Oxide crystal structures: The basics

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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

Ionic radii and Pauling's first rule (the radius ratio rule)

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 AO_2 compounds below. MRR below is the *mimimum radius ratio*.

Compound	r_C (Å)	$r_C + r_O$ (Å)	r_C/r_O	Coordination	MRR
CO_2	-0.19(?)	1.16 (exp.)	?	2	
SiO_2	0.26	1.61	0.19	4	0.225
TiO_2	0.605	1.955	0.45	6	0.414
CeO_2	0.97	2.32	0.72	8	0.732

Pauling, The Nature of the Chemical Bond, 3rd Edn., Cornell University Press, Ithaca 1960

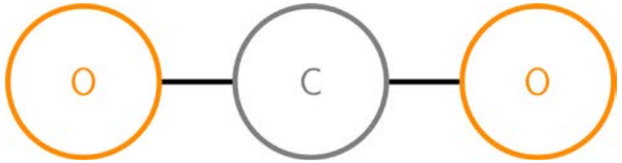
Crystal structures of simple oxides [containing a single cation site]

Crystal structures of simple oxides [containing a single cation site]

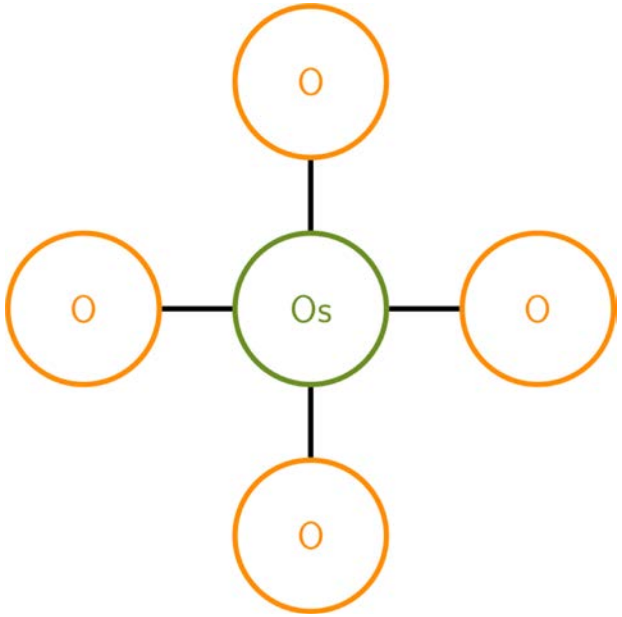
N.B.: CoO is simple, Co_3O_4 is not. $ZnCo_2O_4$ is certainly not !
Co_3O_4 and $ZnCo_2O_4$ are complex oxides.

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

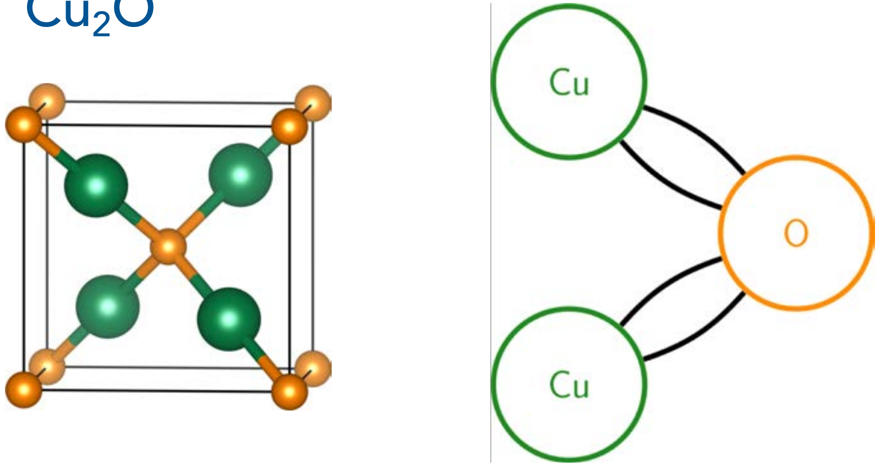


OsO_4: The structure comprises isolated tetrahedra (molecular). The graph is below:
Each Os connected to 4 O and each O to 1 Os



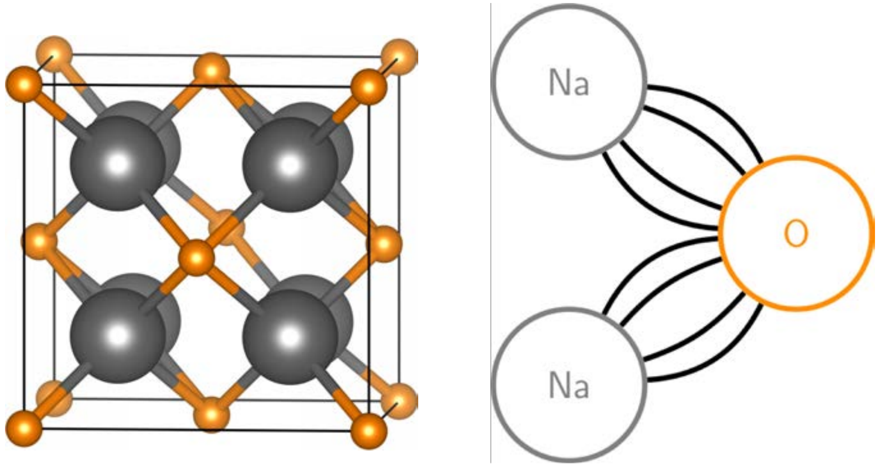
Crystal structures of simple oxides of monovalent ions: A_2O

Cu_2O



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

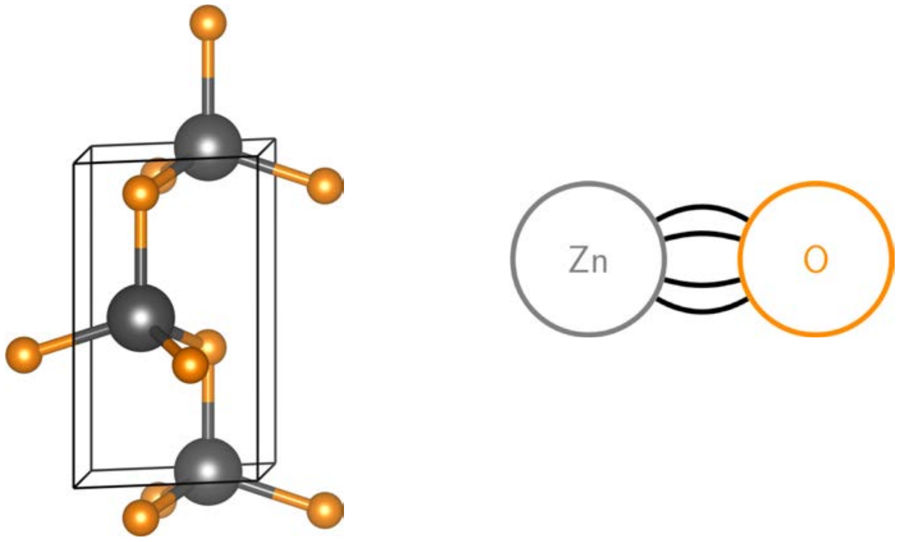
Na_2O (anti-fluorite)



4-coordination for Na^+ and 8-coordination for O^{2-} are unusual.

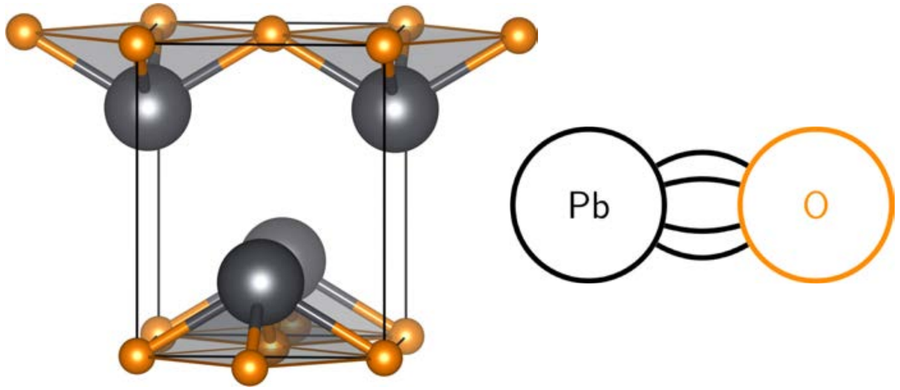
Crystal structures of simple oxides of divalent ions: *A*O

ZnO (wurtzite), sp^3

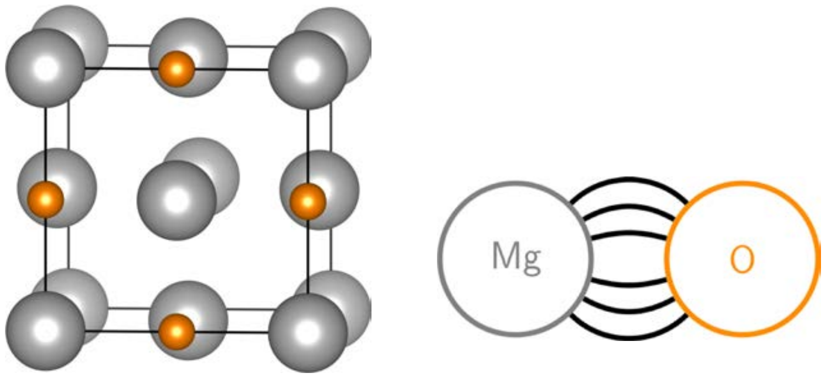


PbO (litharge), lone pairs

Pb^{2+} is $[Xe]4f^{14}5d^{10}6s^{2}6p^{0}$



MgO (rock-salt)

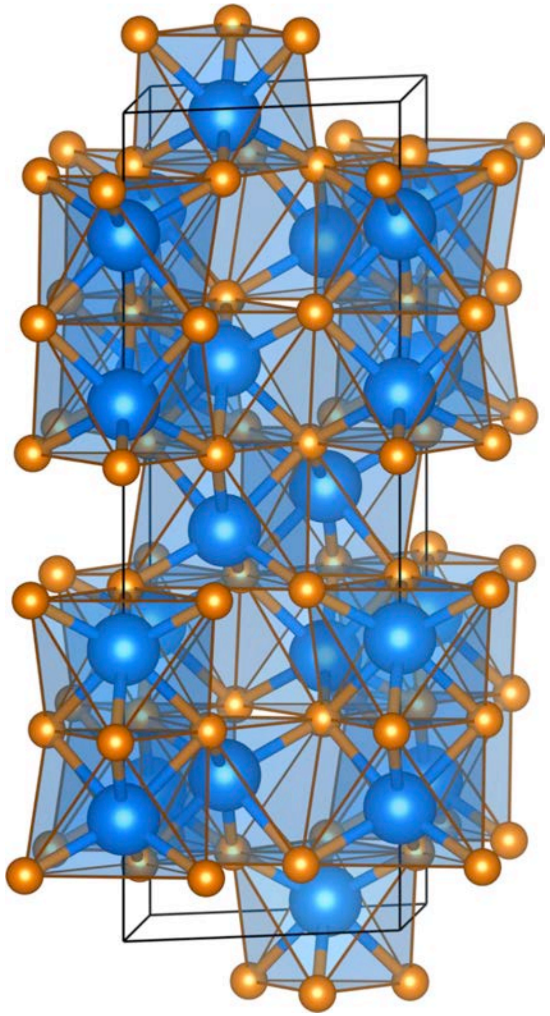


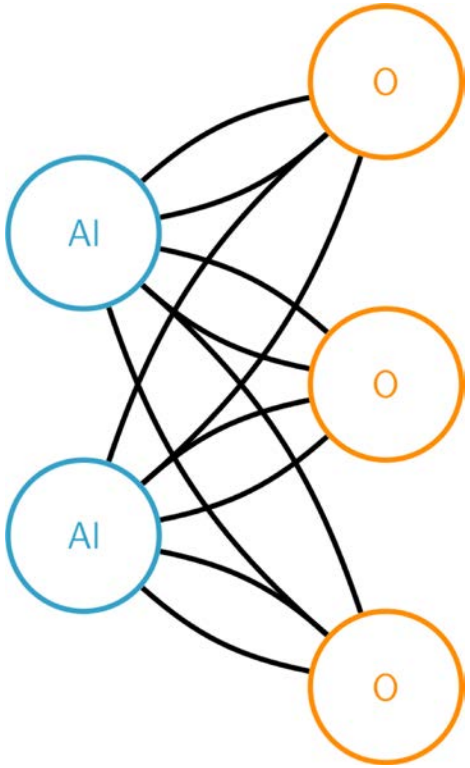
Ubiquitous for *A*O oxides including transition metals (distorted for CuO and NbO).

