Oxide crystal structures: The basics

Ram Seshadri
Materials Department and Department of Chemistry & Biochemistry
Materials Research Laboratory, University of California, Santa Barbara CA 93106 USA
seshadri@mrl.ucsb.edu
en.wikipedia.org:

“Helen Dick Megaw (1 June 1907 – 26 February 2002) was an Irish crystallographer who was a pioneer in X-ray crystallography. She made measurements of the cell dimensions of ice and established the Perovskite crystal structure.”
This lecture

Brief description of oxide crystal structures

1. Ionic radii and Pauling’s rules
2. Electrostatic valence
3. Bond valence, and bond valence sums

Connectivity and bandwidth

1. First rule: the radius ratio rule
2. Second rule: the electrostatic valence rule
3. Third rule: sharing of polyhedron corners, edges and faces
4. Fourth rule: crystals containing different cations
5. Fifth rule: the rule of parsimony
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 $\text{AO}_2$ compounds below. MRR below 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>$\text{CO}_2$</td>
<td>$-0.19(?)$</td>
<td>1.16 (exp.)</td>
<td>?</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>$\text{SiO}_2$</td>
<td>0.26</td>
<td>1.61</td>
<td>0.19</td>
<td>4</td>
<td>0.225</td>
</tr>
<tr>
<td>$\text{TiO}_2$</td>
<td>0.605</td>
<td>1.955</td>
<td>0.45</td>
<td>6</td>
<td>0.414</td>
</tr>
<tr>
<td>$\text{CeO}_2$</td>
<td>0.97</td>
<td>2.32</td>
<td>0.72</td>
<td>8</td>
<td>0.732</td>
</tr>
</tbody>
</table>

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, Co$_3$O$_4$ is not. ZnCo$_2$O$_4$ is certainly not! Co$_3$O$_4$ and ZnCo$_2$O$_4$ are complex oxides.

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

**CO$_2$:** The molecular structure is O=C=O. The graph is:
Each C connected to 2 O, each O connected to a 1 C

**OsO$_4$:** 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: $A_2O$

$Cu_2O$
Linear coordination is unusual. Found usually in $Cu^+$ and $Ag^+$.

$Na_2O$ (anti-fluorite)
4-coordination for $Na^+$ and 8-coordination for $O^{2-}$ are unusual.
Crystal structures of simple oxides of divalent ions: \( \text{AO} \)

- **ZnO (wurtzite), \( \text{sp}^3 \)**
  
- **PbO (litharge), lone pairs**
  \( \text{Pb}^{2+} \) is \([\text{Xe}]4f^{14}5d^{10}6s^26p^0\)

- **MgO (rock-salt)**

  Ubiquitous for \( \text{AO} \) oxides including transition metals (distorted for \( \text{CuO} \) and \( \text{NbO} \)).

  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).
B$_2$O$_3$ (chiral, $P3_12_1$)

B$_2$O$_3$ (hugely important for glass industry).

NB: This structure is not in scale with the others.
Crystal structures of simple oxides of tetravalent ions: $\text{AO}_2$

$\text{TiO}_2$ (rutile)

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

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

$\text{CeO}_2$ (fluorite)

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

Ordered variants abound.

The radius ratio rule at play:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Coordination</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CO}_2$</td>
<td>Linear</td>
</tr>
<tr>
<td>$\text{SiO}_2$</td>
<td>Tetrahedral</td>
</tr>
<tr>
<td>$\text{TiO}_2$</td>
<td>Octahedral</td>
</tr>
<tr>
<td>$\text{HfO}_2$</td>
<td>7-coordinate</td>
</tr>
<tr>
<td>$\text{CeO}_2$</td>
<td>Cubic</td>
</tr>
</tbody>
</table>
Oxides versus sulfides: TiS$_2$

1T–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$_4$
Pauling’s second rule: The electrostatic valence rule

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

\[ \text{electrostatic bond strength or valence} \quad s = \text{charge on cation/coordination number} \]

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.

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 \( B \) (≈ 0.37 Å) are parametrized for the specific ion pair.

