Lecture 2
Structural Aspects of Perovskites: Symmetry, Ordering and Intergrowths

Patrick Woodward
Department of Chemistry
Ohio State University

Structural & Compositional Flexibility

Ordering
• B-site Cation Ordering (i.e. Ba\textsubscript{2}MgWO\textsubscript{6})
• A-site Cation Ordering (i.e. NdAgTi\textsubscript{2}O\textsubscript{6})
• Anion/Vacancy Ordering (i.e. Ca\textsubscript{2}Fe\textsubscript{2}O\textsubscript{5})

Intergrowth Structures
• Ruddlesden-Popper Family (i.e. Sr\textsubscript{3}Ti\textsubscript{2}O\textsubscript{7})
• Dion-Jacobson Family (i.e. RbCa\textsubscript{2}Ta\textsubscript{3}O\textsubscript{10})
• Aurivillius Family (i.e. Bi\textsubscript{2}SrNb\textsubscript{2}O\textsubscript{6})

Distortions (covered next lecture)
• Octahedral Tilting Distortions (i.e. CaTiO\textsubscript{3})
• 1\textsuperscript{st} Order Jahn-Teller Distortions (i.e. LaMnO\textsubscript{3})
• 2\textsuperscript{nd} Order Jahn-Teller Distortions (i.e. BaTiO\textsubscript{3})
**Crystallography of the Ideal Cubic Perovskite Structure**

**The Aristotype (Ideal) Structure**

**Space Group:** $Pm3m$ *(Cubic)*  
**Lattice Parameters:**  
$a \cong 4 \text{ Å}$

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A(Sr)</td>
<td>1b</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
</tr>
<tr>
<td>B(Ti)</td>
<td>1a</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>X(O)</td>
<td>3d</td>
<td>$\frac{1}{2}$</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

![A-site Cubo-octahedron](image1)

![B-site Octahedron](image2)

![Anion](image3)
Crystallographic Directions

[001]

[010]

[100]

[110]

[111]

Body Diagonal

Face Diagonal
### 3D Crystal Systems

<table>
<thead>
<tr>
<th>Crystal System</th>
<th>Required Symmetry Elements</th>
<th>Unit Cell Dimensions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triclinic</td>
<td>None</td>
<td>(a \neq b \neq c)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(\alpha \neq \beta \neq \gamma)</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>Mirror (glide) plane or a 2-fold (2₁) axis</td>
<td>(a \neq b \neq c)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(\alpha = \beta = 90^\circ, \gamma \neq 90^\circ)</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>Three mutually (\perp) 2-fold axes or mirror planes</td>
<td>(a \neq b \neq c)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(\alpha = \beta = \gamma = 90^\circ)</td>
</tr>
<tr>
<td>Rhombohedral/Trigonal</td>
<td>One 3-fold axis</td>
<td>(a = b \neq c)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(\alpha = \beta = 90^\circ, \gamma = 120^\circ)</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>One 6-fold axis</td>
<td>(a = b \neq c)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(\alpha = \beta = 90^\circ, \gamma = 120^\circ)</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>One 4-fold axis</td>
<td>(a = b \neq c)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(\alpha = \beta = \gamma = 90^\circ)</td>
</tr>
<tr>
<td>Cubic</td>
<td>Four 3-fold axes along the body diagonals</td>
<td>(a = b = c)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(\alpha = \beta = \gamma = 90^\circ)</td>
</tr>
</tbody>
</table>

### Symmetry in Space Group Pm\(3m\)

Long Herman-Mauguin Space Group Symbol

\[ P \quad 4/m \quad \bar{3} \quad 2/m \]

Symmetry elements \(\parallel\) to (for axes) or \(\perp\) to (for planes) the \(a\)-, \(b\)-, & \(c\)-axes

In this case a 4-fold axis with a perpendicular mirror plane
Symmetry in Space Group Pm3m

Long Herman-Mauguin Space Group Symbol

\[ P 4/m \bar{3} 2/m \]

Symmetry elements $\parallel$ to (for axes) or $\perp$ to (for planes) the body diagonals

In this case a 3-fold rotoinversion axis (rotate by 120° then invert)

Symmetry in Space Group Pm3m

Long Herman-Mauguin Space Group Symbol

\[ P 4/m \bar{3} 2/m \]

Symmetry elements $\parallel$ to (for axes) or $\perp$ to (for planes) the face diagonals

In this case a 2-fold axis with a perpendicular mirror plane
Cation Ordering

Rock Salt Ordering of B-site Cations

\[ \text{SrTiO}_3 \rightarrow \text{Sr}_2\text{MgWO}_6 \]

This type of cation ordering doesn’t destroy the 4-, 3- or 2-fold axes, but we need a larger unit cell now.
Rock Salt Ordering of B-site Cations

Stoichiometry: $\text{A}_2\text{BB'}\text{O}_6$

Crystal System: Cubic

Space Group: Fm3m

Lattice Parameter: $a \approx 2a_p$ (~8 Å)

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A(Sr)</td>
<td>8c</td>
<td>$\frac{1}{4}$</td>
<td>$\frac{1}{4}$</td>
<td>$\frac{1}{4}$</td>
</tr>
<tr>
<td>B(Mg)</td>
<td>4a</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>B'(W)</td>
<td>4b</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
</tr>
<tr>
<td>X(O)</td>
<td>24e</td>
<td>$x$</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Rock salt ordering can also be described as ordering of cations onto alternating planes running perpendicular to [111]. This is seen in the XRD pattern by the appearance of the $\frac{1}{2} \frac{1}{2} \frac{1}{2}$ peak and the $\frac{3}{2} \frac{1}{2} \frac{1}{2}$ peaks.
Layered Ordering of the B-site Cations

