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

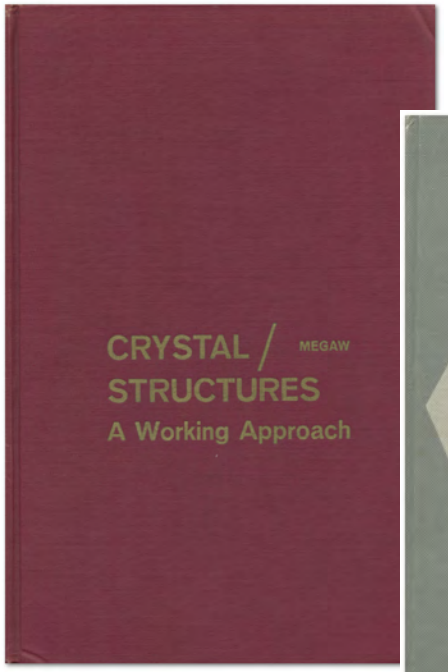
This lecture

1. Brief description of oxide crystal structures (simple and complex)

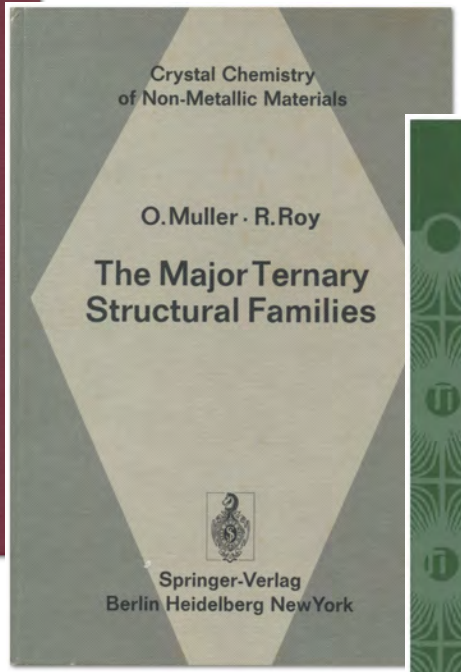
    a. Ionic radii and Pauling's rules
    b. Electrostatic valence
    c. Bond valence, and bond valence sums

Why do certain combinations of atoms take on specific structures?

