Oxide crystal structures: The basics

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Originally created for the:
ICMR mini-School at UCSB: Computational tools for functional oxide materials – An introduction for experimentalists
1. Brief description of oxide crystal structures (simple and complex)
   
a. Ionic radii and Pauling’s rules
b. Electrostatic valence
c. Bond valence, and bond valence sums

Why do certain combinations of atoms take on specific structures?
My bookshelf

H. D. Megaw

O. Muller & R. Roy

I. D. Brown

B. G. Hyde & S. Andersson
Crystal structures of simple oxides [containing a single cation site]
Crystal structures of simple oxides [containing a single cation site]

N.B.: CoO is simple, Co₃O₄ is not. ZnCo₂O₄ is certainly not! Co₃O₄ and ZnCo₂O₄ are complex oxides.

**Graphs** of connectivity in crystals: Atoms are nodes and edges (the lines that connect nodes) indicate short (near-neighbor) distances.

CO₂: The molecular structure is O=C=O. The graph is:
Each C connected to 2 O, each O connected to a 1 C

OsO₄: The structure comprises isolated tetrahedra (molecular). The graph is below:
Each Os connected to 4 O and each O to 1 Os
Crystal structures of simple oxides of monovalent ions: $A_2O$

**Cu$_2$O**

Linear coordination is unusual. Found usually in Cu$^+$ and Ag$^+$.  

**Na$_2$O (anti-fluorite)**

4-coordination for Na$^+$ and 8-coordination for O$^{2-}$ are unusual.
Crystal structures of simple oxides of divalent ions: AO

**ZnO (wurtzite), sp³**

**PbO (litharge), lone pairs**

**MgO (rock-salt)**

Ubiquitous for AO oxides including transition metals (distorted for CuO and NbO).

Insulators, metals (TiO), magnetic, ...
Crystal structures of simple oxides. $\text{Al}_2\text{O}_3$ as an example of a sesquioxide.

$\alpha$-$\text{Al}_2\text{O}_3$ (corundum)

Also the structure of $\text{Cr}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3$.

$\text{Ga}_2\text{O}_3$ does funny things.

$\text{In}_2\text{O}_3$ is different (bixbyite).
Crystal structures of simple oxides of tetravalent ions: $\text{AO}_2$

- $\text{TiO}_2$ (rutile)
- $\text{CeO}_2$ (fluorite)

$\text{TiO}_2$ also crystallizes as anatase and brookite.

$\text{SiO}_2$ takes on this structure, and can be quenched to it, (stishovite) under pressure.

Also the structure of $\text{ThO}_2$, and of $\text{ZrO}_2$ and $\text{HfO}_2$ at elevated temperatures.

Ordered variants abound.
Oxides versus sulfides: TiS$_2$

$2H$–TiS$_2$

van der Waals gap (unlikely in oxides or fluorides, but occurs frequently in hydroxides)

This is the CdI$_2$ structure.
Crystal structures of an oxide with an octavalent ion: OsO$_4$
Shannon-Prewitt (ionic) radii

Radii assigned by systematically examining cation-anion pairs in oxides, fluorides etc. May not work for other kinds of compounds

Be sensitive to coordination number and spin state
In brief: The cation-anion distance is the sum of cation and anion radii, and the number of anions around a cation (the coordination number) is a function of the radius ratio. Exemplified by AO₂ compounds below. MRR is the minimum radius ratio.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$r_C$ (Å)</th>
<th>$r_C + r_O$ (Å)</th>
<th>$r_C/r_O$</th>
<th>Coordination</th>
<th>MRR</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>-0.19(?)</td>
<td>1.16 (exp.)</td>
<td>?</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
<td>0.26</td>
<td>1.61</td>
<td>0.19</td>
<td>4</td>
<td>0.225</td>
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<tr>
<td>TiO₂</td>
<td>0.605</td>
<td>1.955</td>
<td>0.45</td>
<td>6</td>
<td>0.414</td>
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<tr>
<td>CeO₂</td>
<td>0.97</td>
<td>2.32</td>
<td>0.72</td>
<td>8</td>
<td>0.732</td>
</tr>
</tbody>
</table>

Pauling’s second rule: The electrostatic valence rule

In brief: Charges going out from cations should balance anions and *vice-versa*

Why is OsO$_4$ a molecule? Radius ratio + electrostatic valence

Pauling, and later Brown and Shannon, noted that the Pauling bond strength (the electrostatic valence) correlates very well with distance for many oxides: Short bonds (distances) correspond to strong bonds and vice-versa.