Insulators, metals (TiO), magnetic, …

Crystal structures of simple oxides. Al_2O_3 as an example of a sesquioxide

α-Al_2O_3 (corundum)





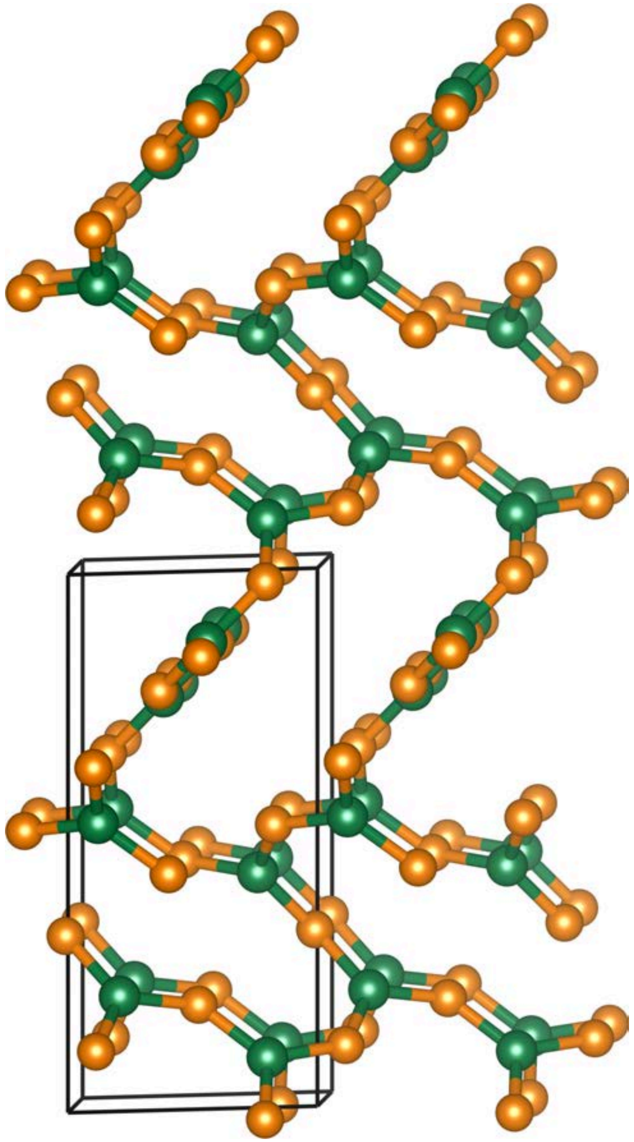
Also the structure of Cr_2O_3 and Fe_2O_3.

Ga_2O_3 does funny things.

In_2O_3 is different (bixbyite).

B_2O_3 (chiral, $P3_12_1$)

B_2O_3 (hugely important for glass industry).



NB: This structure is not in scale with the others.

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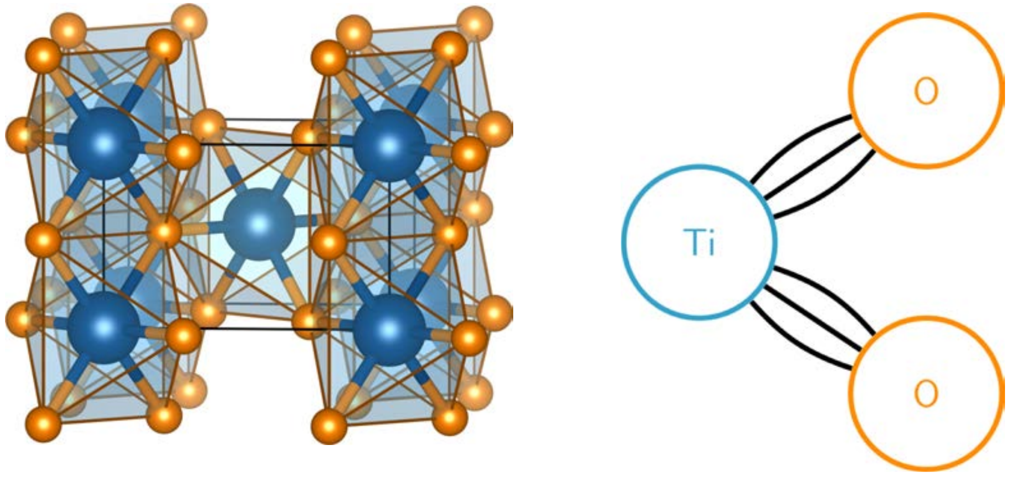
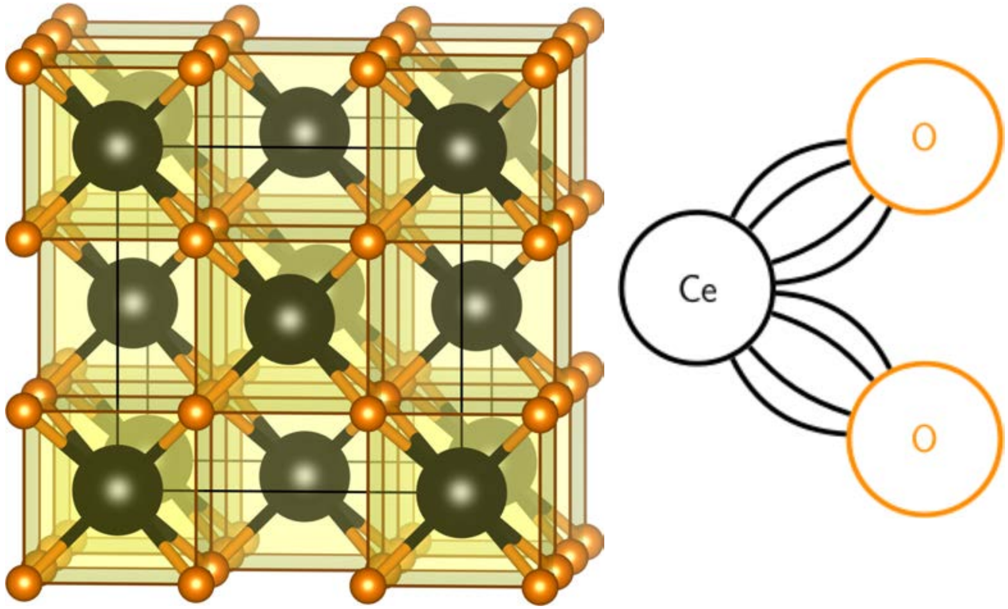
Crystal structures of simple oxides of tetravalent ions: AO_2

TiO_2 (rutile)



CeO_2 (fluorite)



TiO_2 also crystallizes as anatase and brookite.

SiO_2 takes on this structure, and can be quenched to it, (stishovite) under pressure.

Also the structure of ThO_2, and of ZrO_2 and HfO_2 at elevated temperatures.

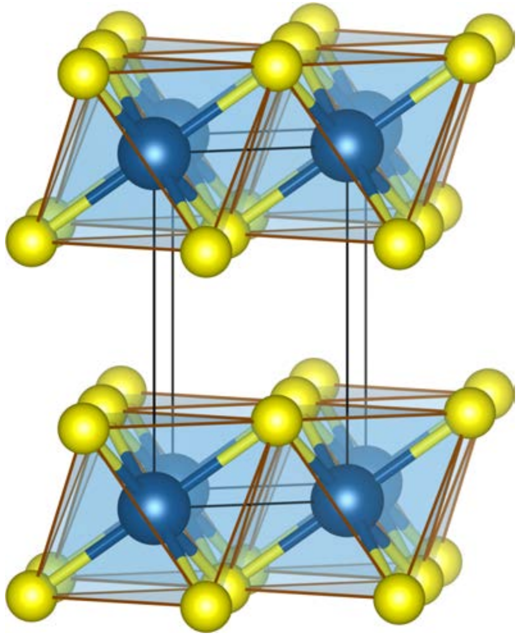
Ordered variants abound.

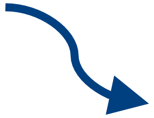
The radius ratio rule at play:

CO_2	Linear
SiO_2	Tetrahedral
TiO_2	Octahedral
HfO_2	7-coordinate
CeO_2	Cubic

Oxides versus sulfides: TiS_2

1T–TiS_2



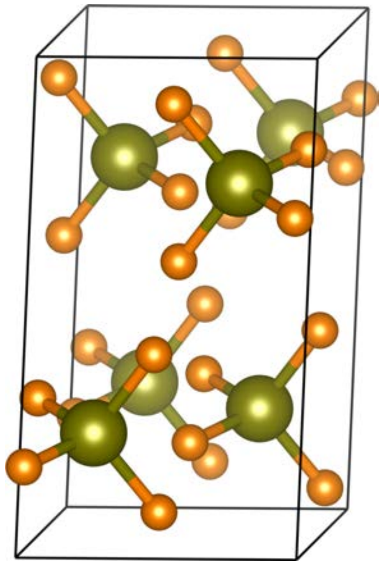


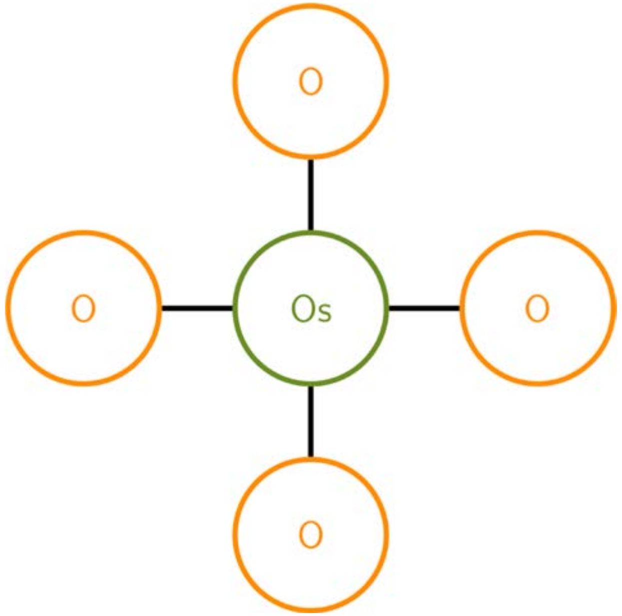
van der Waals gap (unlikely in oxides or fluorides, but occurs frequently in hydroxides)

This is the CdI_2 structure.

Crystal structures of an oxide with an octavalent ion: OsO_4

OsO_4





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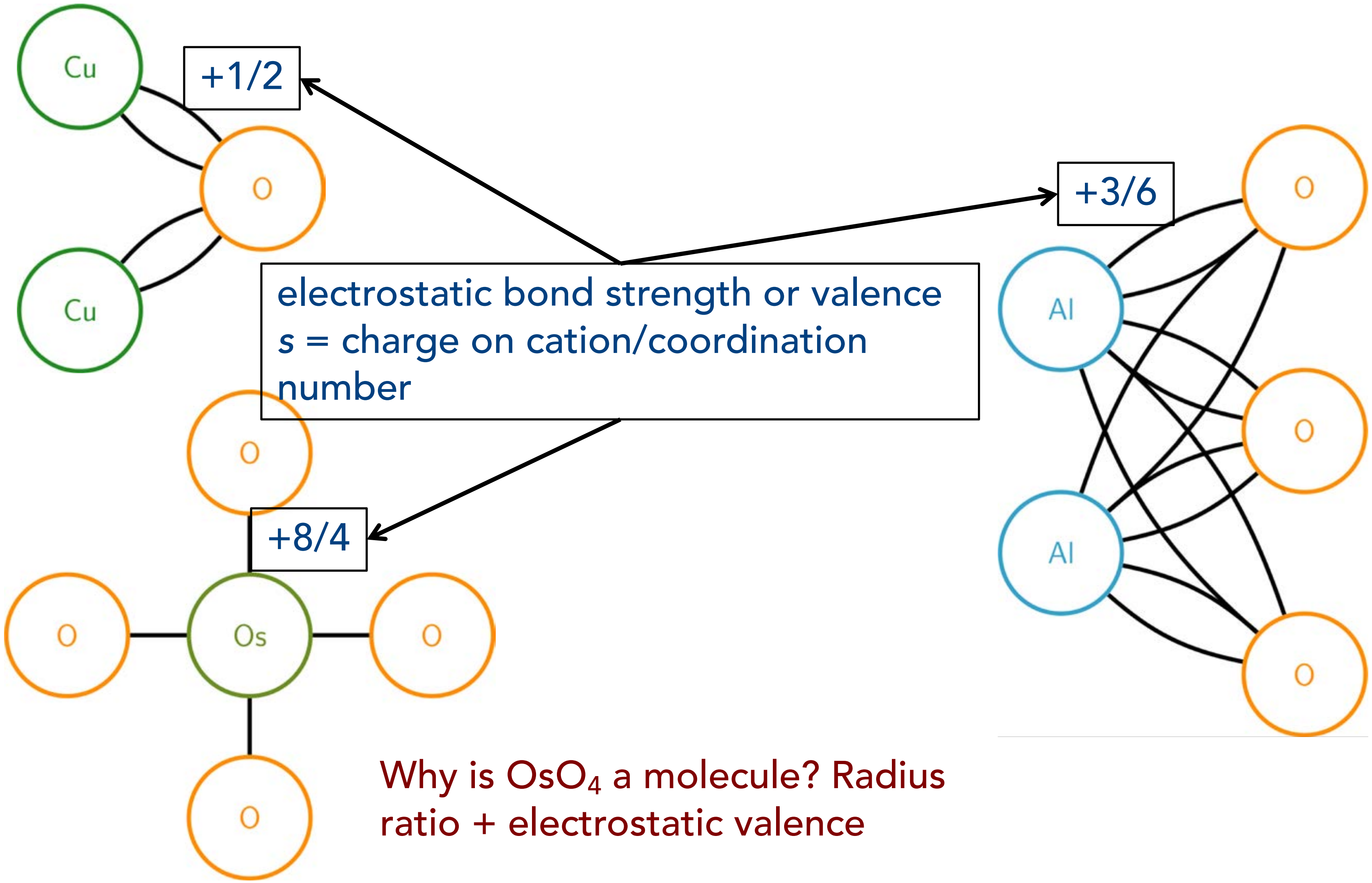
Pauling's second rule: The electrostatic valence rule