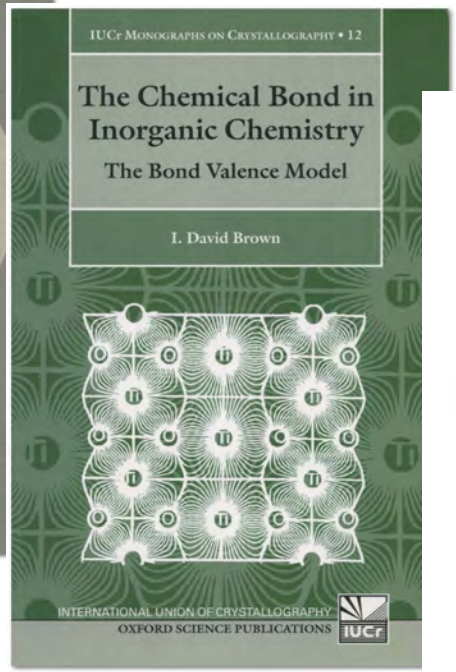
My bookshelf



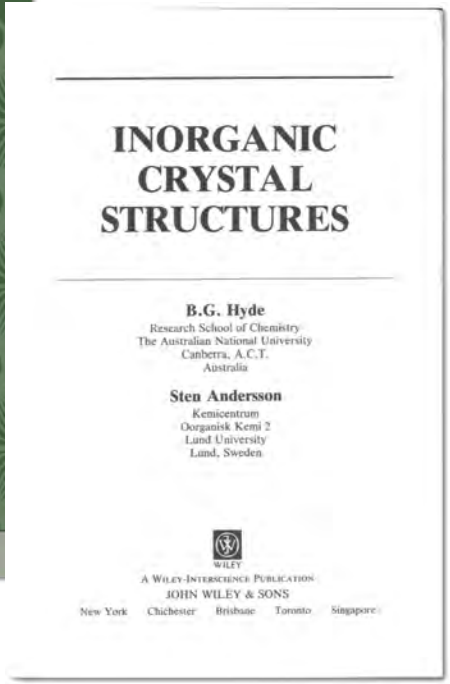
H. D. Megaw



O. Muller &
R. Roy

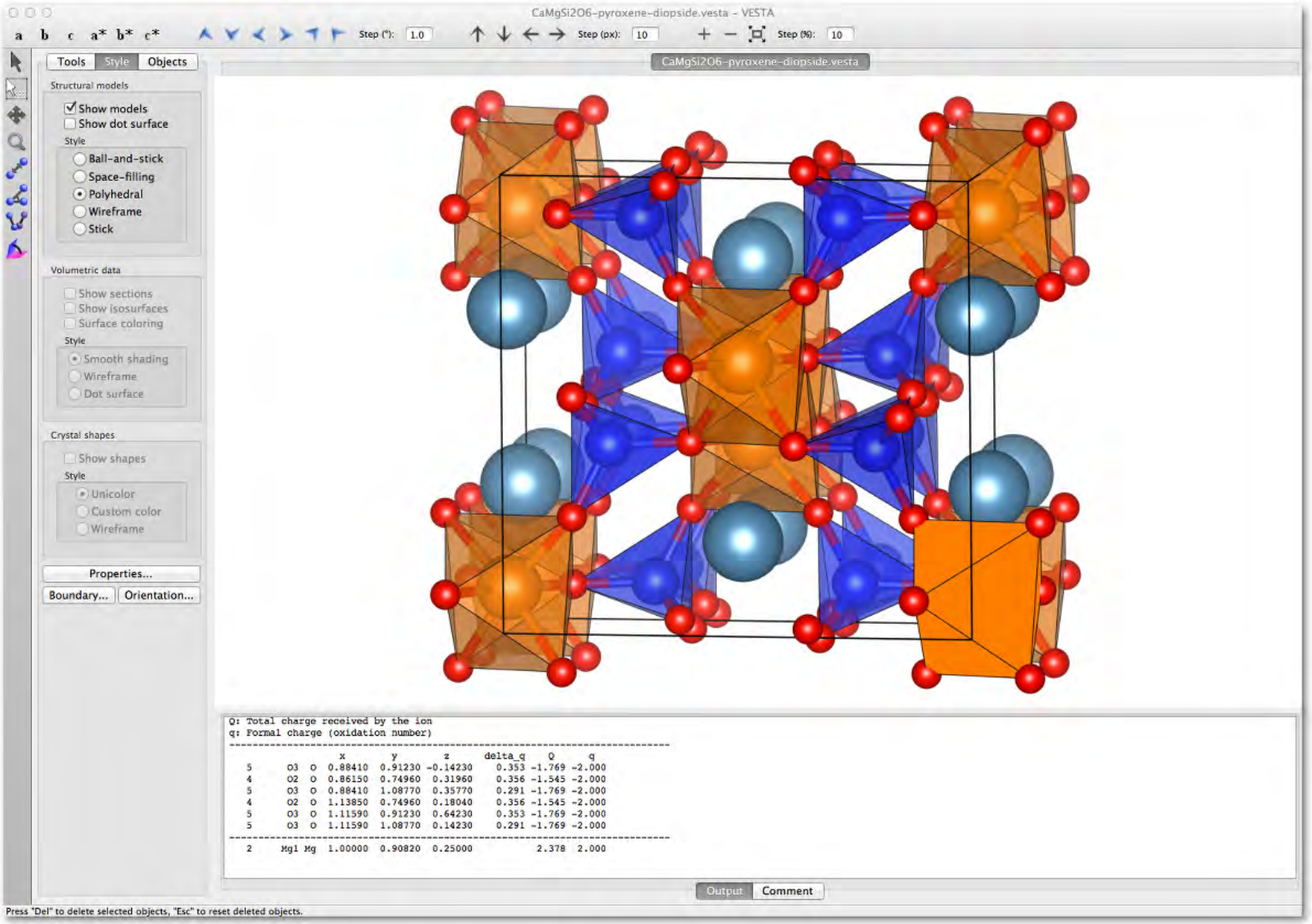


I. D. Brown



B. G. Hyde &
S. Andersson

Software: ICSD + VESTA



K. Momma and F. Izumi, VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data, *J. Appl. Cryst.* **44** (2011) 1272–1276. [doi:10.1107/S0021889811038970]

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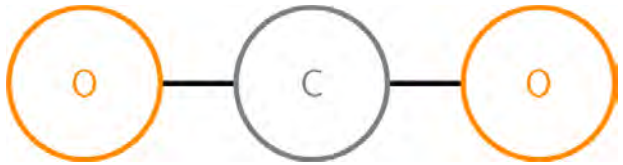
Crystal structures of simple oxides [containing a single cation site]

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

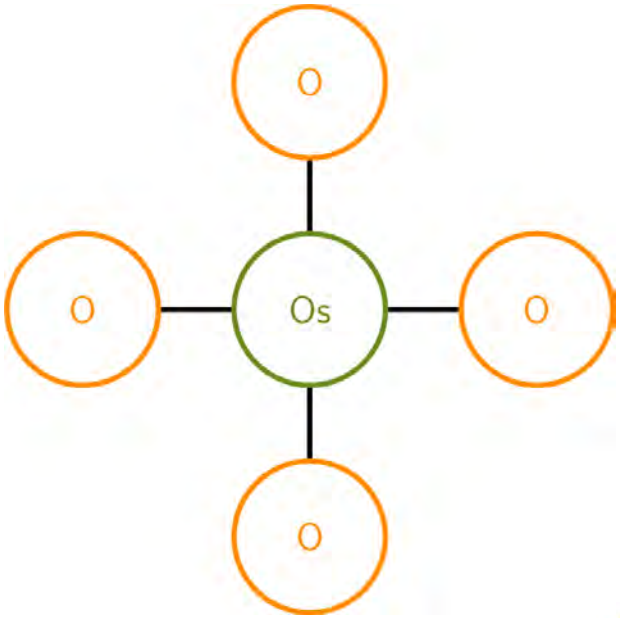
N.B.: CoO is simple, Co_3O_4 is not. $ZnCo_2O_4$ is certainly not !
Co_3O_4 and $ZnCo_2O_4$ are complex oxides.

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

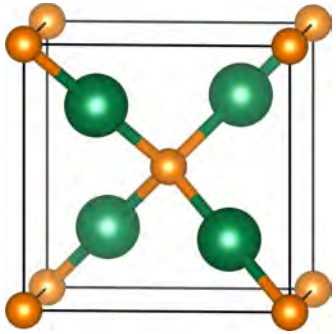


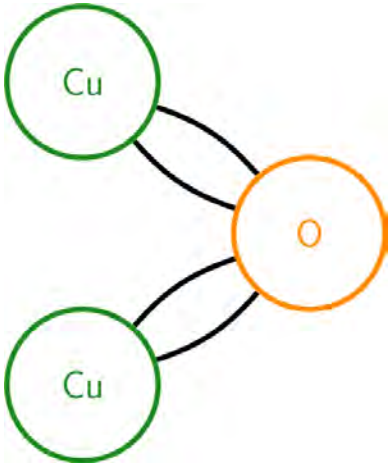
OsO_4: The structure comprises isolated tetrahedra (molecular). The graph is below:
Each Os connected to 4 O and each O to 1 Os