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

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
<table>
<thead>
<tr>
<th>Mn</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
<th>Radii</th>
<th>Valency</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>O</td>
<td>-2</td>
<td>1.790</td>
<td>0.37</td>
<td>a</td>
</tr>
<tr>
<td>2</td>
<td>O</td>
<td>-2</td>
<td>1.765</td>
<td>0.37</td>
<td>j</td>
</tr>
<tr>
<td>2</td>
<td>S</td>
<td>-2</td>
<td>2.22</td>
<td>0.37</td>
<td>e</td>
</tr>
<tr>
<td>2</td>
<td>F</td>
<td>-1</td>
<td>1.698</td>
<td>0.37</td>
<td>a</td>
</tr>
<tr>
<td>2</td>
<td>Cl</td>
<td>-1</td>
<td>2.133</td>
<td>0.37</td>
<td>a</td>
</tr>
<tr>
<td>2</td>
<td>Br</td>
<td>-1</td>
<td>2.34</td>
<td>0.37</td>
<td>e</td>
</tr>
<tr>
<td>2</td>
<td>I</td>
<td>-2</td>
<td>2.52</td>
<td>0.37</td>
<td>e</td>
</tr>
<tr>
<td>2</td>
<td>N</td>
<td>-3</td>
<td>1.849</td>
<td>0.37</td>
<td>j</td>
</tr>
<tr>
<td>2</td>
<td>N</td>
<td>-3</td>
<td>1.85</td>
<td>0.35</td>
<td>e</td>
</tr>
<tr>
<td>3</td>
<td>O</td>
<td>-2</td>
<td>1.760</td>
<td>0.37</td>
<td>a</td>
</tr>
<tr>
<td>3</td>
<td>O</td>
<td>-2</td>
<td>1.732</td>
<td>0.37</td>
<td>j</td>
</tr>
<tr>
<td>3</td>
<td>F</td>
<td>-1</td>
<td>1.66</td>
<td>0.37</td>
<td>b</td>
</tr>
<tr>
<td>3</td>
<td>Cl</td>
<td>-1</td>
<td>2.14</td>
<td>0.37</td>
<td>b</td>
</tr>
<tr>
<td>3</td>
<td>N</td>
<td>-3</td>
<td>1.84</td>
<td>0.37</td>
<td>j</td>
</tr>
<tr>
<td>4</td>
<td>O</td>
<td>-2</td>
<td>1.753</td>
<td>0.37</td>
<td>a</td>
</tr>
<tr>
<td>4</td>
<td>O</td>
<td>-2</td>
<td>1.750</td>
<td>0.37</td>
<td>j</td>
</tr>
<tr>
<td>4</td>
<td>F</td>
<td>-1</td>
<td>1.71</td>
<td>0.37</td>
<td>b</td>
</tr>
<tr>
<td>4</td>
<td>Cl</td>
<td>-1</td>
<td>1.63</td>
<td>0.37</td>
<td>e</td>
</tr>
<tr>
<td>4</td>
<td>Cl</td>
<td>-1</td>
<td>2.13</td>
<td>0.37</td>
<td>b</td>
</tr>
<tr>
<td>4</td>
<td>C1</td>
<td>-1</td>
<td>1.822</td>
<td>0.37</td>
<td>j</td>
</tr>
<tr>
<td>6</td>
<td>O</td>
<td>-2</td>
<td>1.827</td>
<td>0.37</td>
<td>e</td>
</tr>
<tr>
<td>7</td>
<td>O</td>
<td>-2</td>
<td>1.827</td>
<td>0.37</td>
<td>e</td>
</tr>
<tr>
<td>7</td>
<td>O</td>
<td>-2</td>
<td>1.79</td>
<td>0.37</td>
<td>b</td>
</tr>
<tr>
<td>7</td>
<td>F</td>
<td>-1</td>
<td>1.72</td>
<td>0.37</td>
<td>b</td>
</tr>
<tr>
<td>7</td>
<td>Cl</td>
<td>-1</td>
<td>2.17</td>
<td>0.37</td>
<td>b</td>
</tr>
</tbody>
</table>

bvsparm.cif
Crystal structures of some complex oxides [containing two or more cation sites]
The major ternary structural families (Muller and Roy, page 3, redrawn and modified)

**Ternary structural families**

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

- **ABX₄**
  - Zircon (ZrSiO₄)
  - Scheelite (CaWO₄)
  - Barite (BaSO₄)
  - Ordered SiO₂ derivatives
  - Ordered rutile derivatives

- **A₂BX₄**
  - K₂NiF₄ (m = 1 Ruddlesden-Popper)
  - β-K₂SO₄
  - Olivine (Mg₂SiO₄ and for eg. LiFePO₄)
  - Spinel (MgAl₂O₄)
  - CaFe₂O₄
  - Phenacite (Be₂SiO₄)

- **others**
  - **ABX₂** (eg. LiCoO₂ and CuFeO₂)
  - **A₂BX₇** (eg. pyrochlore Y₂Ti₂O₇)
  - **A₂BX₅**
  - **A₂BX₆**
  - **A₃BX₅**