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



+1/2

+3/6

electrostatic bond strength or valence
s = charge on cation/coordination number

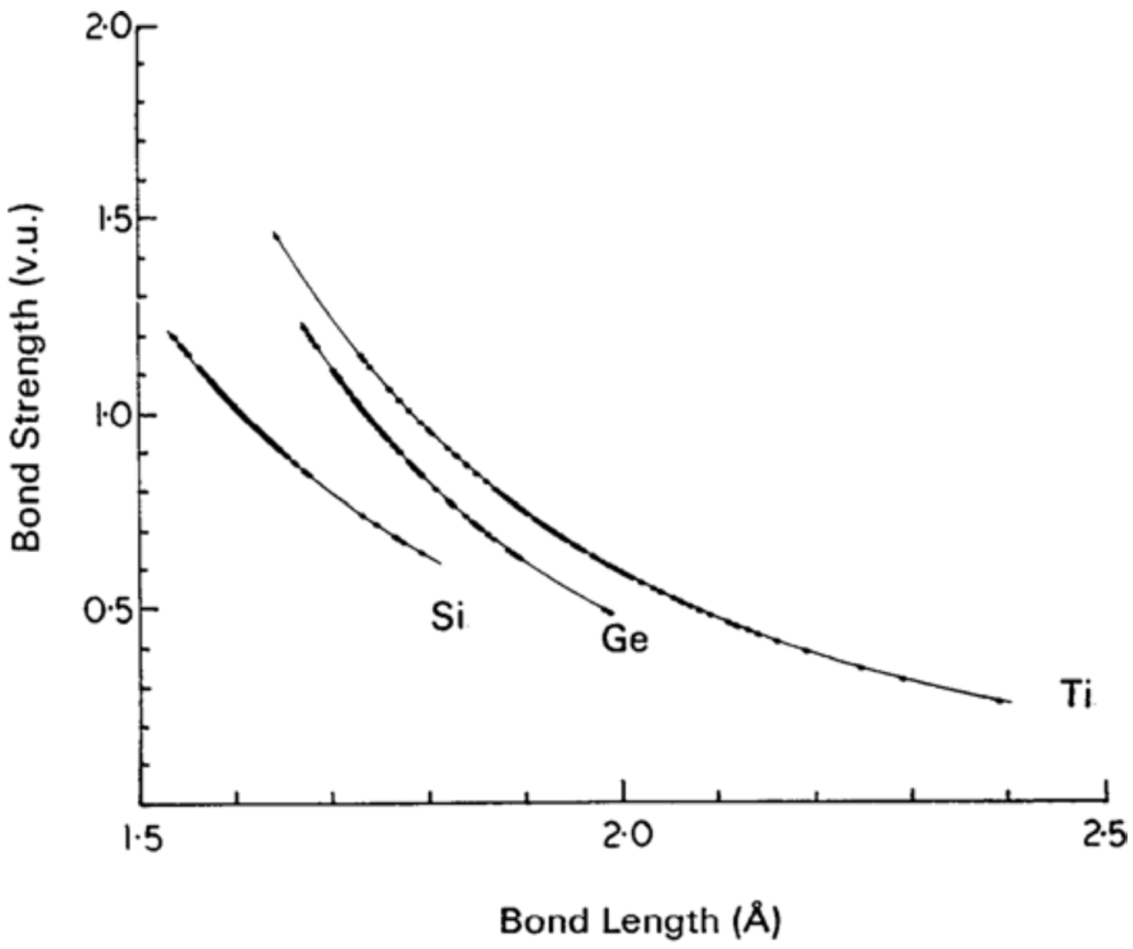
+8/4

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

Pauling, The Nature of the Chemical Bond, 3rd Edn., Cornell University Press, Ithaca 1960

Electrostatic valence and bond 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*



Brown, Shannon, Empirical bond-strength-bond-length curves for oxides, *Acta Cryst. A* **29** (1973) 266–281

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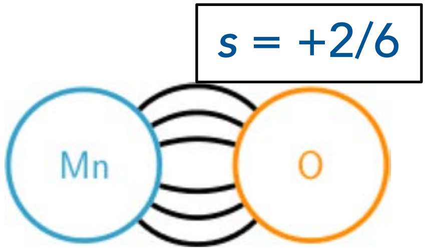
Electrostatic valence and bond valence

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

When all *s* are calculated: $\sum_{\mathrm{CN}} s =$ valence of the ion



For Mn^{2+}–O^{2-}, $R_0 = 1.790$ Å, $B = 0.37$ Å.

This means $R = 2.20$ Å.
experiment: 2.22 Å

Brown, Shannon, Empirical bond-strength-bond-length curves for oxides, *Acta Cryst. A* **29** (1973) 266–281.

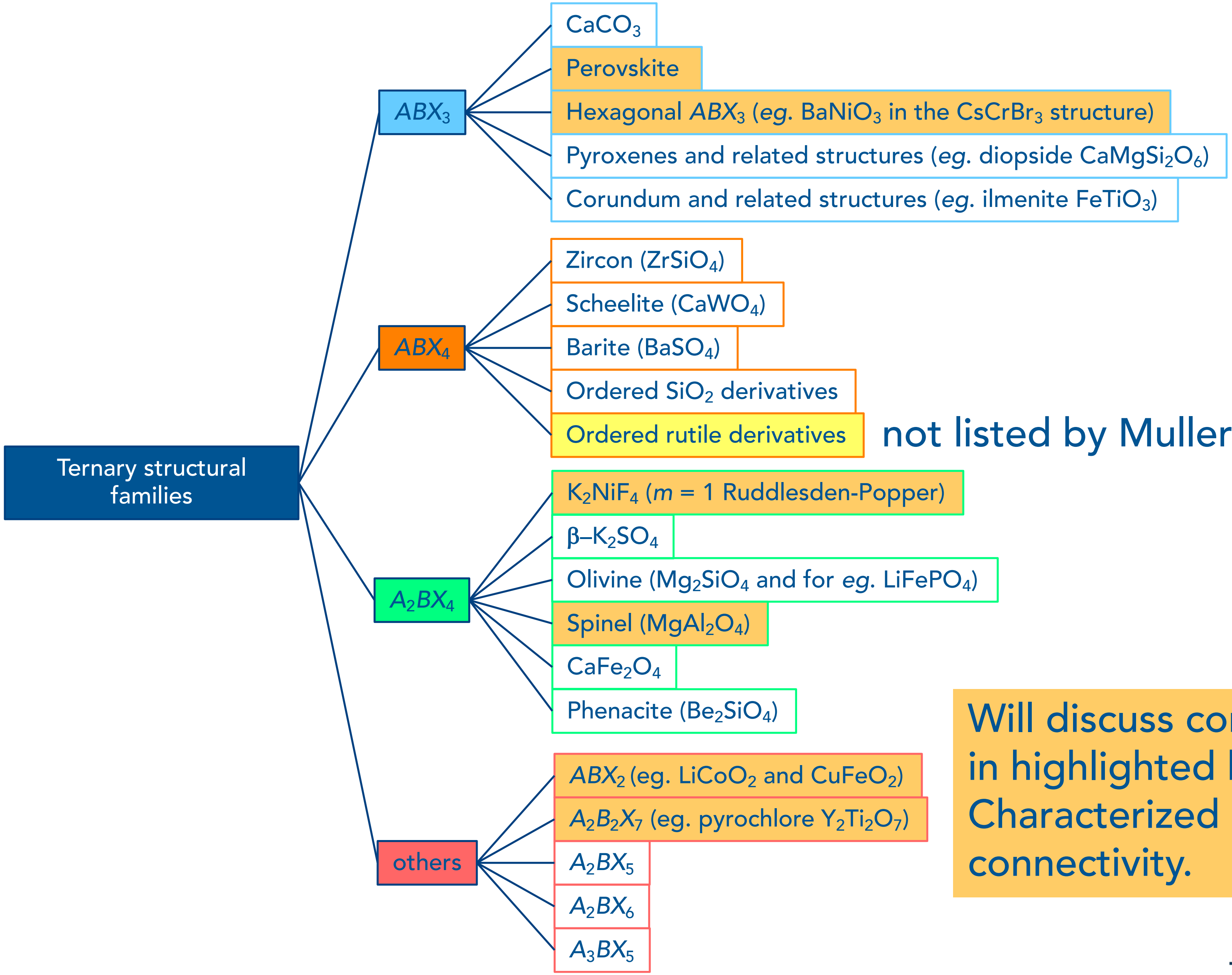
Electrostatic valence and bond valence: Parameters for Mn

```
Mn 2   O  -2    1.790    0.37     a
Mn 2   O  -2    1.765    0.37     j
Mn 2   S  -2    2.22     0.37     e
Mn 2   F  -1    1.698    0.37     a
Mn 2   Cl -1    2.133    0.37     a
Mn 2   Br -1    2.34     0.37     e
Mn 2   I  -2    2.52     0.37     e
Mn 2   N  -3    1.849    0.37     j
Mn 2   N  -3    1.65     0.35     e
Mn 3   O  -2    1.760    0.37     a
Mn 3   O  -2    1.732    0.37     j
Mn 3   F  -1    1.66     0.37     b
Mn 3   Cl -1    2.14     0.37     b
Mn 3   N  -3    1.837    0.37     j
Mn 4   O  -2    1.753    0.37     a
Mn 4   O  -2    1.750    0.37     j
Mn 4   F  -1    1.71     0.37     b
Mn 4   F  -1    1.63     0.37     e
Mn 4   Cl -1    2.13     0.37     b
Mn 4   N  -3    1.822    0.37     j
Mn 6   O  -2    1.79     0.37     e
Mn 7   O  -2    1.827    0.37     e
Mn 7   O  -2    1.79     0.37     b
Mn 7   F  -1    1.72     0.37     b
Mn 7   Cl -1    2.17     0.37     b
```

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
  - ABX_3
    - $CaCO_3$
    - Perovskite
    - Hexagonal ABX_3 (*eg.* $BaNiO_3$ in the $CsCrBr_3$ structure)
    - Pyroxenes and related structures (*eg.* diopside $CaMgSi_2O_6$)
    - Corundum and related structures (*eg.* ilmenite $FeTiO_3$)
  - ABX_4
    - Zircon ($ZrSiO_4$)
    - Scheelite ($CaWO_4$)
    - Barite ($BaSO_4$)
    - Ordered SiO_2 derivatives
    - Ordered rutile derivatives
  - A_2BX_4
    - K_2NiF_4 (m = 1 Ruddlesden-Popper)
    - β–K_2SO_4
    - Olivine (Mg_2SiO_4 and for *eg.* $LiFePO_4$)
    - Spinel ($MgAl_2O_4$)
    - $CaFe_2O_4$
    - Phenacite (Be_2SiO_4)
  - others
    - ABX_2 (eg. $LiCoO_2$ and $CuFeO_2$)
    - $A_2B_2X_7$ (eg. pyrochlore $Y_2Ti_2O_7$)
    - A_2BX_5
    - A_2BX_6
    - A_3BX_5

not listed by Muller and Roy

Will discuss compounds in highlighted boxes: Characterized by dense connectivity.

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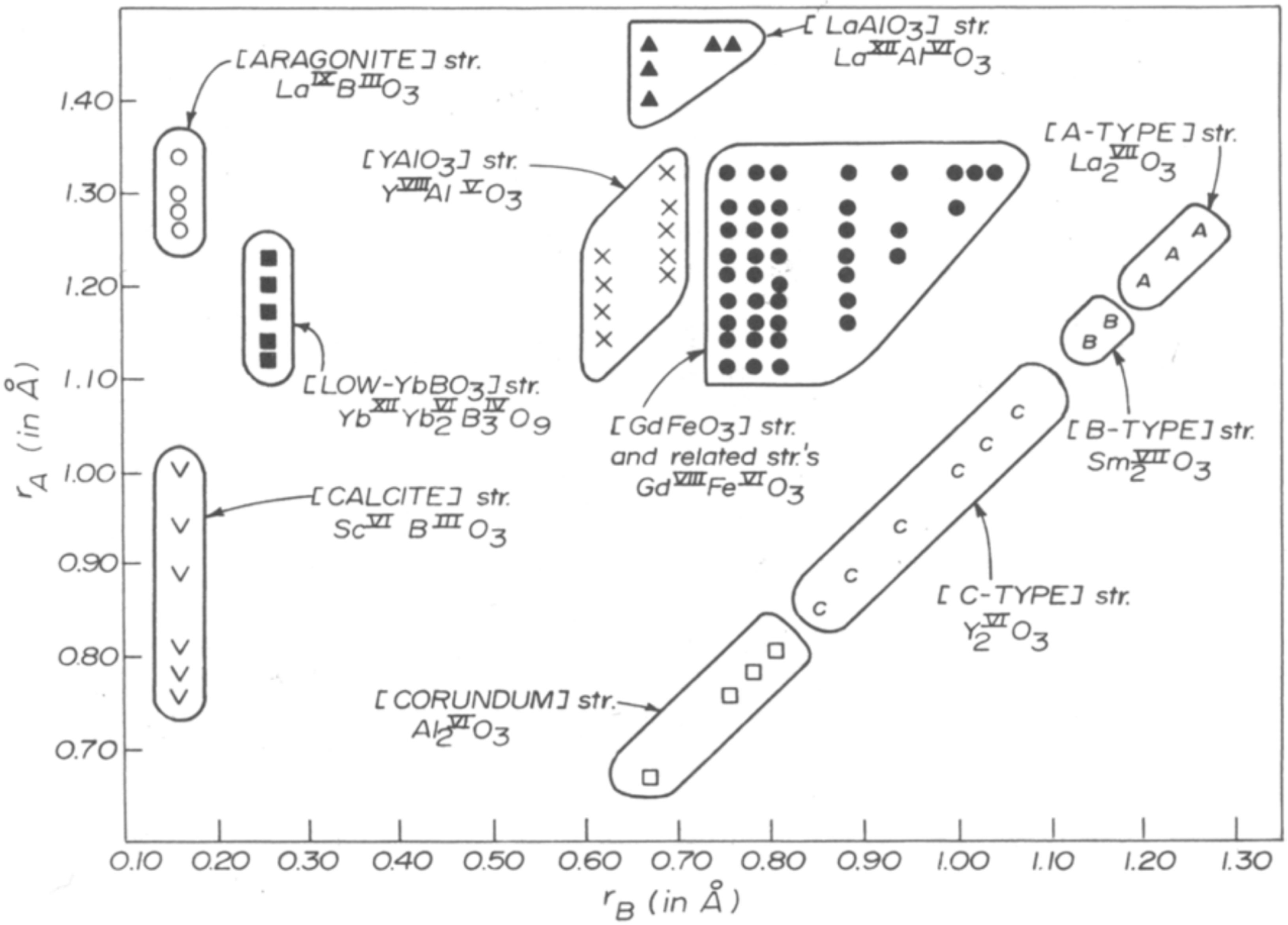
The *ABO*$_3$ structure-sorting field (from Muller and Roy)



The superscripted roman numerals indicate coordination number.