Crystal structures of simple oxides of monovalent ions: A_2O

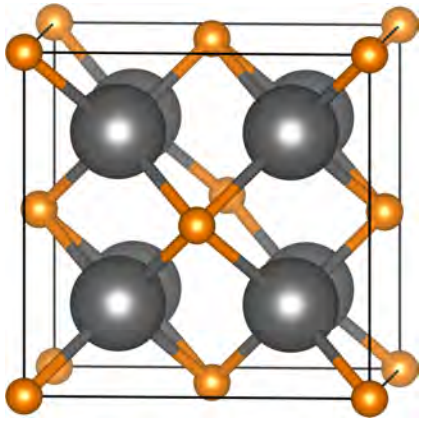
Cu_2O

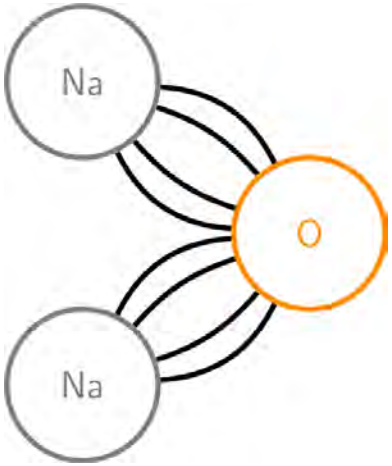




Linear coordination is unusual. Found usually in Cu^+ and Ag^+.

Na_2O (anti-fluorite)

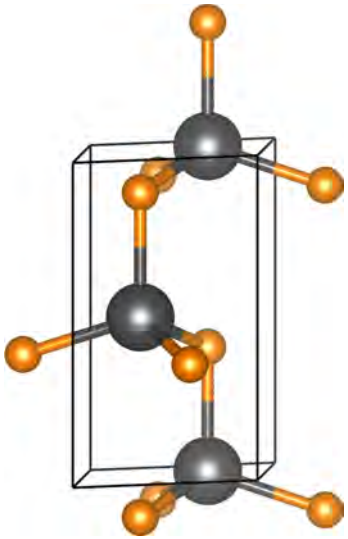




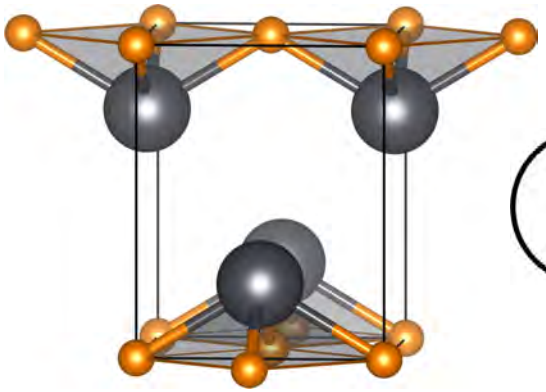
4-coordination for Na^+ and 8-coordination for O^{2-} are unusual.

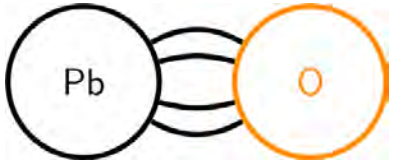
Crystal structures of simple oxides of divalent ions: AO

ZnO (wurtzite), sp^3

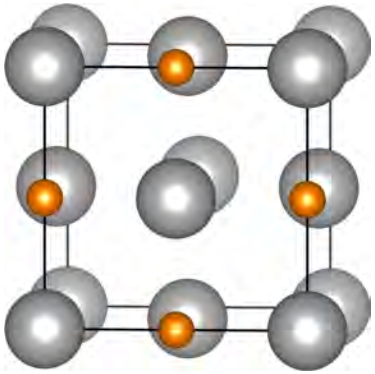


PbO (litharge), lone pairs





MgO (rock-salt)