Electrostatic valence and bond valence

The modern bond valence relationship:

\[
s = \exp \left( \frac{R_0 - R}{B} \right)
\]

Where \( s \) is the strength of the bond, \( R \) is the cation to anion distance, and \( R_0 \) and \( B \approx 0.37 \, \text{Å} \) are parametrized for the specific ion pair.

When all \( s \) are calculated: \( \sum \limits_{\text{CN}} s = \text{valence of the ion} \)

\[
s = +2/6
\]

For Mn\(^{2+}\)--O\(^{2-}\), \( R_0 = 1.790 \, \text{Å}, B = 0.37 \, \text{Å} \).

This means \( R = 2.20 \, \text{Å} \).

experiment: 2.22 Å

### Electrostatic valence and bond valence: Parameters for Mn

<table>
<thead>
<tr>
<th>Element</th>
<th>Charge</th>
<th>Bond Valence</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn 2 O</td>
<td>-2</td>
<td>1.790</td>
<td>a</td>
</tr>
<tr>
<td>Mn 2 O</td>
<td>-2</td>
<td>1.765</td>
<td>j</td>
</tr>
<tr>
<td>Mn 2 S</td>
<td>-2</td>
<td>2.22</td>
<td>e</td>
</tr>
<tr>
<td>Mn 2 F</td>
<td>-1</td>
<td>1.698</td>
<td>a</td>
</tr>
<tr>
<td>Mn 2 Cl</td>
<td>-1</td>
<td>2.133</td>
<td>a</td>
</tr>
<tr>
<td>Mn 2 Br</td>
<td>-1</td>
<td>2.34</td>
<td>e</td>
</tr>
<tr>
<td>Mn 2 I</td>
<td>-2</td>
<td>2.52</td>
<td>e</td>
</tr>
<tr>
<td>Mn 2 N</td>
<td>-3</td>
<td>1.849</td>
<td>j</td>
</tr>
<tr>
<td>Mn 2 N</td>
<td>-3</td>
<td>1.65</td>
<td>e</td>
</tr>
<tr>
<td>Mn 3 O</td>
<td>-2</td>
<td>1.760</td>
<td>a</td>
</tr>
<tr>
<td>Mn 3 O</td>
<td>-2</td>
<td>1.732</td>
<td>j</td>
</tr>
<tr>
<td>Mn 3 F</td>
<td>-1</td>
<td>1.66</td>
<td>b</td>
</tr>
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<td>Mn 3 Cl</td>
<td>-1</td>
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<td>b</td>
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<td>Mn 3 N</td>
<td>-3</td>
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<td>j</td>
</tr>
<tr>
<td>Mn 4 O</td>
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<td>1.753</td>
<td>a</td>
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<td>Mn 4 O</td>
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<td>j</td>
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<tr>
<td>Mn 4 F</td>
<td>-1</td>
<td>1.71</td>
<td>b</td>
</tr>
<tr>
<td>Mn 4 Cl</td>
<td>-1</td>
<td>1.63</td>
<td>e</td>
</tr>
<tr>
<td>Mn 4 N</td>
<td>-3</td>
<td>1.822</td>
<td>j</td>
</tr>
<tr>
<td>Mn 6 O</td>
<td>-2</td>
<td>1.79</td>
<td>e</td>
</tr>
<tr>
<td>Mn 7 O</td>
<td>-2</td>
<td>1.827</td>
<td>e</td>
</tr>
<tr>
<td>Mn 7 O</td>
<td>-2</td>
<td>1.79</td>
<td>b</td>
</tr>
<tr>
<td>Mn 7 F</td>
<td>-1</td>
<td>1.72</td>
<td>b</td>
</tr>
<tr>
<td>Mn 7 Cl</td>
<td>-1</td>
<td>2.17</td>
<td>b</td>
</tr>
</tbody>
</table>

The major ternary structural families (Muller and Roy, page 3, redrawn and modified)

- **ABX₃**
  - CaCO₃
  - Perovskite
  - Hexagonal ABX₃ (e.g., BaNiO₃ in the CsCrBr₃ structure)
  - Pyroxenes and related structures (e.g., diopside CaMgSi₂O₆)
  - Corundum and related structures (e.g., ilmenite FeTiO₃)