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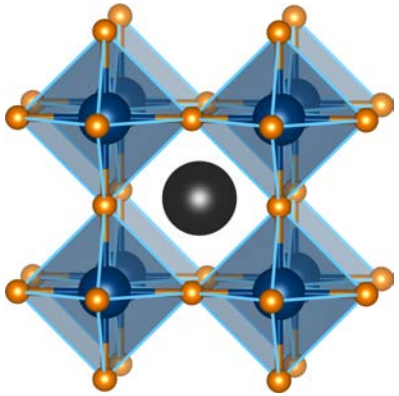
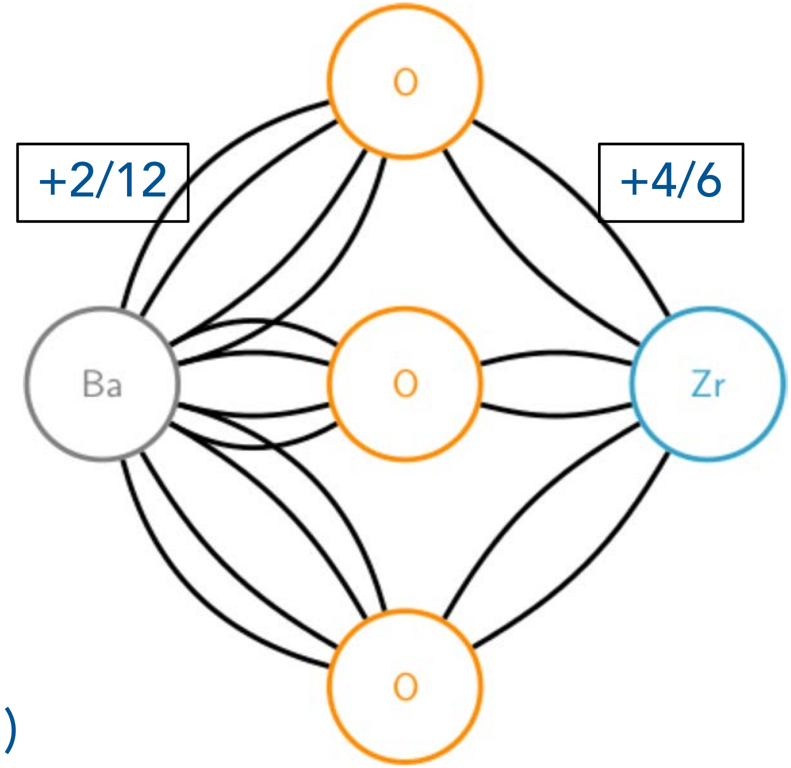
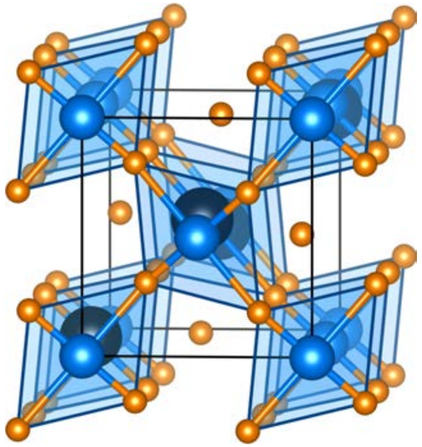
Perovskite

$BaZrO_3$





$LaMnO_3$ *Pnma*
(Jahn-Teller distorted)



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

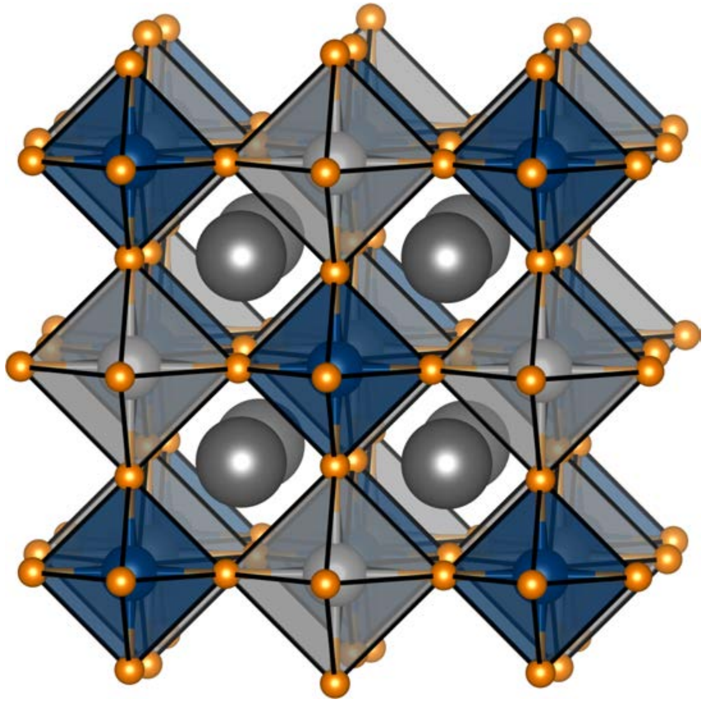
This is the most common perovskite space group.

In the next so many structures, BO_6-polyhedra are depicted.

Ordered double perovskites (elpasolites), obtained through *charge forking*

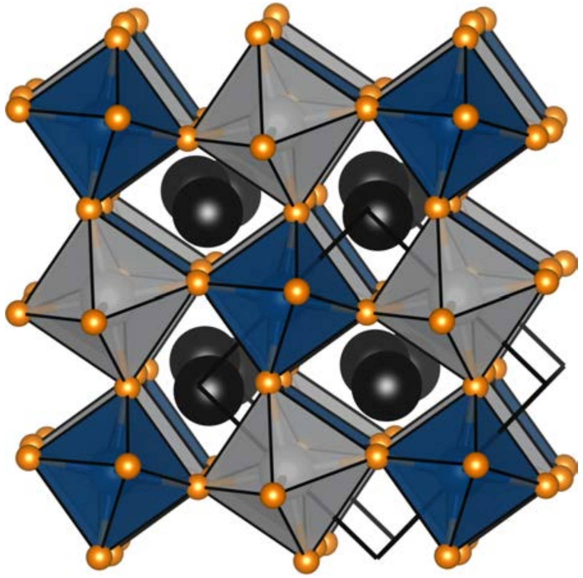
$2BaZr^{4+}O_3 = Ba_2(Mg^{2+} + W^{6+})O_6$

Ba_2MgWO_6



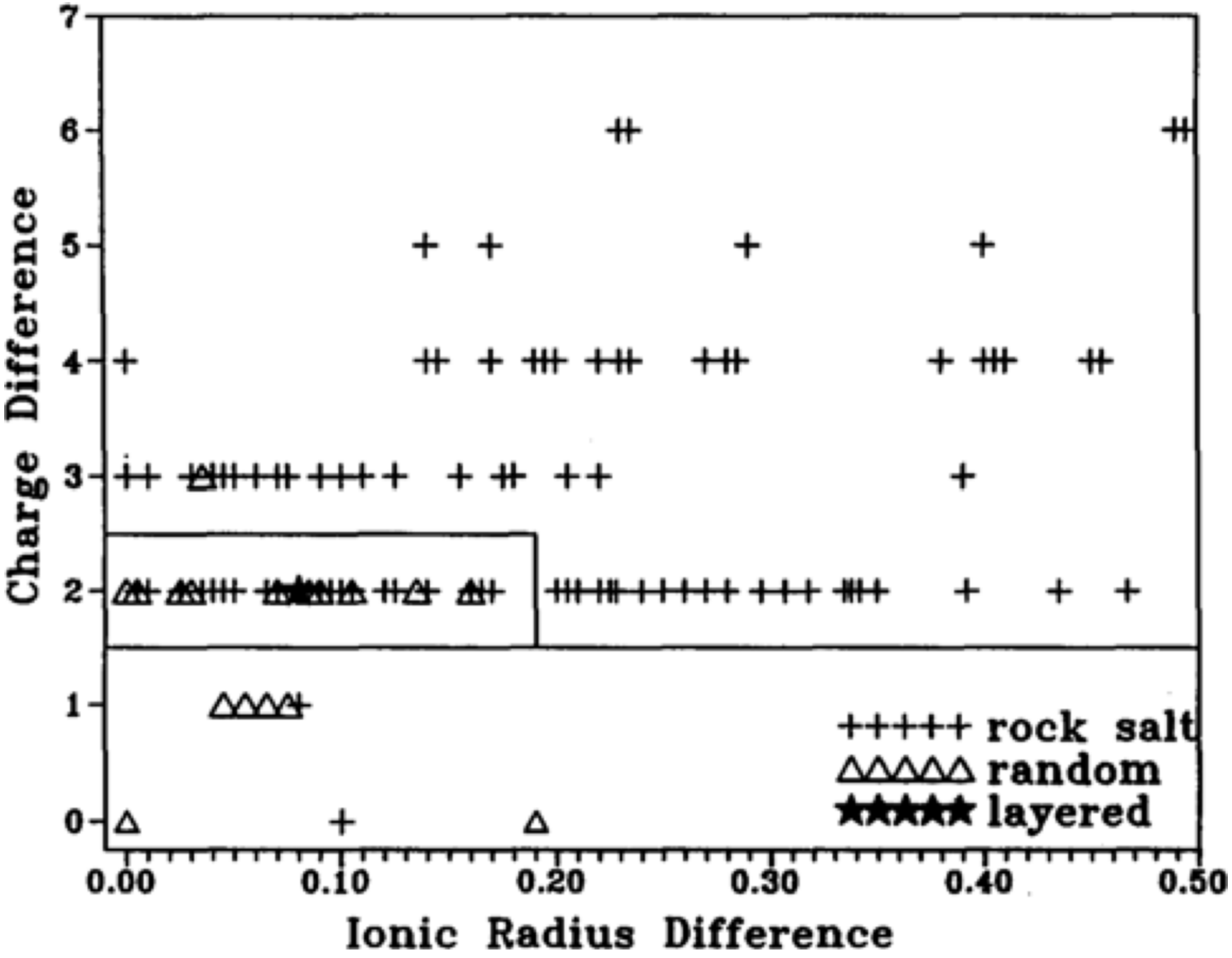
Rock-salt like ordering of dissimilar octahedra. Space group same as rock-salt: *Fm–3m*

Ca_2MgWO_6



Smaller *A*-ions associated with tilting as in simple perovskites.

The double perovskite field: Charge and radius



Anderson, Greenwood, Poeppelmeier, *Prog. Solid State Chem.* **22** (1993) 197–233.