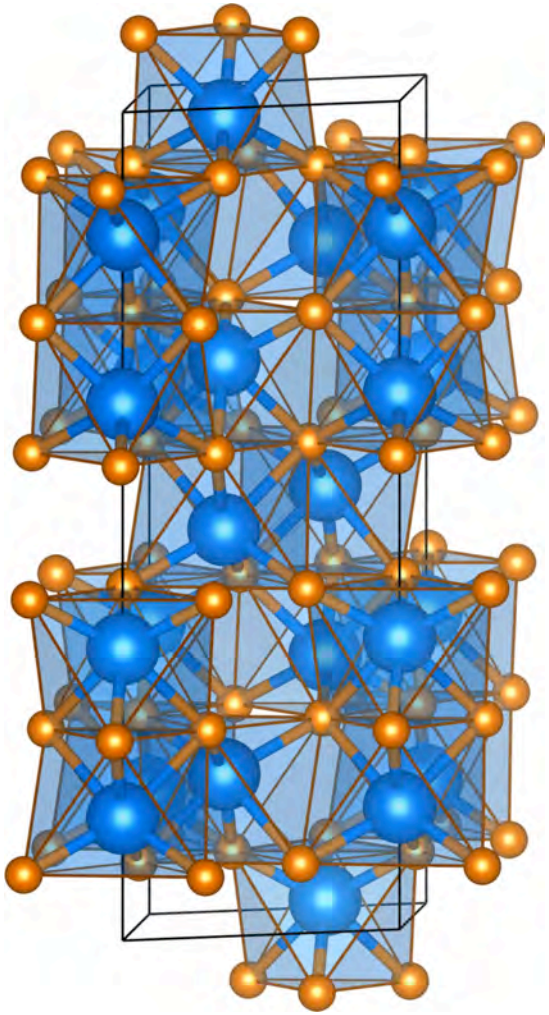


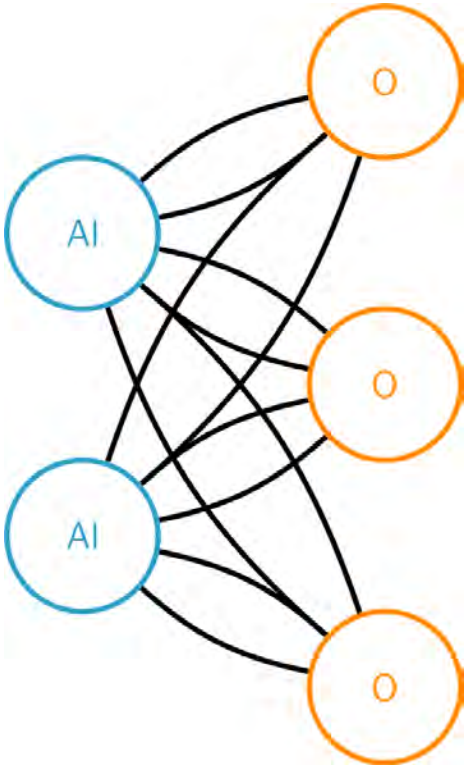
Ubiquitous for AO oxides including transition metals (distorted for CuO and NbO).

Insulators, metals (TiO), magnetic, …

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

α-Al_2O_3 (corundum)





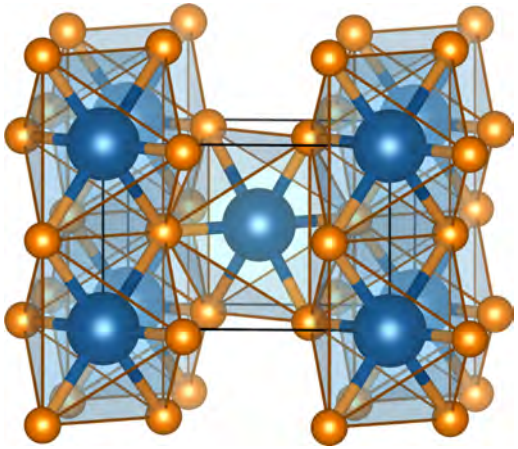
Also the structure of Cr_2O_3 and Fe_2O_3.

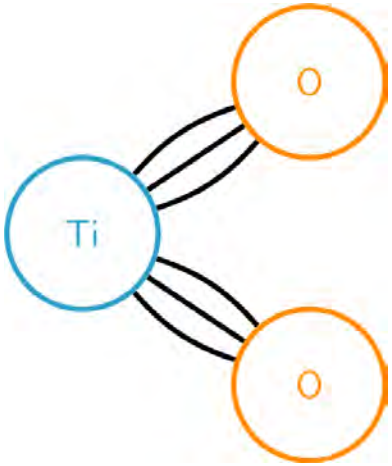
Ga_2O_3 does funny things.

In_2O_3 is different (bixbyite).

Crystal structures of simple oxides of tetravalent ions: AO_2

TiO_2 (rutile)

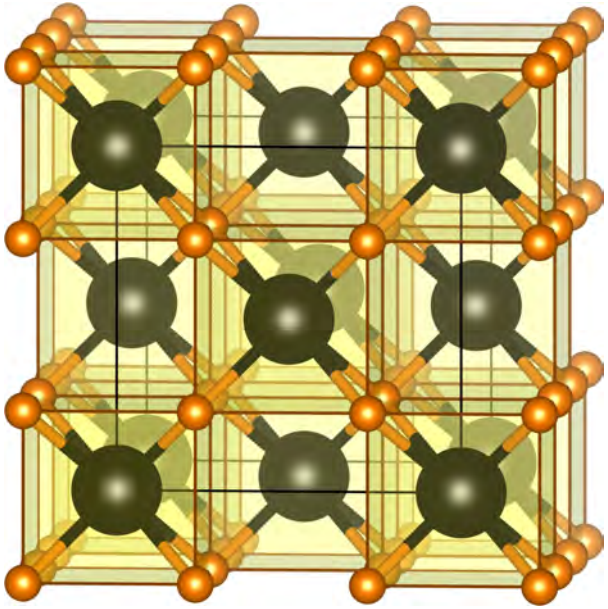


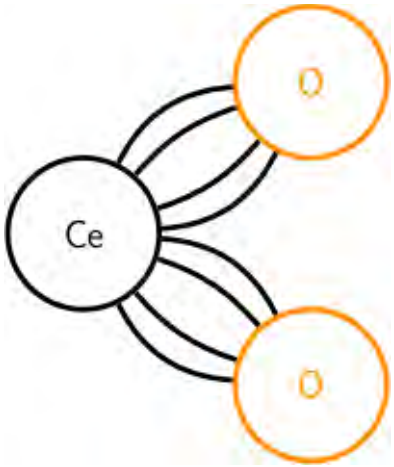


TiO_2 also crystallizes as anatase and brookite.

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

CeO_2 (fluorite)



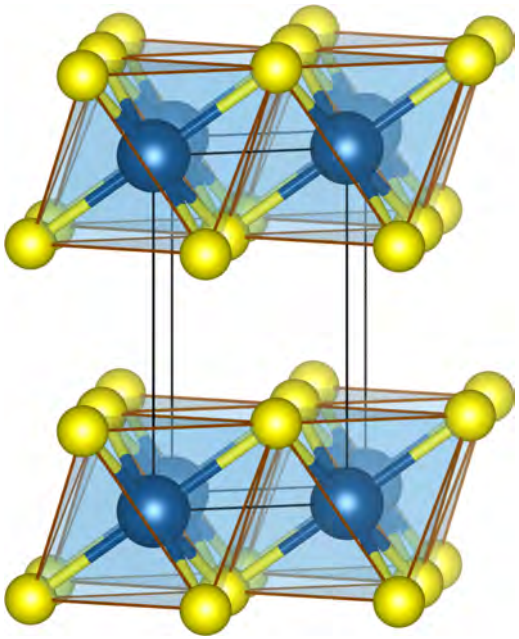


Also the structure of ThO_2, and of ZrO_2 and HfO_2 at elevated temperatures.

