covalent Bonding in Simple Ceramics

- **Mixture of Ionic and Covalent Types.**
- **Depends on electronegativity difference.**

<table>
<thead>
<tr>
<th>Ceramic compound</th>
<th>Bonding atoms</th>
<th>Electronegativity difference</th>
<th>% ionic character</th>
<th>% covalent character</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zirconium dioxide, ZrO₂</td>
<td>Zr–O</td>
<td>2.3</td>
<td>73</td>
<td>27</td>
</tr>
<tr>
<td>Magnesium oxide, MgO</td>
<td>Mg–O</td>
<td>2.2</td>
<td>69</td>
<td>31</td>
</tr>
<tr>
<td>Aluminum oxide, Al₂O₃</td>
<td>Al–O</td>
<td>2.0</td>
<td>63</td>
<td>37</td>
</tr>
<tr>
<td>Silicon dioxide, SiO₂</td>
<td>Si–O</td>
<td>1.7</td>
<td>51</td>
<td>49</td>
</tr>
<tr>
<td>Silicon nitride, Si₃N₄</td>
<td>Si–N</td>
<td>1.3</td>
<td>34.5</td>
<td>65.5</td>
</tr>
<tr>
<td>Silicon carbide, SiC</td>
<td>Si–C</td>
<td>0.7</td>
<td>11</td>
<td>89</td>
</tr>
</tbody>
</table>

\[
\% \text{ ionic character} = \left[1 - e^{-\frac{(X_A - X_B)^2}{4}}\right] \times 100\% 
\]

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Simple Ionic Arrangements

• Packing of Ions depends upon
  ➢ Size:
  ➢ Charge: Neutrality

• Radius ratio \( = \frac{r_{\text{cation}}}{r_{\text{anion}}} \)

• Critical radius ratio for stability
  for coordination numbers 8, 6, 4 and 3 are >0.732, >0.414, >0.225 and > 0.155
**Critical radius ratio**

<table>
<thead>
<tr>
<th>Disposition of ions about central ion</th>
<th>CN</th>
<th>Range of cation radius ratio to anion radius</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corners of cube</td>
<td>8</td>
<td>$\geq 0.732$</td>
</tr>
<tr>
<td>Corners of octahedron</td>
<td>6</td>
<td>$\geq 0.414$</td>
</tr>
<tr>
<td>Corners of tetrahedron</td>
<td>4</td>
<td>$\geq 0.225$</td>
</tr>
<tr>
<td>Corners of triangle</td>
<td>3</td>
<td>$\geq 0.155$</td>
</tr>
</tbody>
</table>

*CN = Coordination number*
Cesium Chloride Crystal Structure

- CsCl is *ionically bonded* with radius ratio = 0.94 and CN = 8.
Sodium Chloride Crystal Structure

- Highly Ionically bonded with Na\(^+\) ions occupying interstitial sites between FCC and Cl\(^-\) ions.
- Radius ratio = 0.56, CN = 6.
Interstitial Sites in FCC Crystal Lattices

- **Octahedral interstitial sites**: Six nearest atoms or ions equidistant from central void.
- **Tetrahedral Interstitial Sites**: Four nearest atoms or ions equidistant from central void.
- There are **four** octahedral sites and **eight** tetrahedral sites per unit cell of FCC.
Calcium Fluorite (CaF$_2$) Crystal Structure

- Ca$^{2+}$ ions occupy the FCC lattice sites while the F$^-$ ions are located at eight tetrahedral sites.
Zinc Blende (ZnS) Crystal Structure

- One type (Zn or S) occupies lattice points and another occupies half (4) of interstitial sites of FCC unit cell.
- Tetrahedrally covalently bonded
- \( \text{CN} = 4 \)
Other Crystal Structures

- **Antifluorite**: Anions occupy lattice points and cations occupy eight tetrahedral sites of FCC. Examples: Li$_2$O, Na$_2$O
Corundum

- Oxygen ions in lattice points of HCP unit cell.
  - Two Al$^{3+}$ ions in octahedral sites for every three O$^-$ ions
    - Al$^{3+}$ occupy 2/3 of the octahedral sites
    - distortion of structure.
Spinel (MgAl$_2$O$_4$) or (AB$_2$O$_4$)

- Oxygen ions form FCC lattice and Mg and M1 ions occupy interstitial sites
Other Crystal Structures

• **Perovskite** \((\text{CaTiO}_3)\): \(\text{Ca}^{2+}\) and \(\text{O}^{2-}\) ions form FCC unit cell.
  - \(\text{Ca}^{2+}\) Ions occupy corners
  - \(\text{O}^{2-}\) Ions occupy face centers.
  - \(\text{Ti}^{4+}\) ions are at octahedral sites.
Carbon structures

- **Graphite**: Polymorphic form of compound.
- Layered structure with carbon atoms in hexagonal arrays.
- Good **lubricating** properties
- **Diamond**:
- Carbon Nanotubes
- C60 (buckyball)
Silicate Structures

- **Silicate** ($\text{SiO}_4^{4-}$) is building block of silicates.
- **Chain/ring structure:** Two corners of each $\text{SiO}_4^{4-}$ tetrahedron bonds with corners of other tetrahedron.
Sheet Structures of Silicates

- **Sheet structure:** Three corners of same planes of silicate tetrahedron bonded to the corners of three other silicate tetrahedra.
- If the bondings are weak, sheets slide over each other easily.
Silicate Networks

- **Silica:** All four corners of the SiO$_4^{4-}$ tetrahedra share oxygen atoms.
- **Basic structures:** Quartz, tridynute and cristobalite.
- Important compound of many ceramic and glasses.
- **Feldspars:** Infinite 3D networks.
- Some Al$^{3+}$ Ions replace Si$^{4+}$ Ions: **Net negative charge.**
- Alkaline and alkaline fit into interst
Homework

• Example problems: 11.1, 11.2, 11.3, 11.4, 11.7, 11.8,
• HW: download from website
• Reading assignment: Sections 11.6, 11.8