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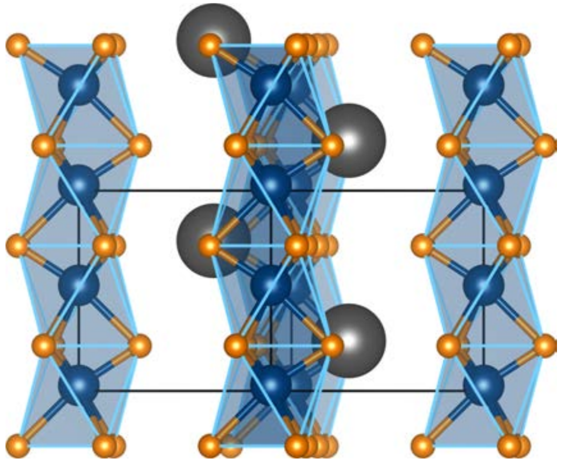
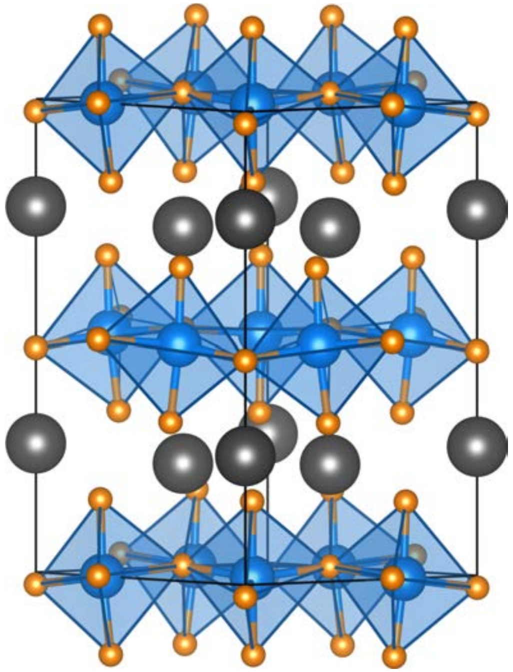
Hexagonal ABO_3 structures

$BaNiO_3$

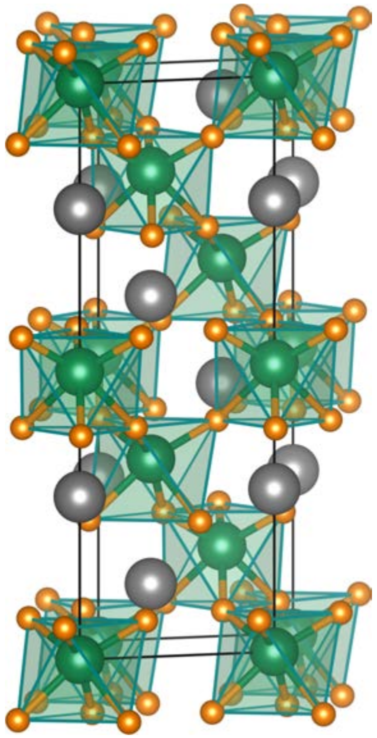


Ferroelectric $YMnO_3$ (“$YAlO_3$”)



Unusual 5-fold coordination (trigonal bibyramid) of MnO_5

$LiNbO_3$ (ferroelectric $R3c$)



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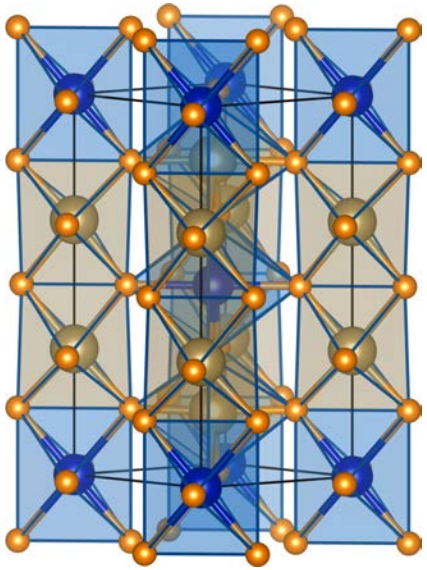
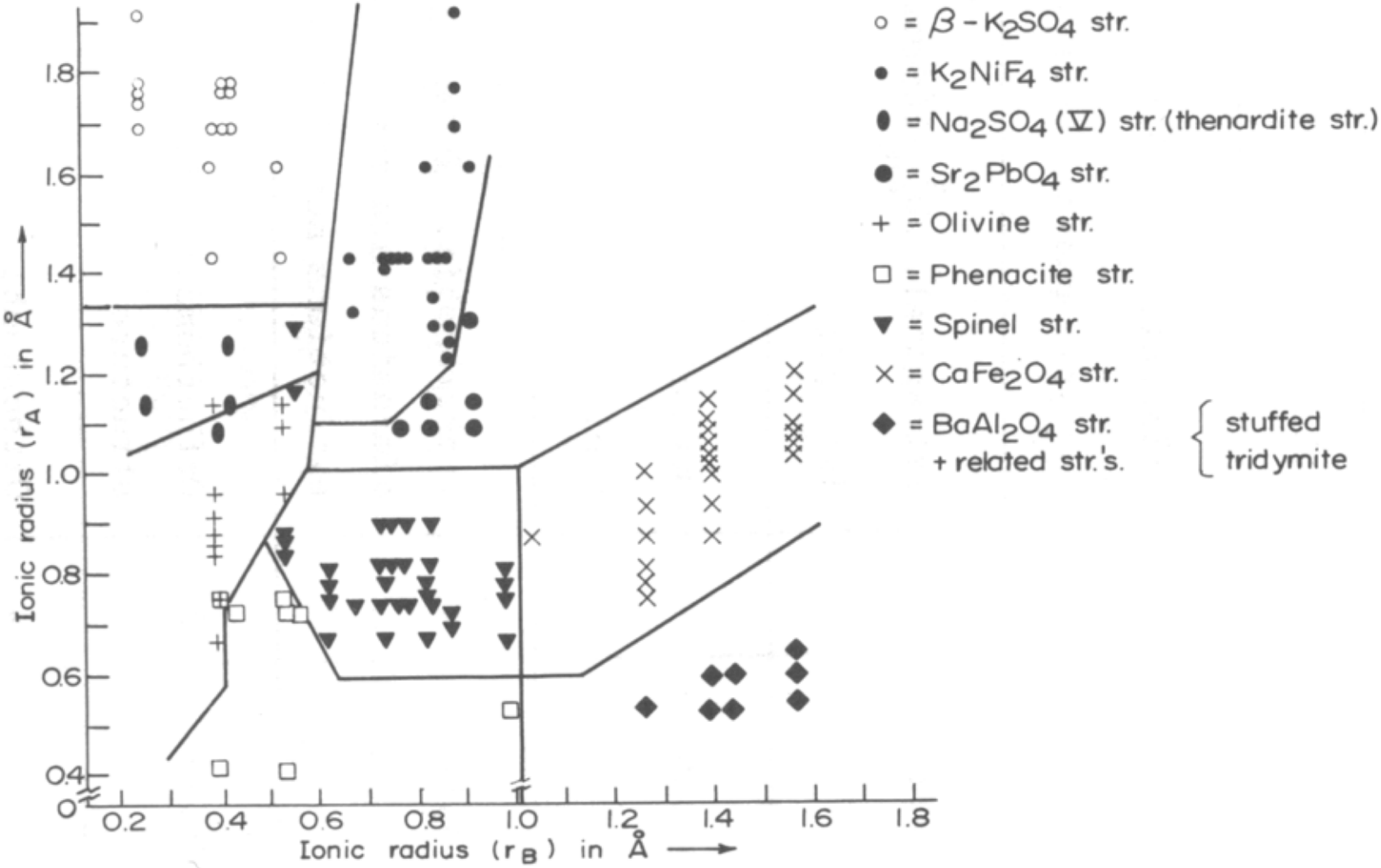
Ordered rutiles (the trirutile), obtained through *charge forking*

$CoTa_2O_6$: $3 \times TiO_2 = Ti_3O_6$; $3 \times Ti^{4+} = Co^{2+} + 2 \times Ta^{5+}$



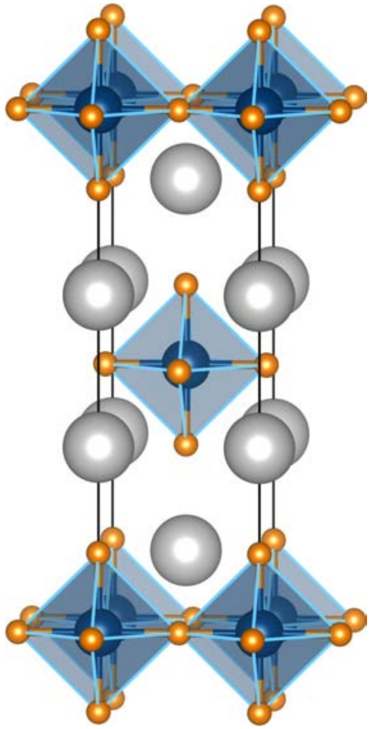
The A_2BO_4 structure-sorting field (from Muller and Roy)



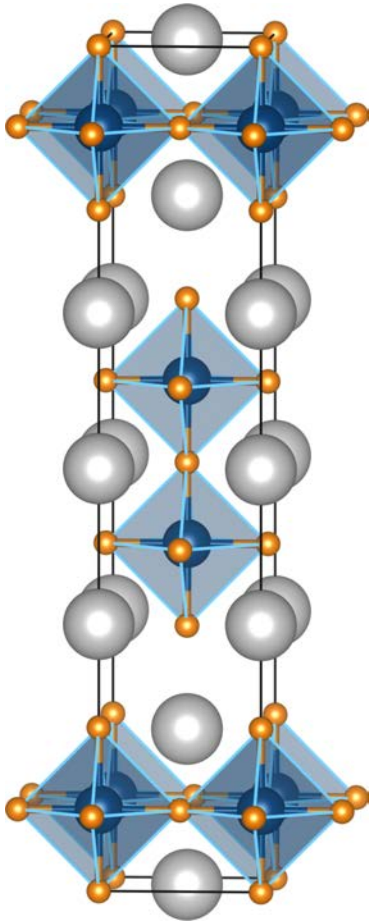
The superscripted roman numerals indicate coordination number.

