Chemistry 524
Inorganic Materials Chemistry

Prototypical Structures
Rock Salt (NaCl) has two interpenetrated *fcc* lattices (AX)

\[ Fm\bar{3}m, \alpha = 5.6573\text{Å} \]

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Cl</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
</tr>
</tbody>
</table>
Rock Salt (NaCl) has two interpenetrated $fcc$ lattices (AX).
LiCoO$_2$ adopts an ordered rocksalt structure

The rock salt structure is a dense network of edge-sharing octahedrally coordinated cations.
LiCoO$_2$ adopts an ordered rocksalt structure

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Orienting in the correct fashion we can start to see the potential for a layered structure
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LiCoO$_2$ adopts an ordered rocksalt structure

The structure of LiCoO$_2$ is formed by ordering the site occupancy of Li and Co between the layers.

Interestingly, LiNiO$_2$ has a similar structure, but Ni$^{2+}$ and Li$^+$ have similar ionic radii, thus there is substantial mixing between the Li and Ni layers.
LiCoO$_2$ has “brucite”-like layers of edge-sharing octahedra
Carbon and Silicon both adopt the diamond structure

**Fd\(\bar{3}m\), \(a = 3.5667\text{Å}\)**

<table>
<thead>
<tr>
<th>Atom</th>
<th>(x)</th>
<th>(y)</th>
<th>(z)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>
Carbon and Silicon both adopt the diamond structure.
If there are different atoms, diamond becomes zinc blende

\[
\text{ZnS} \quad F\bar{4}3m, \quad a = 5.4090\text{Å}
\]

<table>
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<tr>
<th>Atom</th>
<th>(x)</th>
<th>(y)</th>
<th>(z)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Zn</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
</tr>
</tbody>
</table>
Stereographic projection of zinc blende

$z = 0.00$

$z = 0.25$

$z = 0.50$

$z = 0.75$
Wurtzite and Zinc Blende differ in stacking sequence

Zinc blende has a cubic unit cell with an fcc lattice of anions...

Thus the anions form a cubically close packed network with half of the tetrahedral interstitials containing a different cation

The principle difference in the wurtzite structure is that the anionic lattice is hexagonally close packed
The wurtzite unit cell is hexanal (hcp oxygen)

\[ P63mc, \quad a = 3.2499, \quad c = 5.2066 \]

<table>
<thead>
<tr>
<th>Atom</th>
<th>( x )</th>
<th>( y )</th>
<th>( z )</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>0.3333</td>
<td>0.66667</td>
<td>0.00</td>
</tr>
<tr>
<td>Zn</td>
<td>0.3333</td>
<td>0.6667</td>
<td>0.3333+( \delta )</td>
</tr>
</tbody>
</table>
The fluorite structure has general composition $AX_2$

Many very important engineering materials adopt the fluorite structure – $\text{CeO}_2$, $\text{ZrO}_2$, $\text{UO}_2$

$\text{CeO}_2$ is an oxygen ion conductor commonly used in oxygen sensors and fuel cell membranes

$\text{Y:ZrO}_2$ (commonly called yttria stabilized zirconia) is a widely used structural material due to its exceptionally high hardness as well as a thermal barrier coating due to its low thermal conductivity
The fluorite has general composition $AX_2$.

$z = 0.00$

$z = 0.25$

$z = 0.50$

$z = 0.75$
The fluorite has general composition $AX_2$

Looking at the polyhedral connectivity of the cations shows an unusual coordination environment compared to the octahedral and tetrahedral sites we have previously seen.
The fluorite has general composition $AX_2$

Looking at the polyhedral connectivity of the cations shows an unusual coordination environment compared to the octahedral and tetrahedral sites we have previously seen.

Easier to understand the structure as a cubic close packing of the A cations with all of the tetrahedral interstitials occupied by the anions!
You should know how to draw these structures in projection.
Al\textsubscript{2}O\textsubscript{3}, Cr\textsubscript{2}O\textsubscript{3}, and Fe\textsubscript{2}O\textsubscript{3} adopt the corundum structure

The oxide ions in corundum form a hexagonal close packed lattice (along the c-direction). \(2/3\) of the octahedral sites are occupied
Al$_2$O$_3$, Cr$_2$O$_3$, and Fe$_2$O$_3$ adopt the corundum structure.

The oxide ions in corundum form a hexagonal close packed lattice (along the c-direction). 2/3 of the octahedral sites are occupied.

Small impurities of Cr in Al$_2$O$_3$ give ruby its brilliant red color.
Two variants of ordered corundum exist.

Fe and Ti form alternating layers along the c-axis to form ilmenite FeTiO$_3$.

LiNbO$_3$ forms another ordered variant of corundum.
Both rutile and anatase have the composition AX$_2$

The ideal anion packing is hexagonally close-packed and the difference is principally in the interstitials which are occupied – easy to transform between the two.

Rutile $E_g = 3.0$ eV

Anatase $E_g = 3.2$ eV

Anatase proves more efficient at hydrogen production, but both structures are very important in the physics and chemistry of TiO$_2$. 
The perovskite structure has the formula $\text{ABX}_3$

**Functional properties include:**

- High-$T_c$ cuprate superconductors
- Colossal Magneto-Resistance ($\text{La,SrMnO}_3$)
- Fast ion conduction ($\text{Li}^+, \text{O}^{2-}$), batteries, fuel cells
- Mixed electronic/ionic conduction, fuel cells
- Oxidation/reduction catalysts
- Ferroelectric / piezoelectric ceramics ($\text{BaTiO}_3$, $\text{Pb(ZrTi)}_3\text{O}_3$)
- Important mineral structure in lower mantle ($\text{MgSiO}_3$)
- Frequency filters for wireless communications: $\text{Ba(Zn}_{1/3}\text{Ta}_{2/3})_3\text{O}_3$
Perovskite in stereographic projection

Bear in mind this is the projection for a perfectly symmetric and undistorted perovskite!