Ordered variants abound.

Oxides versus sulfides: TiS_2

$2H$–TiS_2

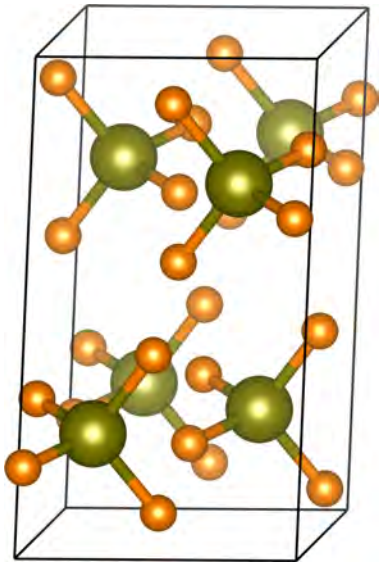


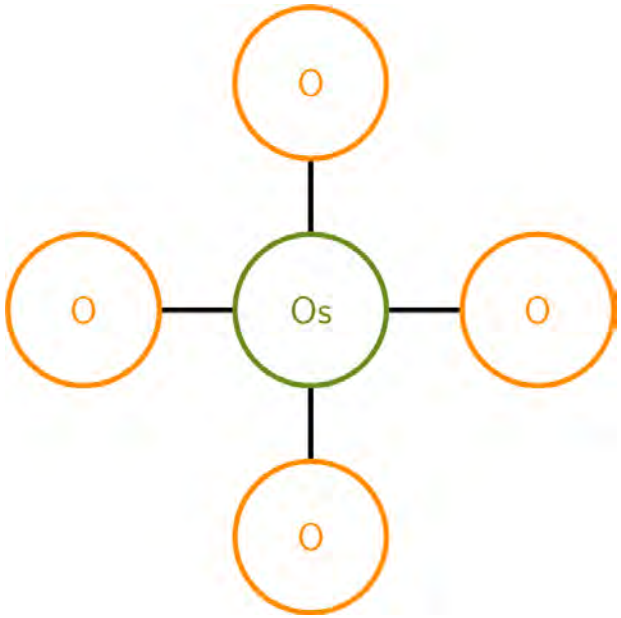
van der Waals gap (unlikely in oxides or fluorides, but occurs frequently in hydroxides)

This is the CdI_2 structure.