K_2NiF_4 and Ruddlesden-Popper (m = 1, 2, 3)
General formula $[SrO][SrTiO_3]_m$

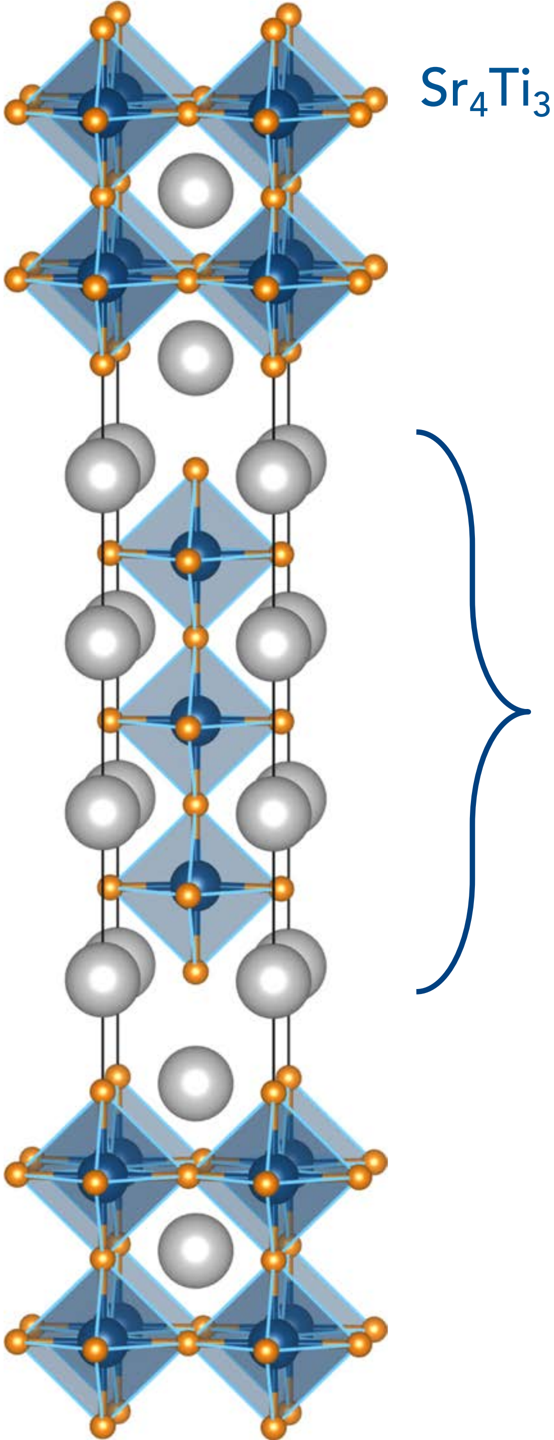
Sr_2TiO_4



$Sr_3Ti_2O_7$

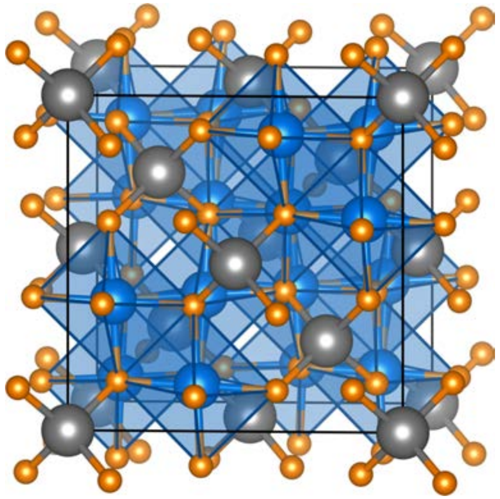


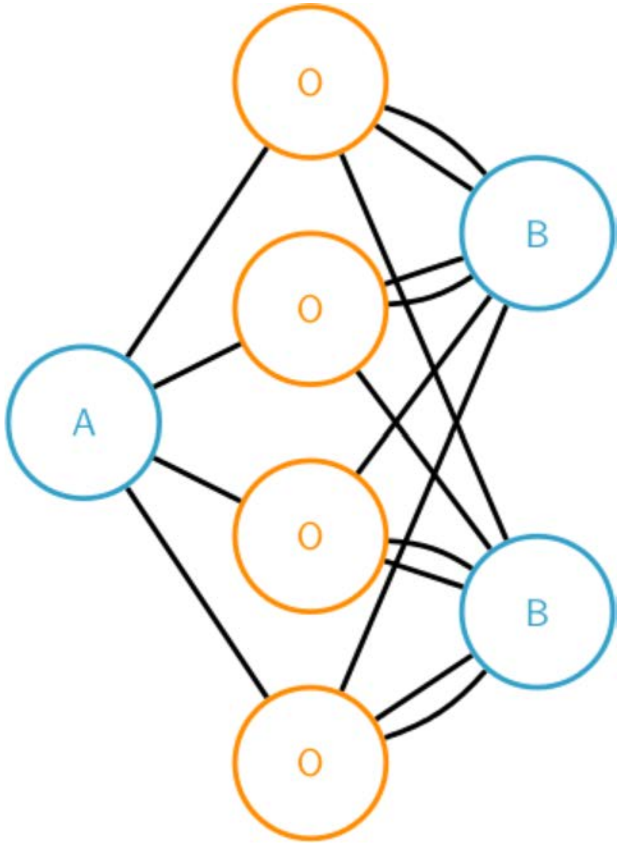
$Sr_4Ti_3O_{10}$



Spinel AB_2O_4

$MgAl_2O_4$



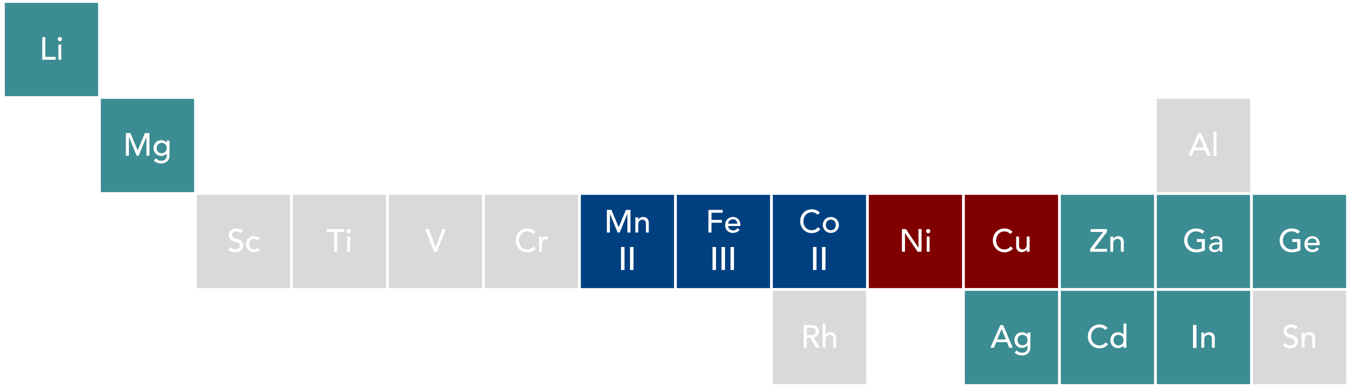


Ubiquitous structure when ions have similar sizes, around 0.6 Å.
A is tetrahedrally coordinated, and *B* octahedral (actually with a slight trigonal distortion).

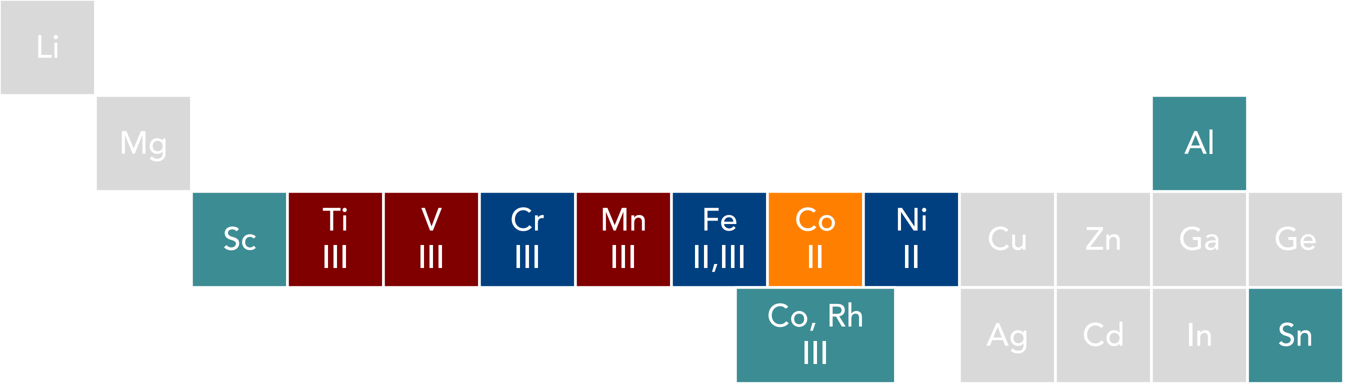
In general, lower oxidation states and smaller bandwidths than in perovskites.

Spinel AB_2O_4

ions on the *A* site



ions on the *B* site



A,*B* Jahn-Teller active

A,*B* Diamagnetic

Co II High single-ion anisotropy

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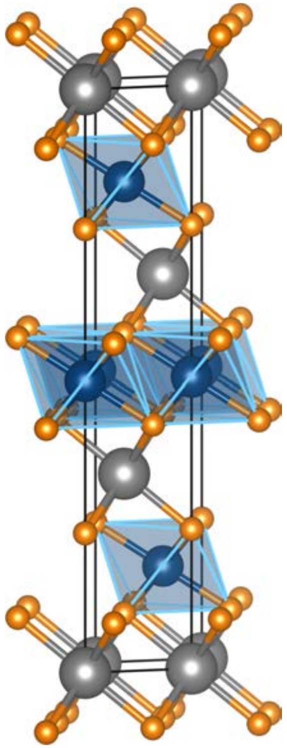
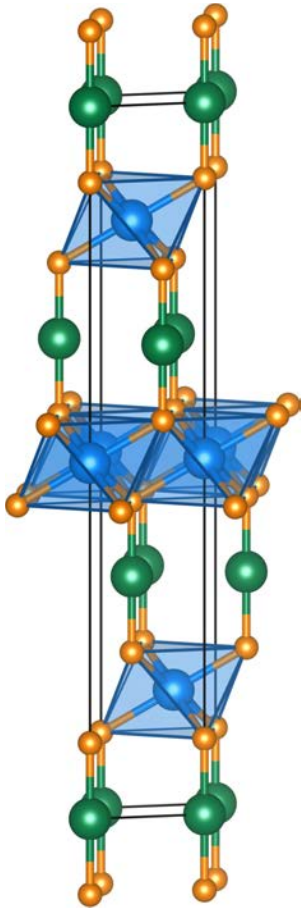
Some ABO_2 structures: Highly dense in-plane, and frequently metallic

$LiCoO_2$ (ordered rock-salt)



111-ordered with alternating octahedral LiO_6 and CoO_6 stacking

3*R*–$CuFeO_2$ (delafossite)



BO_2 (CdI_2) slabs separated by two-coordinate atoms, usually Cu^+ and Ag^+. Also unusually, Pd^{1+} and Pt^{1+}.

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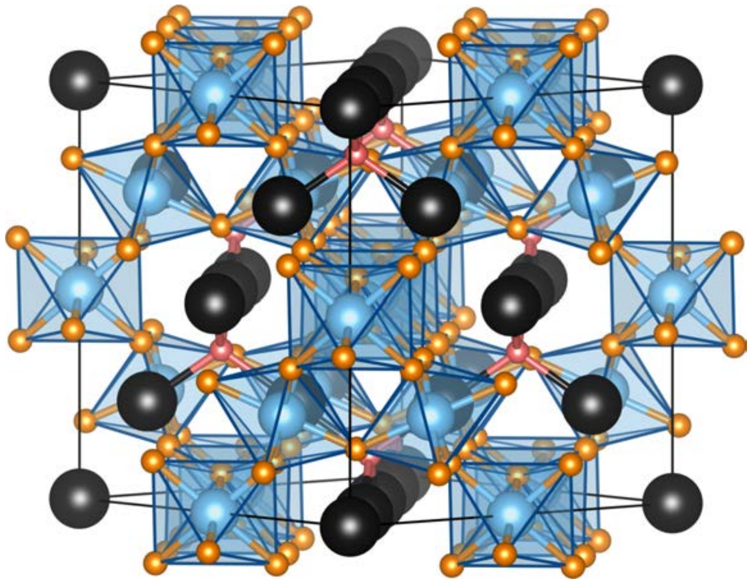
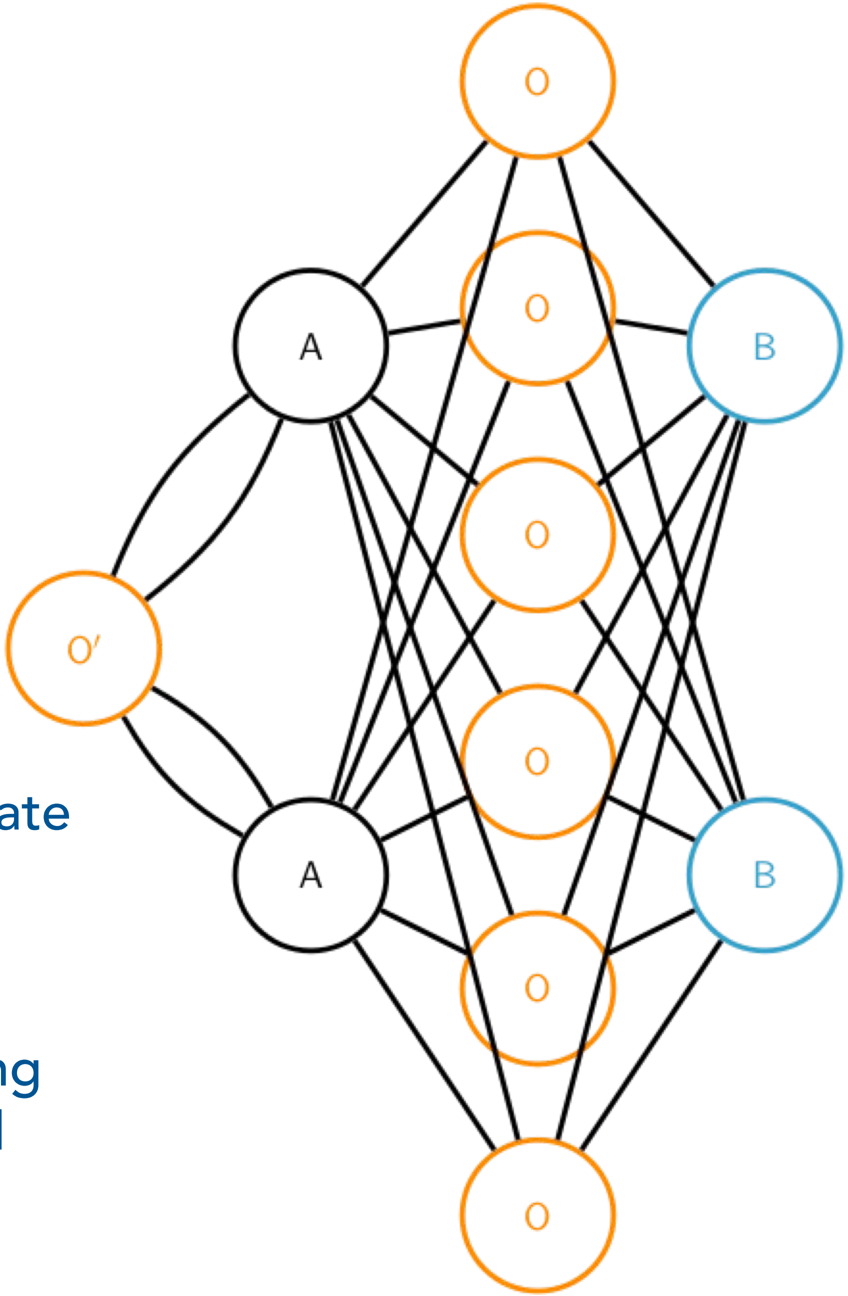
$A_2B_2O_7$ pyrochlore

$Y_2Ti_2O_7 = Y_2Ti_2O_6O'$



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.



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Some examples of the structural principles covered

Research Articles

Angewandte Chemie

Solid-State Chemistry

International Edition: DOI: 10.1002/anie.202000829
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The Limited Predictive Power of the Pauling Rules**

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Abstract: *The Pauling rules have been used for decades to rationalise the crystal structures of ionic compounds. Despite their importance, there has been no statistical assessment of the performances of these five empirical rules so far. Here, we rigorously and automatically test all five Pauling rules for a large data set of around 5000 known oxides. We discuss each Pauling rule separately, stressing their limits and range of application in terms of chemistries and structures. We conclude that only 13 % of the oxides simultaneously satisfy the last four rules, indicating a much lower predictive power than expected.*

Introduction

Understanding and predicting the crystal structure of inorganic materials is an important goal of chemistry. In 1929, Linus Pauling published a series of five empirical rules rationalising inorganic crystal structures.[1] The Pauling rules apply to ionic compounds and describe what are the preferred local environments of a cation and how these environments connect to each other. These rules have become a cornerstone of solid-state chemistry and remain the main empirical theory rationalising crystal-structure stability. Pauling developed these five rules by combining his knowledge of inorganic crystal structures and simple electrostatic arguments. Though, in response to observed deviations, these rules have been slightly improved over the years, nowadays they remain widely used in their original form.[2–8]

The Pauling rules are not laws of nature. It is thus expected that they are not always correct. While previous studies have looked at their application on specific chemistries (for example, silicates) or at their fundamental orbital origin,[9–13] they have not yet been assessed statistically on a large scale. The absence of such a rigorous assessment of the validity of the Pauling rules inhibits their use for true prediction and prevents the development of improved and alternative rules. Building on recent advances in crystal-structure-analysis tools including the automatic identification of local environments and their connectivity,[14–16] we report here on the first statistical evaluation of the Pauling rules on several thousands of compounds. Our work shines light on their strengths and limits, enables a more cautious use of them and offers a first necessary step towards their future improvement.