The precise details of the structural distortions are extremely rich and continue to be studied quite actively.
Perovskites allow for extremely good orbital overlap.
The Goldschmidt Tolerance factor predicts distortion

Goldschmidt Tolerance Factor:

\[ a = 2(r_B + r_X) = \sqrt{2}(r_A + r_X) \]

\[ t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)} \]

<table>
<thead>
<tr>
<th>Goldschmidt tolerance factor (t)</th>
<th>Structure</th>
<th>Explanation</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt;1</td>
<td>Hexagonal</td>
<td>A ion too big or B ion too small.</td>
<td>•BaNiO₃</td>
</tr>
<tr>
<td>0.9-1</td>
<td>Cubic</td>
<td>A and B ions have ideal size.</td>
<td>•SrTiO₃ •BaTiO₃</td>
</tr>
<tr>
<td>0.71 - 0.9</td>
<td>Orthorhombic/Rhombohedral</td>
<td>A ions too small to fit into B ion interstices.</td>
<td>•GdFeO₃ •CaTiO₃</td>
</tr>
<tr>
<td>&lt;0.71</td>
<td>Different structures</td>
<td>A ions and B have similar ionic radii.</td>
<td>•Ilmenite</td>
</tr>
</tbody>
</table>
If the radii are not well matched, perovskites distort!

ortho-CaMnO₃

BaNiO₃
Glazer notation is shorthand to describe octahedral tilting

The tilt system is described by specifying the rotation about each of the cartesian axes

\( a^0a^0a^0 \) \hspace{2cm} \( a^+a^+a^+ \) \hspace{2cm} \( a^+a^-c^+ \)

Undistorted system \hspace{2cm} Rotation is identical in all directions \hspace{2cm} Very complicated tilting pattern

The letter denotes the RELATIVE magnitude of the rotation around the xyz axes

The superscript denotes the RELATIVE rotation with respect to other axes

Patrick Woodward (THE Ohio State) is the leading authority on all things perovskites
Perovskites allow us to tune properties through composition

Careful! Cl doping in CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ is more about processing than bonding

Walsh et al. APL Mat. 1, 042111 (2013); Walsh et al. Mater. Horiz., 2, 228 (2015)
$ABX_3$ composition gives us many knobs to turn


Chemical flexibility of I-II-VI$_3$ perovskites

**A site:**
organic cation or inorganic cation
- Size
- Shape
- Polarisation

**B site:**
inorganic cation
- Size
- Redox

**X site:**
inorganic anion or polyanion
- Size
- Shape
- Redox
Ruddleson-Popper phases – (AO)(ABX$_3$)$_n$
Many useful materials adopt the spinel structure!

The spinel structure contains a cubically close packed layer of oxygen anions.

Only half of the octahedral sites and one eigth of the tetrahedral sites are fully occupied

The A and B sites can both accommodate transition metals
The connectivity of spinels is very complex
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The connectivity of spinels is very complex
Spinel structure – $AB_2X_4$

Both sites can accommodate most 3d transition metals: versatility and substitutional control

Edge sharing octahedra (pyrochlore)

Isolated tetrahedra (diamond)

$Fd\overline{3}m, a = 8.3346\text{Å}$

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<tbody>
<tr>
<td>Co</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Cr</td>
<td>0.625</td>
<td>0.625</td>
<td>0.625</td>
</tr>
<tr>
<td>O</td>
<td>$u$</td>
<td>$u$</td>
<td>$u$</td>
</tr>
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$u$ is typically near 0.25, as it gets larger the tetrahedral site gets larger and the octahedral site shrinks.
The B-sublattice contains a Kagome net – very frustrated

The A-sublattice is actually just a diamond net

Both sublattices exhibit lots of geometric frustration and are therefore a great testing ground for properties and physics
Olivine is directly analogous to spinels – $\text{B}_2\text{AO}_4$

Contains \textit{hcp} layers of oxygen rather than \textit{ccp}

Spinels contain two transition metals on the A or B site, whereas olivine usually contains a main group element like P, S, or Si on the A site.

$\text{LiFePO}_4$ is the prototypical example of the olivine structure
The garnet structure is exceptionally rich – \( \{R_3\}[M_2](XO_4)_3 \)

**MO\(_6\) octahedra share corners with XO\(_4\) tetrahedra to form a 3D network**

**Larger R ions sit in an 8-coordinate position**

Garnets – particularly \( \{Y_3\}[Al_2](Al_3)O_{12} \) (YAG) – are extensively used in phosphors since the Y site can be substituted with other rare earth elements
Garnets are a “fruit fly” for magnetism, complex structure

\[ R_3B_2(AO_4)_3 \]
Most commonly studied for the triangular lattice on $R$ site

$\text{Gd}_3\text{Ga}_2(\text{GaO}_4)_3$ is an archetype for magnetic frustration
Garnets are not close-packed in the traditional sense

When viewed down the (111) axis, four symmetry-related rods consisting of alternating octahedral and trigonal prismatic sites (face of the rare-earth polyhedra) can be seen.

These rods, bound together by the tetrahedral site, form a network of close-packed rods as described by O’Keefe and Andersson.

O’Keefe and Andersson Acta Cryst A 33 914 (1977)
Garnet lattice composed of a network of close-packed rods

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