MATRL 218/CHEM 227: Class VI — Structures 3
More Structures

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AB\(_2\) structures:

**Fluorite CaF\(_2\):** SG = \(Fm\overline{3}m\) (No. 225) \(a = 5.45\ \text{Å}\)

<table>
<thead>
<tr>
<th>Atom</th>
<th>(x)</th>
<th>(y)</th>
<th>(z)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>F</td>
<td>(1/4)</td>
<td>(1/4)</td>
<td>(1/4)</td>
</tr>
</tbody>
</table>

This structure type is also adopted by SrF\(_2\), BaF\(_2\), UO\(_2\), ThO\(_2\), Na\(_2\)O (the anti-type), ZrO\(_2\) at high temperatures . . .

ZrO\(_2\) can be stabilized in the fluorite structure through doping with Ca\(^{2+}\) or Y\(^{3+}\) – these are stabilized zirconias and have many structural and electrochemical applications.

**CdI\(_2\):** SG = \(P\overline{3}m1\) (No. 164) \(a = 4.24\ \text{Å}\ c = 6.84\ \text{Å}\)

<table>
<thead>
<tr>
<th>Atom</th>
<th>(x)</th>
<th>(y)</th>
<th>(z)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>I</td>
<td>(2/3)</td>
<td>(1/3)</td>
<td>(~0.25)</td>
</tr>
</tbody>
</table>

This structure type is also adopted by PbI\(_2\), MgCl\(_2\), FeCl\(_2\), ZnI\(_2\), Cd(OH)\(_2\), Mg(OH)\(_2\), TaS\(_2\), NbS\(_2\) . . .
CdCl$_2$: SG = $R\bar{3}m$ (No. 166) $a = 3.85$ Å $c = 17.46$ Å

<table>
<thead>
<tr>
<th>Atom</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Cl</td>
<td>2/3</td>
<td>1/3</td>
<td>$\sim$ 1/12</td>
</tr>
</tbody>
</table>

The CdCl$_2$ structure is to the CdI$_2$ structure what ABCABC stacking is to ABAB stacking:

On the left is the structure of CdI$_2$ projected down the $b$ axis and on the right is the structure of CdCl$_2$. The cyan-colored box marks the unit cell.
\textbf{MoS}_2: \text{SG } P6_3/mmc \text{ (No. 194) } a = 3.160 \text{ Å } c = 12.294 \text{ Å}

\begin{tabular}{lccc}
Atom & x & y & z \\
\hline
Mo & 1/3 & 2/3 & 1/4 \\
S & 1/3 & 2/3 & 0.621 \\
\end{tabular}

Unlike the CdI\textsubscript{2} structure where the cations are octahedral, in MoS\textsubscript{2}, the cations are in the centers of trigonal prisms formed by the S.
Rutile TiO$_2$: SG = $P4_2/mnm$ (No. 136) $a = 4.592$ Å $c = 2.959$ Å

<table>
<thead>
<tr>
<th>Atom</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>O</td>
<td>0.3051</td>
<td>0.3051</td>
<td>0</td>
</tr>
</tbody>
</table>

Left: The rutile structure showing the TiO$_6$ octahedron within a single unit cell.

Right: The rutile structure showing many TiO$_6$ octahedra sharing corners. The view is down the $c$ axis. This is also the structure of CrO$_2$, MoO$_2$, RuO$_2$ ...

Al$_2$O$_3$: SG = $R3c$ (No. 167) $a = 4.759$ Å $c = 12.992$ Å

<table>
<thead>
<tr>
<th>Atom</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>0</td>
<td>0</td>
<td>0.35217</td>
</tr>
<tr>
<td>O</td>
<td>0.30168</td>
<td>0</td>
<td>1/4</td>
</tr>
</tbody>
</table>

The corundum structure with the $c$ axis going from left to right. Red spheres are O and grey are Al.