Results and Discussion

Our analysis relies on the use of a tool for automatic local-environment detection on a set of oxides coming from the Inorganic Crystal Structure Database (ICSD) and present in the Materials Project database (see Supporting Information for a detailed description).[17] We focused on oxides as they are ionic enough for the Pauling rules to be applicable and because the large number of oxides known makes it possible to obtain a large data set and hence good statistics. In total, more than 5000 oxides (a subset of the structures from Ref. [14]) are considered. The paper presents and discusses the performance of each of the five rules individually and wraps up by commenting on the overall quality of the five rules taken altogether.

Rule 1: Radius-Ratio Rule

The first rule states that "[…] The coordination number of the cation [is determined] by the radius ratio [of cation and anion]."[1] This rule is based on a hard-sphere model of the atoms as shown in Figure 1 a. A coordination environment is stable only if the radius ratio of cation and anion falls within the geometrically derived stability window of this environment.

While several atomic- and ionic-radii schemes were developed after Pauling's original work, we used the simplest here—Pauling's univalent radii.[7] We found a rather unsatisfactory agreement with the first rule in our data set. Only 66 % of the tested local environments agreed with the expectation from Pauling's first rule. Figure 1 b shows an analysis of the fulfilment of the rule by element. By design, the first rule can only work for elements presenting a low diversity in local environments (for instance, Si, P, and S are mainly tetrahedral).[14] In contrast, many of the alkali and alkaline-earth metals and some transition metals are found in a variety of environments and present strong deviations from the rule. We link the failure of the first rule to an inadequate

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Not the first, and not the first …

History of Chemistry

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The Origin of the Ionic-Radius Ratio Rules

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Question

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

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Answer

Generally speaking, the ionic-radius ratio rules are either incorrectly attributed to Linus Pauling in the chemical literature *(1)* or to Victor Goldschmidt in the geochemical literature *(2)*. In actual fact, they were first proposed within the context of the coordination chemistry literature by the Austrian chemist, Gustav F. Hüttig, in a brief note published in 1920 in which he reported the R_-/R_+ ratio for possible geometries corresponding to coordination numbers of 2, 3, 4, 5, 6, 8, 12, and 20 *(3)*. Two years later the German chemist, Alfred Magnus, gave a more detailed treatment explicitly linked to Walther Kossel's recently proposed electrostatic screening theory of complex ion formation and also included values for various alternative coordination geometries, such as square planar versus tetrahedral and hexagonal planar versus octahedral *(4, 5)*. In 1923, Hüttig's original results were cited by Max Lembert in a discussion of the structures of complex hydrates *(6)*, and the following year they were incorporated into the second edition of Rudolf Weinland's textbook, *Einfuhrung in die Chemie der Komplexverbindungen (7)*. In a series of papers published in 1925 by Rudolf Straubel and Hüttig, the rules were further linked to the concept of packing efficiency *(8, 9)*.

The thrust of all of the above papers was the problem of how to predict the maximum coordination numbers for discrete complex ions and of explaining why there were few, if any, known examples of species having coordination numbers of five or seven. While not the first person to propose the radius ratio rules, the Swiss–Norwegian geochemist, Victor Goldschmidt, does appear to have been the first to apply them to infinitely extended ionic lattices rather than to discrete complex ions—an application first described in German in 1926 and 1927 in Parts VII and VIII of his famous series of short monographs dealing with the laws governing the geochemical distribution of the elements in Nature *(10, 11)*, and again in English in 1929 *(12)*. Even this cannot be said of Pauling, however, who was quite late in coming to the rules and who first invoked them in his 1927 paper on ionic radii and once again in his 1929 summary of the various principles governing the structures of complex ionic crystals *(13, 14)*.

In his various monographs, Goldschmidt acknowledged the earlier work of both Hüttig and Magnus, whereas in his own publications, Pauling failed to note either—an oversight that he partially corrected in the case of Magnus a decade later in the first edition of *The Nature of the Chemical Bond (15)*. This neglect, coupled with the unfamiliarity of most American chemists with both the early German literature on coordination chemistry and the geochemical literature, probably accounts for the incorrect association of the rules with Pauling's name. Luckily, this association has never been strong enough to become a full-fledged example of "Stigler's Law of Eponymy" *(16)*: "No scientific discovery is ever named after its original discoverer." This is, however, certainly an example of Robert Merton's more famous "Matthew Effect" *(17)* whereby the famous are often credited, not only with their own discoveries, but occasionally with some they never made: "For unto every one that hath shall be given, and he shall have abundance: but from him that hath not shall be taken away even that which he hath." (from the Gospel of Matthew, quoted in ref *17*).

While the ionic-radius ratio rules are known to have many exceptions, they have remained a standard feature of most inorganic textbooks since the 1950s and have also been the subject of numerous articles in this *Journal (18)*.

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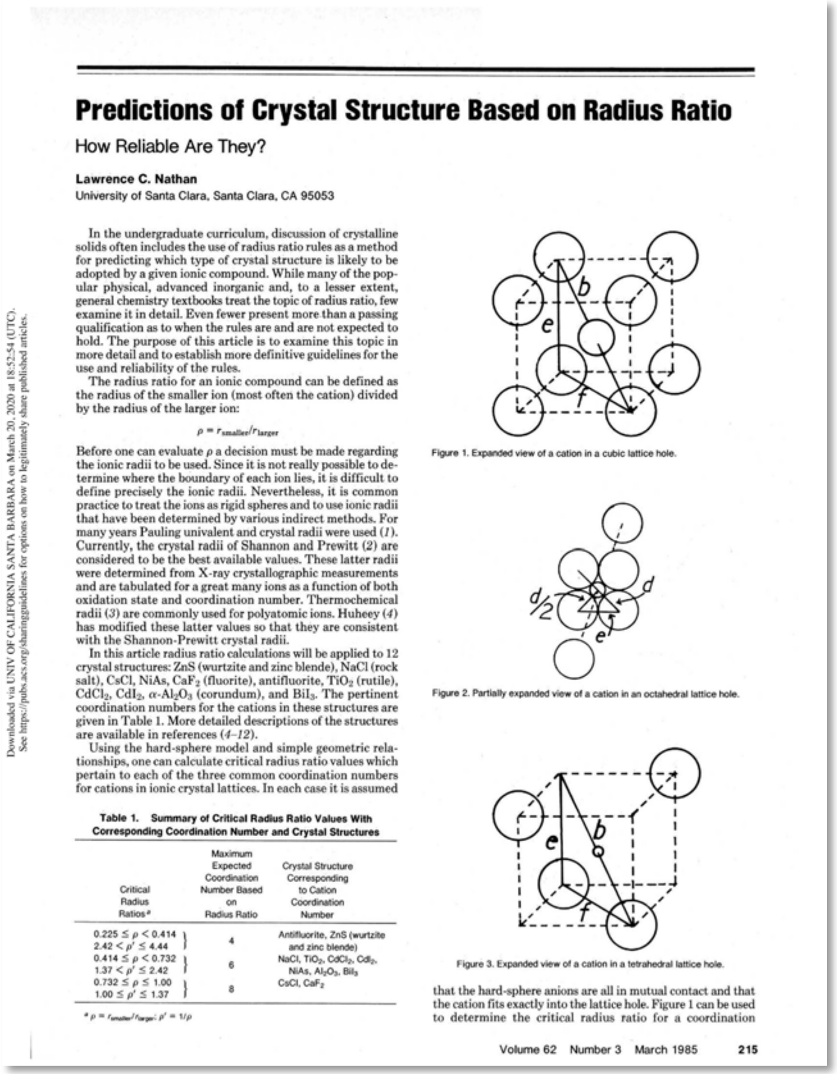

Predictions of Crystal Structure Based on Radius Ratio

How Reliable Are They?

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In the undergraduate curriculum, discussion of crystalline solids often includes the use of radius ratio rules as a method for predicting which type of crystal structure is likely to be adopted by a given ionic compound. While many of the popular physical, advanced inorganic and, to a lesser extent, general chemistry textbooks treat the topic of radius ratio, few examine it in detail. Even fewer present more than a passing qualification as to when the rules are and are not expected to hold. The purpose of this article is to examine this topic in more detail and to establish more definitive guidelines for the use and reliability of the rules.

The radius ratio for an ionic compound can be defined as the radius of the smaller ion (most often the cation) divided by the radius of the larger ion:

$$\rho = r_{\text{smaller}}/r_{\text{larger}}$$

Before one can evaluate ρ a decision must be made regarding the ionic radii to be used. Since it is not really possible to determine where the boundary of each ion lies, it is difficult to define precisely the ionic radii. Nevertheless, it is common practice to treat the ions as rigid spheres and to use ionic radii that have been determined by various indirect methods. For many years Pauling univalent and crystal radii were used (*1*). Currently, the crystal radii of Shannon and Prewitt (*2*) are considered to be the best available values. These latter radii were determined from X-ray crystallographic measurements and are tabulated for a great many ions as a function of both oxidation state and coordination number. Thermochemical radii (*3*) are commonly used for polyatomic ions. Huheey (*4*) has modified these latter values so that they are consistent with the Shannon-Prewitt crystal radii.

In this article radius ratio calculations will be applied to 12 crystal structures: ZnS (wurtzite and zinc blende), NaCl (rock salt), CsCl, NiAs, CaF_2 (fluorite), antifluorite, TiO_2 (rutile), $CdCl_2$, CdI_2, α-Al_2O_3 (corundum), and BiI_3. The pertinent coordination numbers for the cations in these structures are given in Table 1. More detailed descriptions of the structures are available in references (*4–12*).

Using the hard-sphere model and simple geometric relationships, one can calculate critical radius ratio values which pertain to each of the three common coordination numbers for cations in ionic crystal lattices. In each case it is assumed that the hard-sphere anions are all in mutual contact and that the cation fits exactly into the lattice hole. Figure 1 can be used to determine the critical radius ratio for a coordination

Table 1. Summary of Critical Radius Ratio Values With Corresponding Coordination Number and Crystal Structures

Critical Radius Ratios[a]	Maximum Expected Coordination Number Based on Radius Ratio	Crystal Structure Corresponding to Cation Coordination Number
$0.225 \le \rho < 0.414$ $2.42 < \rho' \le 4.44$	4	Antifluorite, ZnS (wurtzite and zinc blende)
$0.414 \le \rho < 0.732$ $1.37 < \rho' \le 2.42$	6	NaCl, TiO_2, $CdCl_2$, CdI_2, NiAs, Al_2O_3, BiI_3
$0.732 \le \rho \le 1.00$ $1.00 \le \rho' \le 1.37$	8	CsCl, CaF_2

[a] $\rho = r_{\text{smaller}}/r_{\text{larger}}$; $\rho' = 1/\rho$

Figure 1. Expanded view of a cation in a cubic lattice hole.

Figure 2. Partially expanded view of a cation in an octahedral lattice hole.

Figure 3. Expanded view of a cation in a tetrahedral lattice hole.

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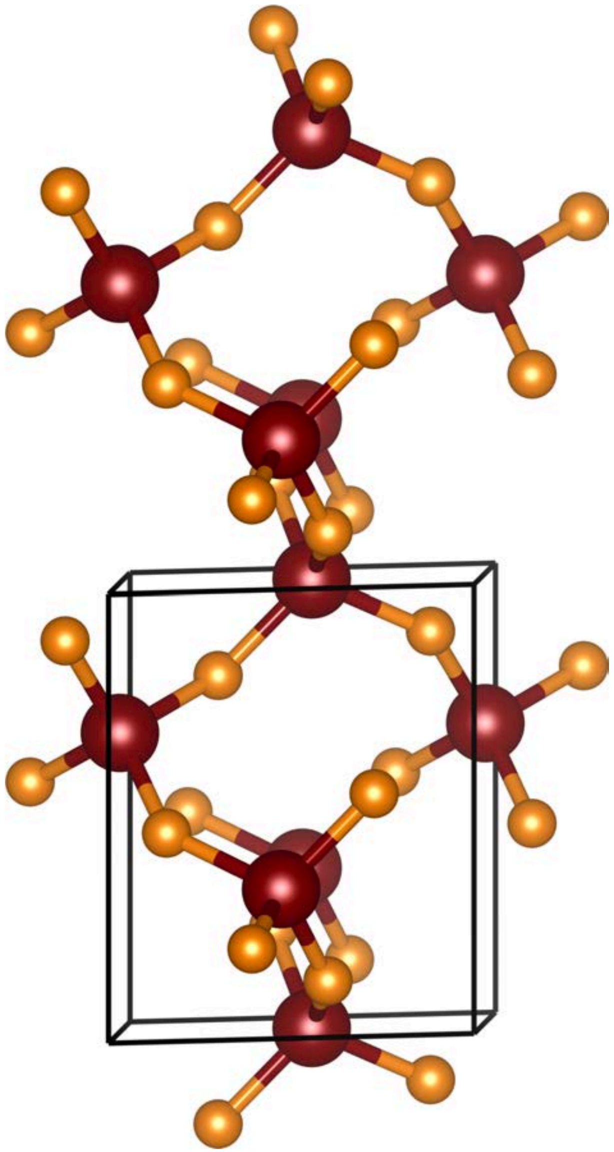
UC SANTA BARBARA