Stoichiometry: \( \text{A}_2\text{BB'}\text{O}_6 \)
Crystal System: Tetragonal
Space Group: \( \text{P}4/\text{mmm} \)
\( a \approx a_p \ (\sim 4 \ \text{Å}) \)
\( c \approx 2a_p \ (\sim 8 \ \text{Å}) \)

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (Sr)</td>
<td>2h</td>
<td>( \frac{1}{2} )</td>
<td>( \frac{1}{2} )</td>
<td>z</td>
</tr>
<tr>
<td>B (Mg)</td>
<td>1a</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>B' (W)</td>
<td>1b</td>
<td>0</td>
<td>0</td>
<td>( \frac{1}{2} )</td>
</tr>
<tr>
<td>X1 (O)</td>
<td>2g</td>
<td>0</td>
<td>0</td>
<td>z</td>
</tr>
<tr>
<td>X2 (O)</td>
<td>2f</td>
<td>( \frac{1}{2} )</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>X3 (O)</td>
<td>2e</td>
<td>( \frac{1}{2} )</td>
<td>0</td>
<td>( \frac{1}{2} )</td>
</tr>
</tbody>
</table>

Rock Salt Ordering of B-site Cations

Layered ordering can also be described as ordering into alternating planes running perpendicular to [001]. This is seen in the XRD pattern by the appearance of the peaks with half-integer values for \( l \).
Why is Layered ordering of B-site cations unfavorable?

**Pauling’s 5th Rule**
The number of chemically different coordination environments for a given ion in a crystal tends to be small. (Rule of Parsimony)

**Brown’s Rule of Maximum Symmetry**
The most stable structure is the most symmetric structure, consistent with the constraints acting on the system
Why is Rock Salt ordering of A-site cations unfavorable?

### $A_2MM'X_6$
- Space Group = Fm3m
- A: 8c 1/4 1/4 1/4
- M: 4a 0 0 0
- M': 4b 1/2 1/2 1/2
- X: 24e x 0 0

Oxygen can displace in response to B/B' size mismatch

### $AA'M_2X_6$
- Space Group = Fm3m
- M: 8c 1/4 1/4 1/4
- A: 4a 0 0 0
- A': 4b 1/2 1/2 1/2
- X: 24d 1/4 1/4 0

Oxygen cannot displace in response to A/A' size mismatch

---

Anion Vacancy Ordering
\[ \text{Ca}_2\text{Fe}_2\text{O}_5 \] (Brownmillerite)

Remove \( \frac{1}{2} \) of the oxygen ions in the middle layer.

“CaFeO\textsubscript{3}”

All Fe\textsuperscript{3.5+} ions in octahedral coordination

\[ \text{CaFeO}_{2.5} \rightarrow \text{Ca}_2\text{Fe}_2\text{O}_5 \]

50\% six coordinate Fe\textsuperscript{3+}
50\% four coordinate Fe\textsuperscript{3+}

Let’s take a closer look at the middle layer, where the oxygen vacancies are located.

“CaFeO\textsubscript{3}”

octahedral coordination

\[ \text{Ca}_2\text{Fe}_2\text{O}_5 \] (Brownmillerite)

Distorted tetrahedral coordination

\[ \text{Ca}_2\text{Fe}_2\text{O}_5 \]
Ca$_2$Mn$_2$O$_5$

“CaMnO$_3$”
All Mn$^{3.5+}$ ions in octahedral coordination

Remove columns of oxygen ions

CaMnO$_{2.5}$ → Ca$_2$Mn$_2$O$_5$
All Mn$^{3+}$ ions in square pyramidal coordination

Intergrowth Structures
**Perovskite Intergrowth Structures**

- **Ruddlesden-Popper Series**
  - Perovskite + Rock Salt

- **Dion-Jacobson Series**
  - Perovskite + CsCl

- **Aurivillius Series**
  - Perovskite + Bi$_2$O$_2$

---

**Constructing an Intergrowth Structure**

**Dion-Jacobson Series**

- **KZnF$_3$**
- **TIAIF$_4$**
  - n=1 Dion-Jacobson Structure

- Break corner sharing topology
- "repair" dangling bonds
**Constructing an Intergrowth Structure**

*Ruddlesden-Popper Series*

![Diagram of SrTiO₄ and Sr₂TiO₄ n=1 Ruddlesden-Popper Structure](image)

1. Break corner sharing topology,
2. Shift by $x=\frac{1}{2}$, $y=\frac{1}{2}$
3. Insert extra $A$-cation

**Constructing an Intergrowth Structure**

*Aurivillius Series*

![Diagram of Bi₂WO₆ and Bi₂O₅²⁺ Layer](image)

1. Bi₂WO₆
2. Bi₂O₅²⁺ Layer
Increasing the Width of the Perovskite Block

*Ruddlesden-Popper Phases*

\[ A_{n+1}B_nO_{3n+1} \]

- Sr\(_2\)TiO\(_4\)  
  *n*=1 layer
- Sr\(_3\)Ti\(_2\)O\(_7\)  
  *n*=2 layer
- Sr\(_4\)Ti\(_3\)O\(_{10}\)  
  *n*=3 layer