Crystal structures of an oxide with an octavalent ion: OsO_4

OsO_4



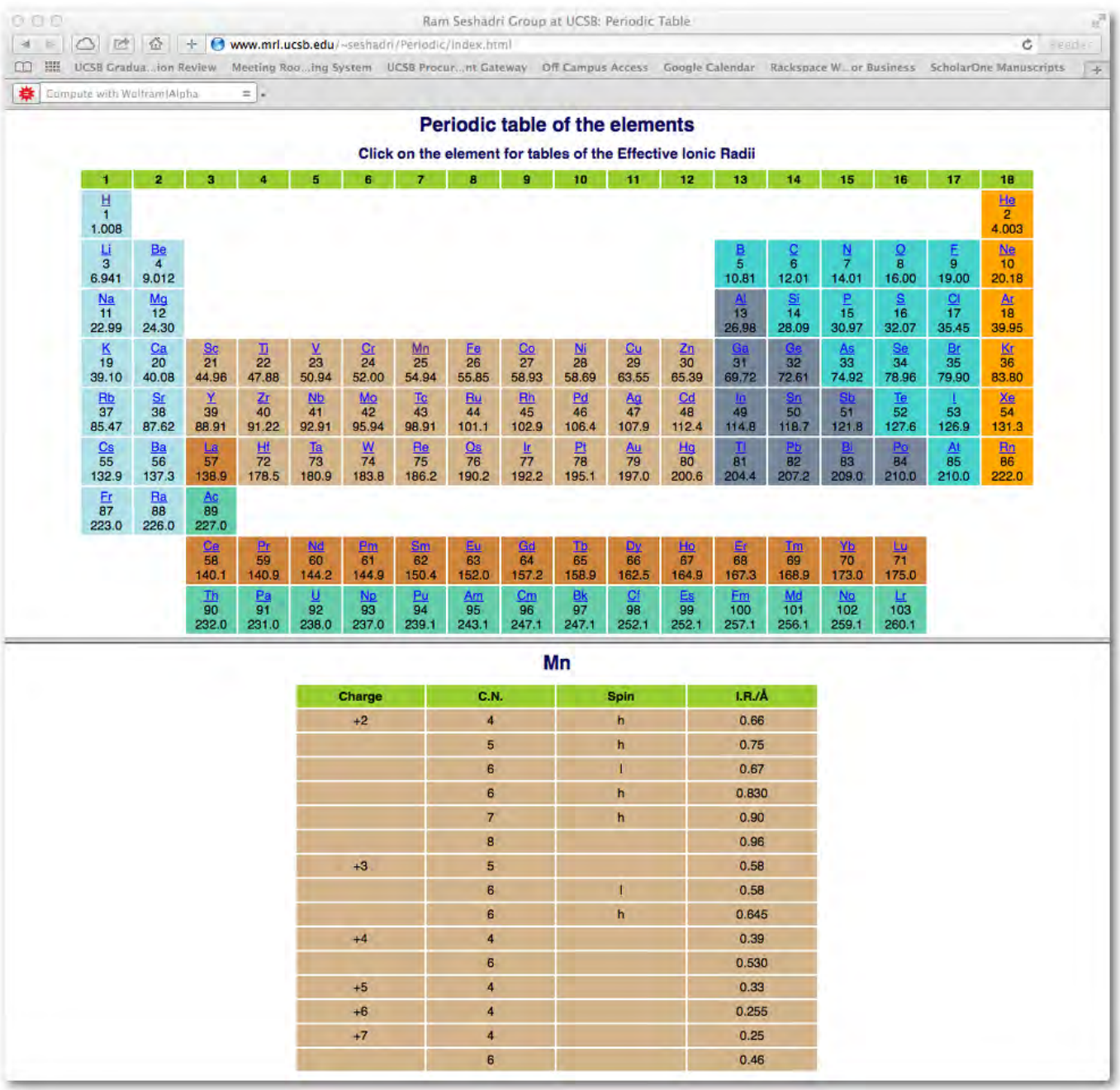


Shannon-Prewitt (ionic) radii

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



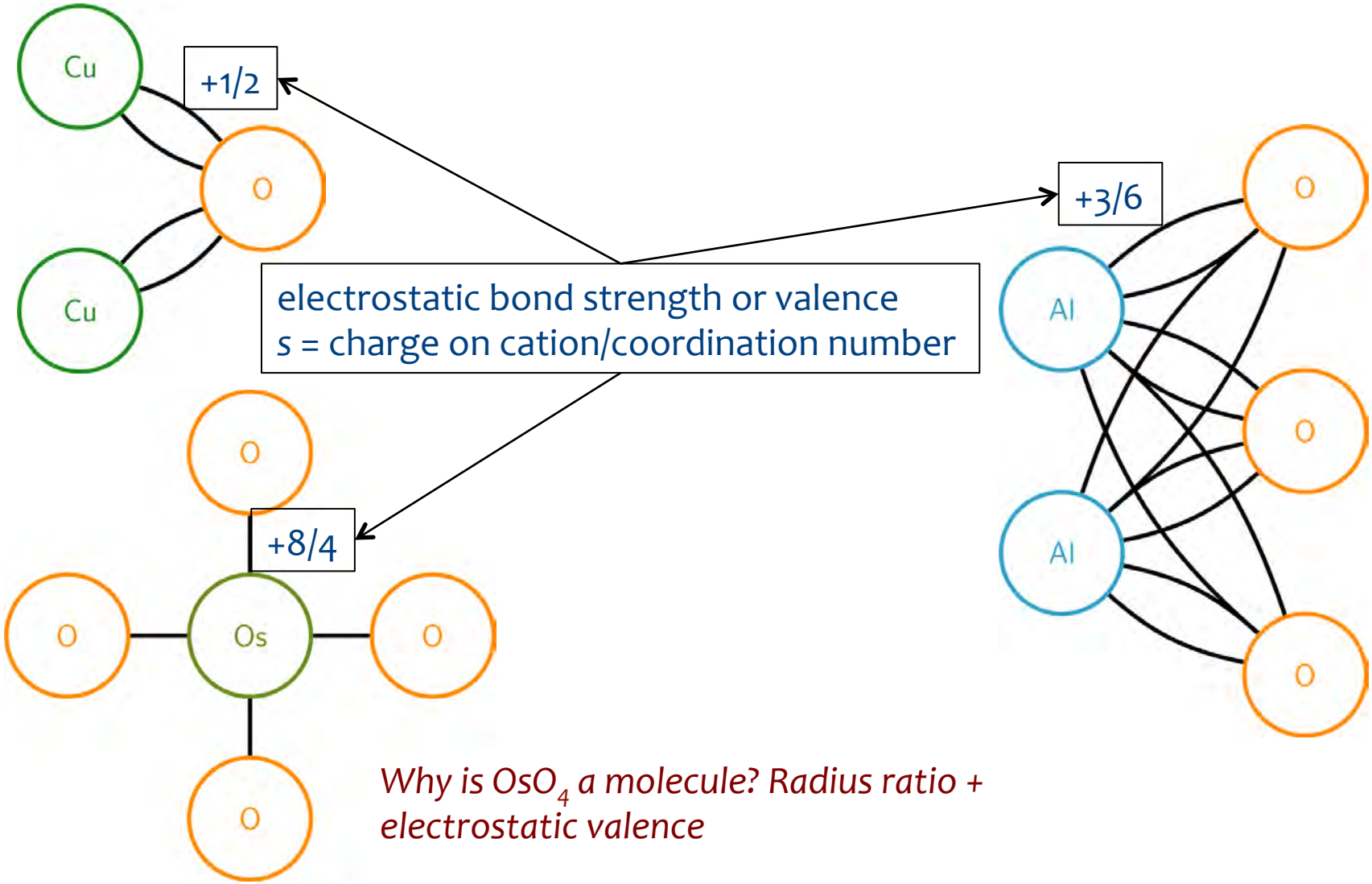
www.mrl.ucsb.edu/~seshadri/Periodic/index.html

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 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