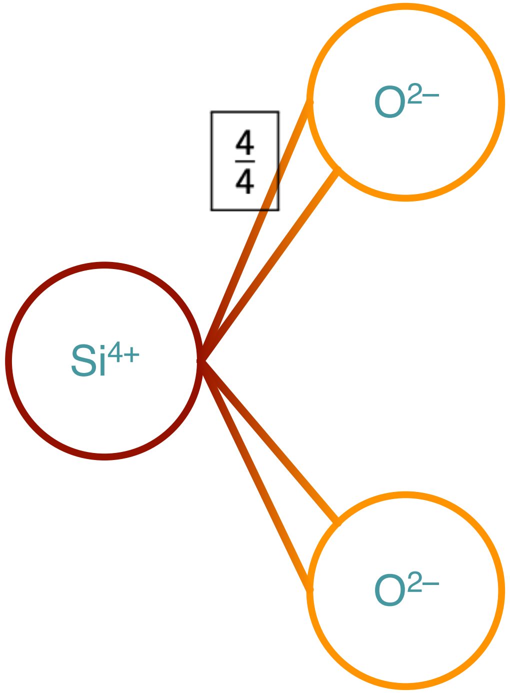
Not the first, and not the first …

Letter from Pauling to W.L. Bragg. October 22, 1928:

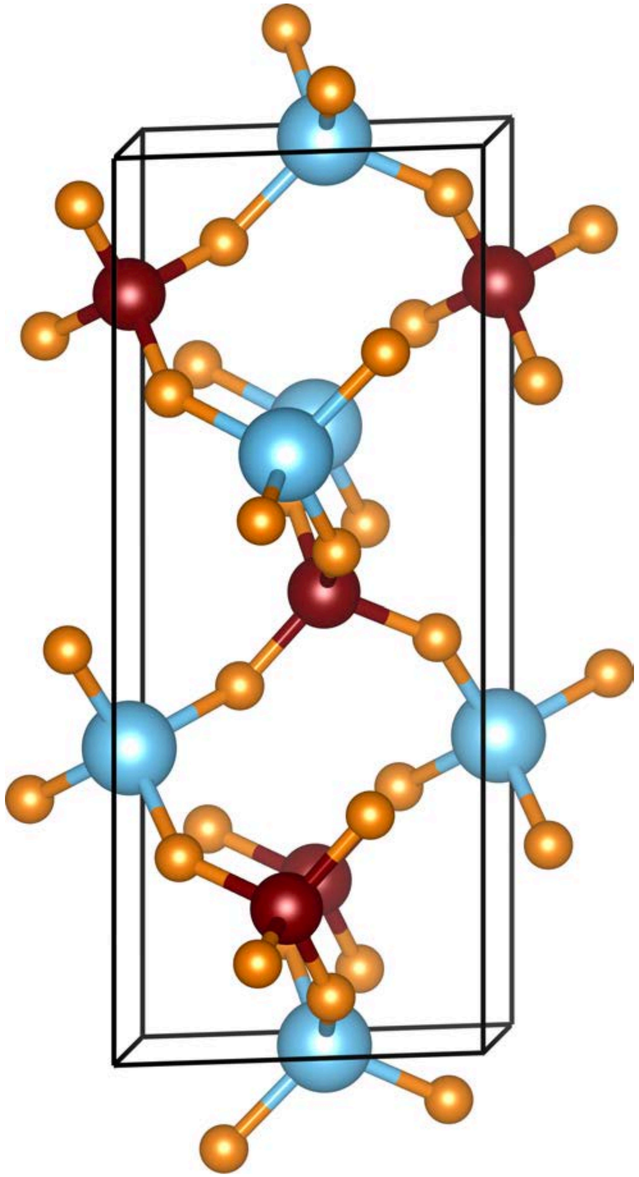
“The last of August I sent two papers to the Editor of the Journal of the American Chemical Society. In one of them are rules governing the structures of complex crystals. I realize that nothing I have done is highly original - in particular was I gratified to read in your letter a statement of the rule governing the sharing of polyhedron elements.”

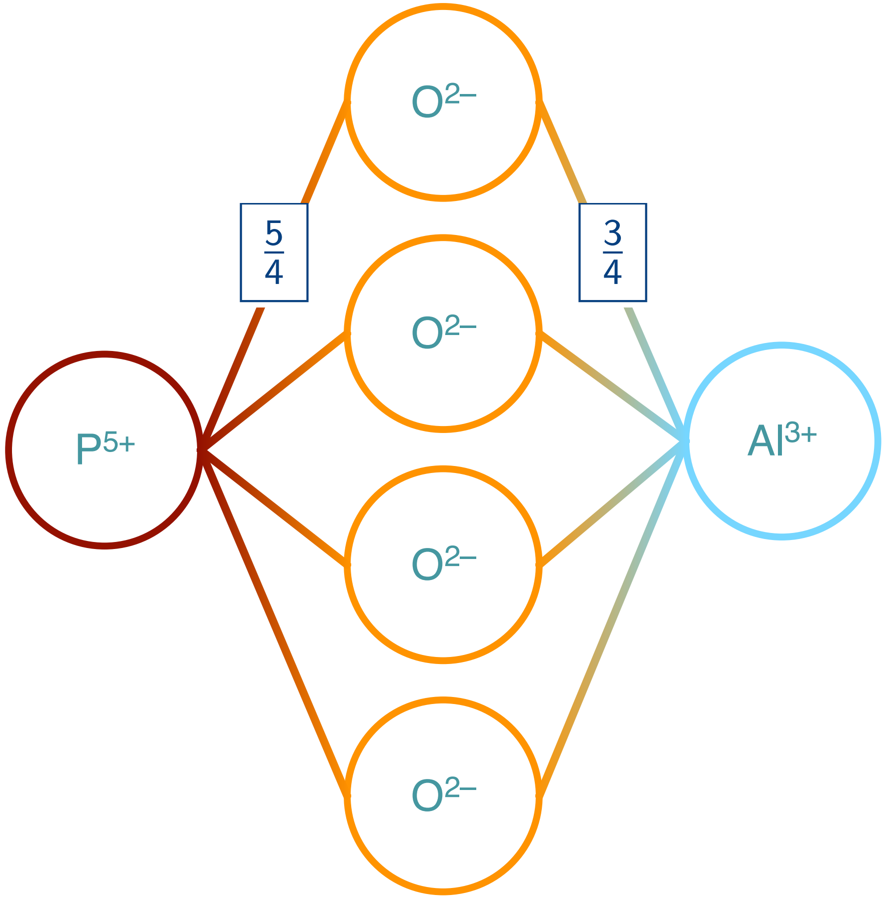
SiO$_2$ (low quartz, $P3_22_1$)



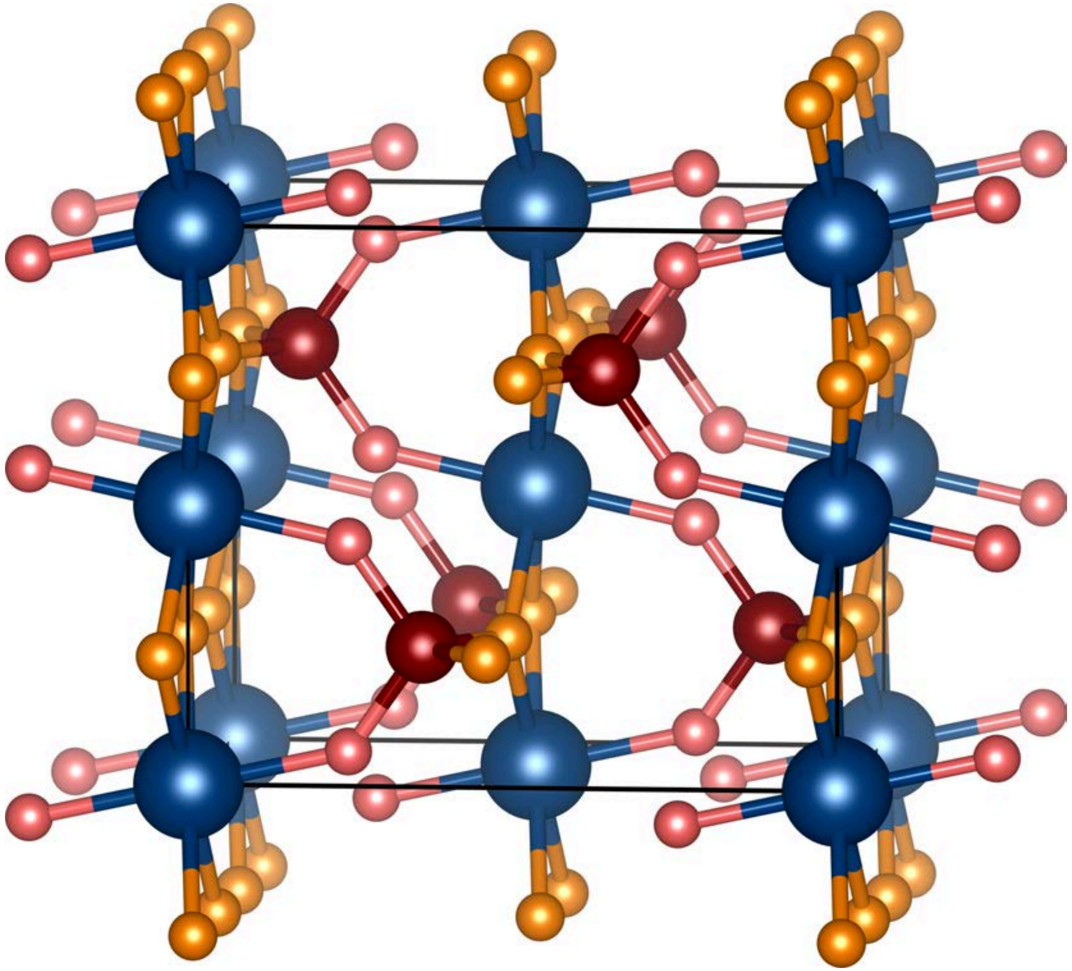


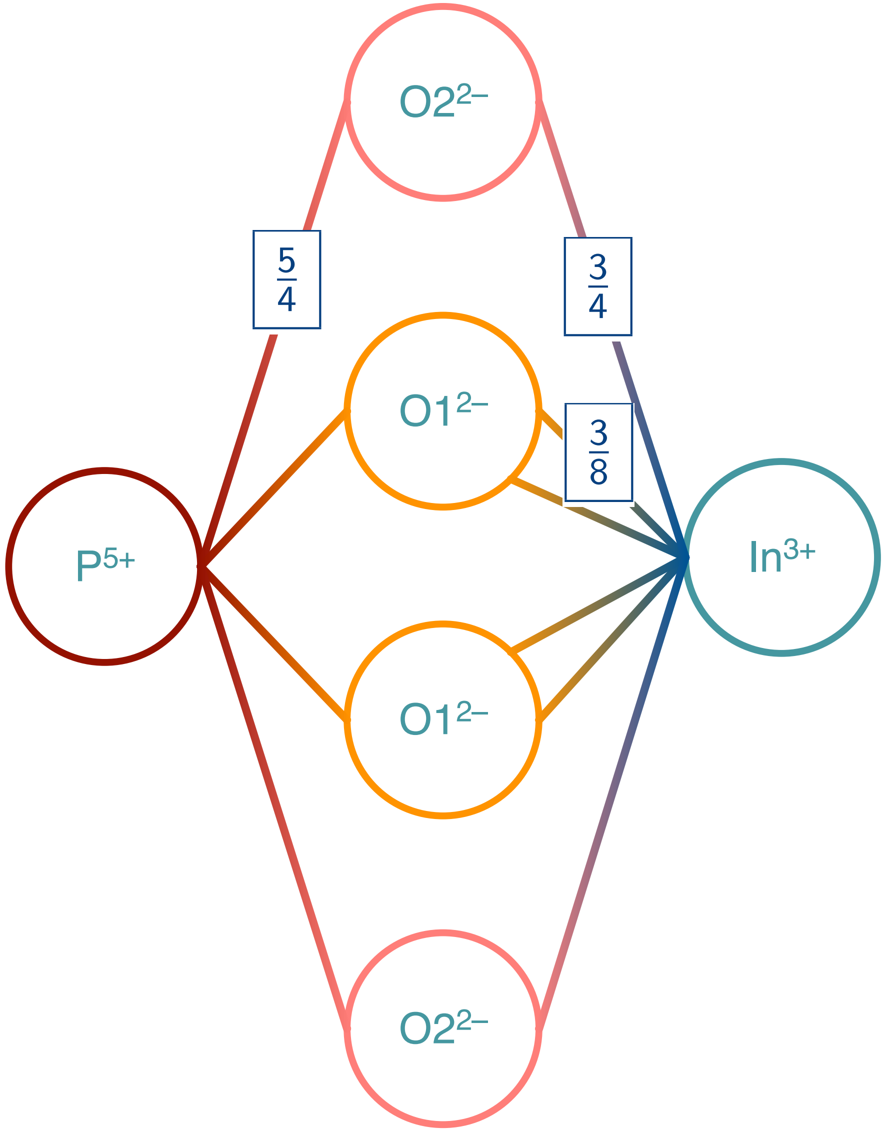
Berlinite, $AlPO_4$, obtained structurally by forking cation charges in SiO_2





IPO$_4$: In^{3+} is too large for 4-coordination





Pyrochlore $Cd_2Ta_2O_7$: The Bond Valence Map