ReO$_3$: SG = $Pm3m$ (No. 221) $a = 3.754$ Å

<table>
<thead>
<tr>
<th>Atom</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Re</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>O</td>
<td>1/2</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
ABO$_3$ perovskite:

BaZrO$_3$ (A = Ba, B = Zr): $SG = Pm\bar{3}m$ (No. 221) $a = 4.194$ Å

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba</td>
<td>1$b$</td>
<td>1/2</td>
<td>1/2</td>
<td>1/2</td>
</tr>
<tr>
<td>Zr</td>
<td>1$a$</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>O</td>
<td>3$d^*$</td>
<td>1/2</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

* $3d$ is $(\frac{1}{2},0,0), (0,\frac{1}{2},0), (0,0,\frac{1}{2})$

Most perovskite structures are not cubic. BaZrO$_3$, BaSnO$_3$, BaHfO$_3$ are a few examples of the cubic ones.

In the cubic perovskite, we have:

$$(r_A + r_O) = (\sqrt{2}/2)a = \sqrt{2}(r_B + r_O)$$
The tolerance factor of an ABO$_3$ perovskite is defined as:

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

For an ideal (cubic) perovskite, \( t = 1 \). Most perovskites have \( t < 1 \), and the structures are distorted. An example is the orthorhombic CaZrO$_3$, whose structure is given below:

\[
\begin{array}{|c|c|c|c|}
\hline
\text{Atom} & \text{Wyckoff} & x & y & z \\
\hline
\text{Ca} & 4c & 0.0065 & 0.0356 & 1/4 \\
\text{Ti} & 4b & 0 & 1/2 & 0 \\
\text{O1} & 4b & 0.5711 & -0.0161 & 1/4 \\
\text{O2} & 8d & 0.2897 & 0.2888 & 0.0373 \\
\hline
\end{array}
\]

Here is the structure looking down the long c axis. The connectivity of the perovskite structure, namely the corner-shared octahedra are clearly seen. The large grey atoms are Ca.

This structure is seen for LnMO$_3$ where Ln is a rare-earth (La, Pr, Nd …) and M is Fe, Al, Sc, Cr, Ga, Co, V, Rh … The structure is also observed in compounds such as UCrS$_3$, NaMgF$_3$, CsCaH$_3$ … MgSiO$_3$ adopts the perovskite structure at high pressures and this is believed to be important for understanding the earth’s mantle.
**AB₂O₄ spinel:**

This structure has a cubic close packing (fcc) arrangement of oxide ions, with cations places in some of the interstitial tetrahedral and octahedral voids.

**MgAl₂O₄:**  
SG = Fd3m (No. 227)  
[a = 8.09 Å]  
Structure described with center at (\(\frac{1}{8}, \frac{1}{8}, \frac{1}{8}\))  

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>(\frac{5}{8})</td>
<td>(\frac{5}{8})</td>
<td>(\frac{5}{8})</td>
</tr>
<tr>
<td>Al</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>O</td>
<td>0.390</td>
<td>0.390</td>
<td>0.390</td>
</tr>
</tbody>
</table>

The spinel, MgAl₂O₄. The Al atoms (hidden) are octahedrally surrounded by O. Mg atoms sit in tetrahedral interstices formed by O. The view is down one of the cubic axes of the structure.

The structure can also be regarded as being formed by strips of edge-sharing octahedra that are laid down forming a trellis. Tetrahedral voids in formed by these strips of octahedra are where the Mg sit.

In MgAl₂O₄, the divalent Mg are in the tetrahedral site, and trivalent Al are in the octahedral site. Such an arrangement corresponds to a normal spinel. In an inverse spinel, the tetrahedral site might have a trivalent ion. An example is MgFe₂O₄, where one Fe³⁺ is tetrahedral and the other is octahedral. The Mg²⁺ is octahedral.

Spinels are formed by a number of transition elements, and by Mg₂TiO₄, Na₂MoO₄, Li₂NiF₄, CuTi₂S₄, Fe₃O₄…. 