Ceramic crystal structures

- Need to consider stoichiometry, relative size of ions, bond hybridization

- Coordination # increases with $\frac{r_{\text{cation}}}{r_{\text{anion}}}$

<table>
<thead>
<tr>
<th>$\frac{r_{\text{cation}}}{r_{\text{anion}}}$</th>
<th>Coord #</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>$T_D$</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.

ZnS (zincblende)

NaCl (sodium chloride)

CsCl (cesium chloride)
Rock salt structure

Example: NaCl (rock salt) structure

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

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

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

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

\[ r_{\text{O}} = 0.140 \text{ nm} \]
\[ r_{\text{Mg}} = 0.072 \text{ nm} \]
\[ \frac{r_{\text{Mg}}}{r_{\text{O}}} = 0.514 \]

∴ cations prefer \( O_H \) sites

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

Adapted from Fig. 12.2, Callister 7e.
AX crystal structures

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

Cesium Chloride structure:

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

\( \therefore \) cubic sites preferred

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

Adapted from Fig. 12.3, Callister 7e.
AX crystal structures

Zinc Blende structure

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

- Size arguments predict Zn\(^{2+}\) in O\(_H\) sites,
- In observed structure Zn\(^{2+}\) in T\(_D\) sites

- Why is Zn\(^{2+}\) in T\(_D\) sites?
  - bonding hybridization of zinc favors T\(_D\) sites

So each Zn\(^{2+}\) has 4 neighboring O\(^{2-}\)

Ex: ZnO, ZnS, SiC

Adapted from Fig. 12.4, Callister 7e.
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

BaTiO₃

Adapted from Fig. 12.6, *Callister 7e.*