- **ABX₄**
  - Zircon (ZrSiO₄)
  - Scheelite (CaWO₄)
  - Barite (BaSO₄)
  - Ordered SiO₂ derivatives
  - **Ordered rutile derivatives**
    - K₂NiF₄ (m = 1 Ruddlesden-Popper)
    - β-K₂SO₄
    - Olivine (Mg₂SiO₄ and for e.g., LiFePO₄)
    - Spinel (MgAl₂O₄)
    - CaFe₂O₄
    - Phenacite (Be₂SiO₄)

- **A₂BX₄**
  - **ABX₂** (e.g., LiCoO₂ and CuFeO₂)
  - A₂B₂X₇ (e.g., pyrochlore Y₂Ti₂O₇)

- **others**
  - A₂BX₅
  - A₂BX₆
  - A₃BX₅

Will discuss compounds in highlighted boxes: Characterized by dense connectivity.
The superscripted roman numerals indicate coordination number.
Perovskite

BaZrO$_3$

LaMnO$_3$ Pnma 
*(Jahn-Teller distorted)*

Note that the space group *Pnma* (#62) can be written in a variety of ways.

This is the most common perovskite space group.

In the next so many structures, BO$_6$-polyhedra are depicted.
Ordered double perovskites (elpasolites)

\[ \text{Ba}_2\text{MgWO}_6 \]

\[ \text{Ca}_2\text{MgWO}_6 \]

Rock-salt like ordering of dissimilar octahedra. Space group same as rock-salt: \( Fm\overline{3}m \)

Smaller A-ions associated with tilting as in simple perovskites.
The double perovskite field: Charge and radius

Hexagonal ABO$_3$ structures

BaNiO$_3$

LiNbO$_3$ (ferroelectric R3c)

Ferroelectric YMnO$_3$ ("YAlO$_3$")

Unusual 5-fold coordination (trigonal bipyramid) of MnO$_5$
Ordered rutiles (the trirutile)

$\text{CoTa}_2\text{O}_6 \cdot 3 \times \text{TiO}_2 = \text{Ti}_3\text{O}_6; 3 \times \text{Ti}^{4+} = \text{Co}^{2+} + 2 \times \text{Ta}^{5+}$
The $\text{A}_2\text{BO}_4$ structure-sorting field (from Muller and Roy)

The superscripted roman numerals indicate coordination number.
$K_2NiF_4$ and Ruddlesden-Popper ($m = 1, 2, 3$)

General formula $[SrO][SrTiO_3]_m$

$Sr_2TiO_4$

$Sr_3Ti_2O_7$

$Sr_4Ti_3O_{10}$

$m = 3$
Ubiquitous structure when ions have similar sizes, around 0.6 Å. A is tetrahedrally coordinated, and B octahedral (actually with a slight trigonal distortion).

In general, lower oxidation states and smaller bandwidths than in perovskites.
Spinel $\text{AB}_2\text{O}_4$

**Ions on the A site**

- Li
- Mg
- Sc
- Ti
- V
- Cr
- Mn
- Fe
- Co
- Ni
- Cu
- Zn
- Ga
- Ge
- Rh
- Ag
- Cd
- Sn

**Ions on the B site**

- Li
- Mg
- Sc
- Ti
- V
- Cr
- Mn
- Fe
- Co
- Ni
- Cu
- Zn
- Ga
- Ge
- Co, Rh
- Ag
- Cd
- In
- Sn

**Properties**

- Jahn-Teller active
- Diamagnetic
- High single-ion anisotropy
Some $\text{ABO}_2$ structures: Highly dense in-plane, and frequently metallic

- **LiCoO$_2$** (ordered rock-salt)
  - 111-ordered with alternating octahedral LiO$_6$ and CoO$_6$ stacking

- **3R–CuFeO$_2$** (delafossite)
  - BO$_2$ (Cdl$_2$) slabs separated by two-coordinate atoms, usually Cu$^+$ and Ag$^+$. Also unusually, Pd$^{1+}$ and Pt$^{1+}$.
$Y_2Ti_2O_7 = Y_2Ti_2O_6O^-$

6+2-coordinate $A$ atoms and 6-coordinate $B$ atoms.

Separately, just connecting $A$ or just connecting $B$ yields two interpenetrating pyrochlore lattices of corner-connected tetrahedra.
fin