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

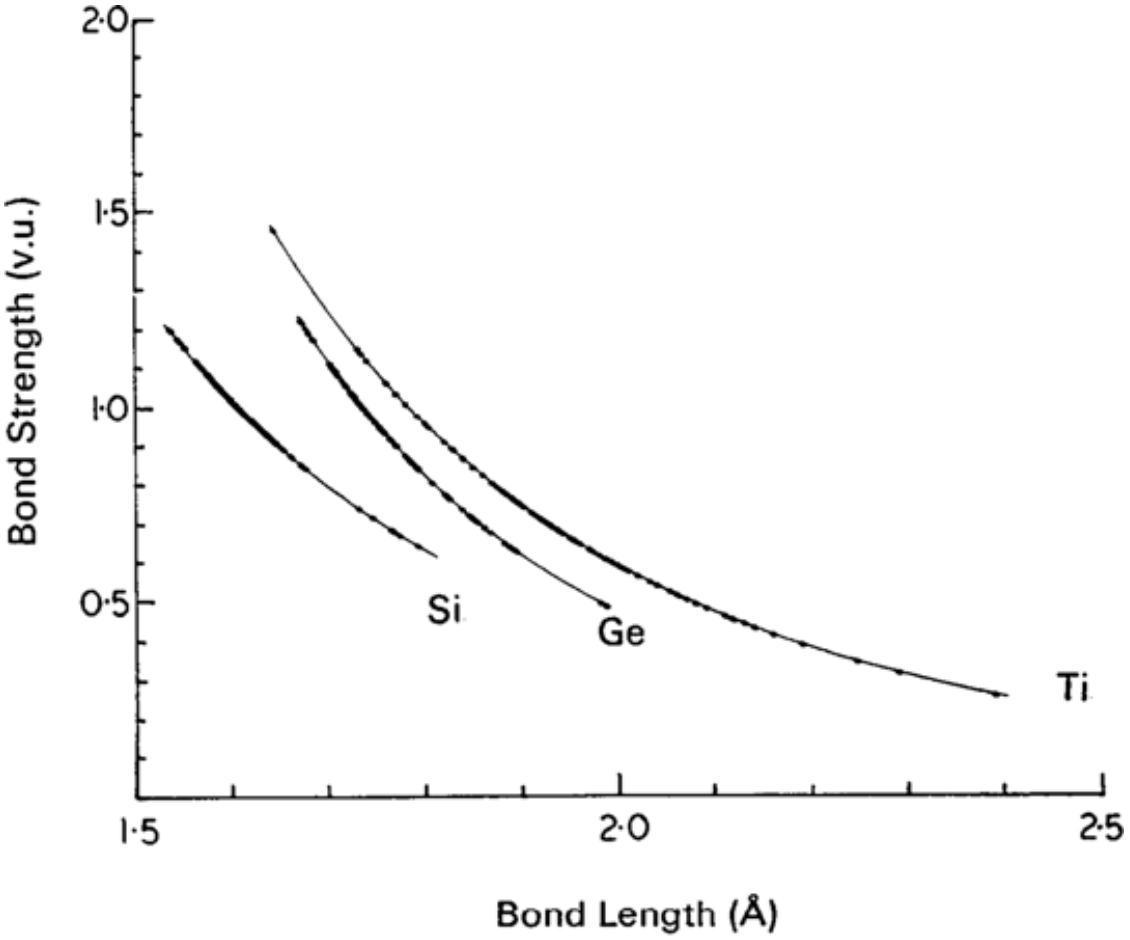
In brief: Charges going out from cations should balance anions and *vice-versa*



Why is OsO_4 a molecule? Radius ratio + electrostatic valence

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

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) correpond to strong bonds and *vice-versa*



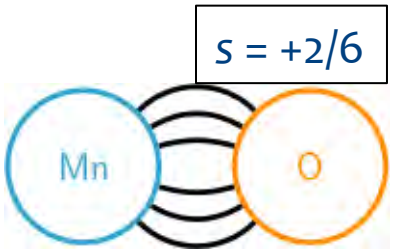
I. D. Brown and R. D. Shannon, Empirical bond-strength-bond-length curves for oxides, *Acta Cryst.* **A29** (1973) 266–281

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 $B \approx 0.37$ 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

I. D. Brown and R. D. Shannon, Empirical bond-strength-bond-length curves for oxides, *Acta Cryst.* **A29** (1973) 266–281.

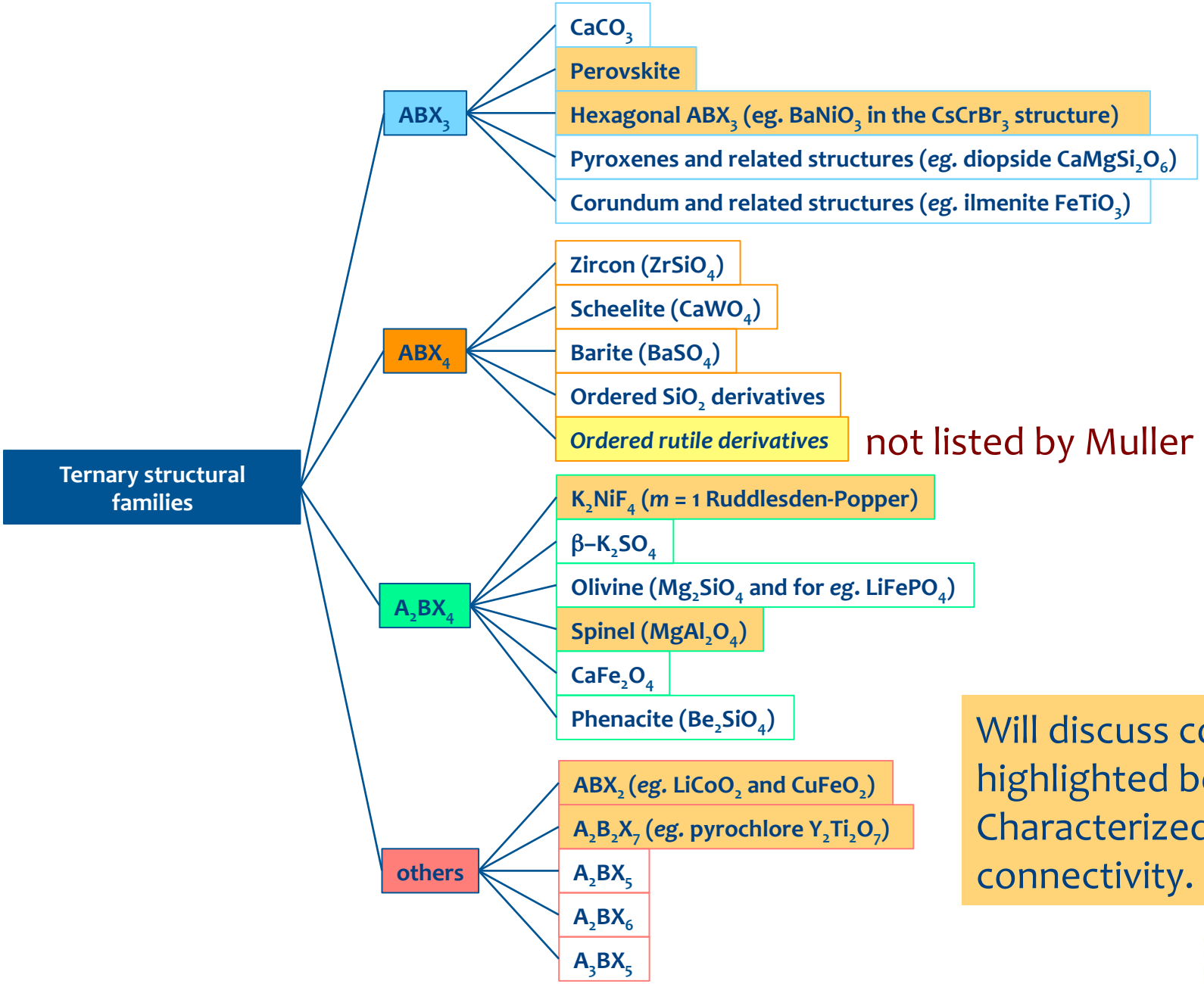
Electrostatic valence and bond valence: Parameters for Mn