**Will discuss compounds in highlighted boxes:** Characterized by dense connectivity.
The $\text{ABO}_3$ structure-sorting field (from Muller and Roy)

The superscripted roman numerals indicate coordination number.
Perovskite

$\text{BaZrO}_3$

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, $\text{BO}_6$-polyhedra are depicted.
Ordered double perovskites (elpasolites), obtained through charge forking

\[ 2\text{BaZr}^{4+}\text{O}_3 = \text{Ba}_2(\text{Mg}^{2+} + \text{W}^{6+})\text{O}_6 \]

\( \text{Ba}_2\text{MgWO}_6 \)

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

\( \text{Ca}_2\text{MgWO}_6 \)

Smaller A-ions associated with tilting as in simple perovskites.
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), obtained through *charge forking*

\[
\text{CoTa}_2\text{O}_6 : 3 \times \text{TiO}_2 = \text{Ti}_3\text{O}_6; 3 \times \text{Ti}^{4+} = \text{Co}^{2+} + 2 \times \text{Ta}^{5+}
\]
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 $[\text{SrO}]\text{SrTiO}_3)_m$

$\text{Sr}_2\text{TiO}_4$

$\text{Sr}_3\text{Ti}_2\text{O}_7$

$\text{Sr}_4\text{Ti}_3\text{O}_{10}$

$m = 3$
Spinel $\text{AB}_2\text{O}_4$

MgAl$_2$O$_4$

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 $AB_2O_4$

ions on the A site
- Li
- Mg

ions on the B site
- Li
- Mg

Jahn-Teller active
- A, B

Diamagnetic
- A, B

High single-ion anisotropy
- Co II
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)

- $\text{BO}_2$ (Cdl$_2$) slabs separated by two-coordinate atoms, usually Cu$^+$ and Ag$^+$. Also unusually, Pd$^{1+}$ and Pt$^{1+}$. 
A$_2$B$_2$O$_7$ pyrochlore

\[ Y_2Ti_2O_7 = Y_2Ti_2O_6O' \]

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.
Some examples of the structural principles covered

"Here, we test rigorously and automatically all five Pauling rules for a large data set of around 5000 known oxides... We conclude that only 13% of the oxides simultaneously satisfy the last four rules, indicating their much lower predictive power than expected."
The Origin of the Ionic-Radius Ratio Rules

Not the first, and not the first ...

Quoted:

What is the origin of the ionic-radius ratio rules?

David Baer

Department of Chemistry

University of California, Los Angeles

LH-501

A few years ago, in 1924, it was proposed that the ratio of the ionic radii of two ions is given by the formula:

\[ r_1 : r_2 = L_1 : L_2 \]

where \( r_1 \) and \( r_2 \) are the ionic radii of the two ions, and \( L_1 \) and \( L_2 \) are the nuclear charges of the two ions.

This formula was derived from the Born model of the atom, which assumes that the ionic radius is proportional to the nuclear charge. However, this formula did not explain why the ratio of the ionic radii is the same for all ionic compounds.

In 1925, Pauling proposed a new theory of ionic bonding, which explained why the ratio of the ionic radii is the same for all ionic compounds.

According to Pauling, the ionic radius is determined by the electrostatic interaction between the positive and negative ions. The ionic radius is proportional to the nuclear charge and inversely proportional to the square of the distance between the ions.

Pauling's theory was based on the idea that the electrostatic interaction between the ions is the primary factor determining the ionic radius. This theory explained why the ratio of the ionic radii is the same for all ionic compounds, because the electrostatic interaction is the same for all ionic compounds.

Since then, many other theories have been proposed to explain the ionic radius, but Pauling's theory remains the most widely accepted theory today.

https://doi.org/10.1021/ed100258f
Letter from Pauling to W.L. Bragg. October 22, 1928:

“The last of August I sent two papers to the Editor of the Journal of the American Chemical Society. In one of them are rules governing the structures of complex crystals. I realize that nothing I have done is highly original - in particular was I gratified to read in your letter a statement of the rule governing the sharing of polyhedron elements.”
SiO$_2$ (low quartz, $P3_22_1$)
Berlinite, AlPO₄, obtained structurally by forking cation charges in SiO₂
IPO$_4$: In$^{3+}$ is too large for 4-coordination
Pyrochlore $\text{Cd}_2\text{Ta}_2\text{O}_7$: The Bond Valence Map

[Diagram showing the bond valence map of the pyrochlore $\text{Cd}_2\text{Ta}_2\text{O}_7$ structure, with bond valences indicated by fractions next to the bond connections.]