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

I. D. Brown and R. D. Shannon, Empirical bond-strength-bond-length curves for oxides, *Acta Cryst.* **A29** (1973) 266–281.

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



not listed by Muller and Roy

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

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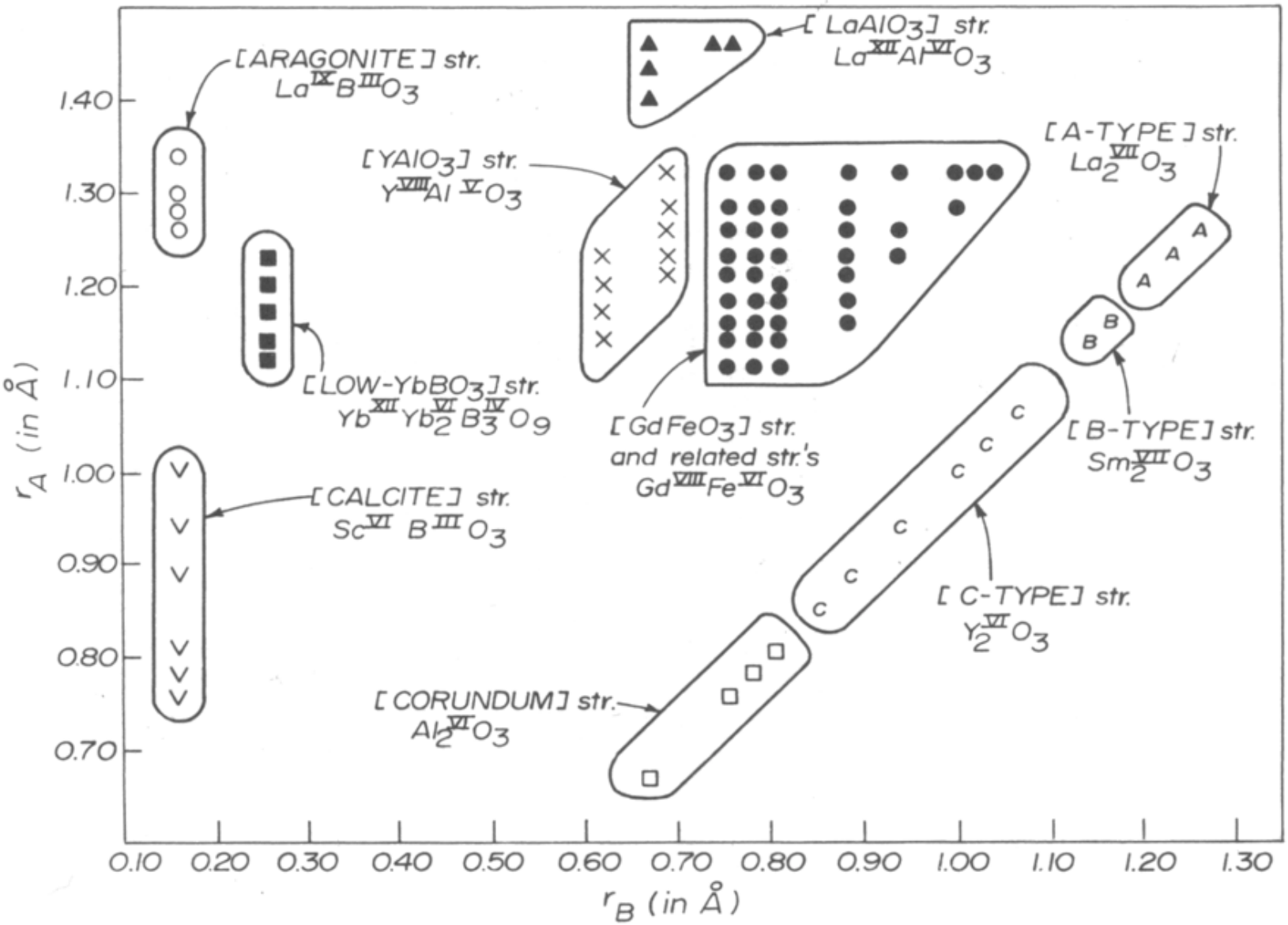
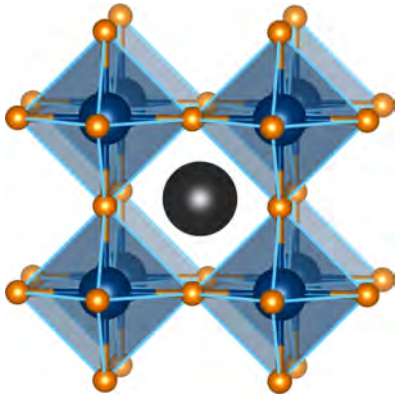
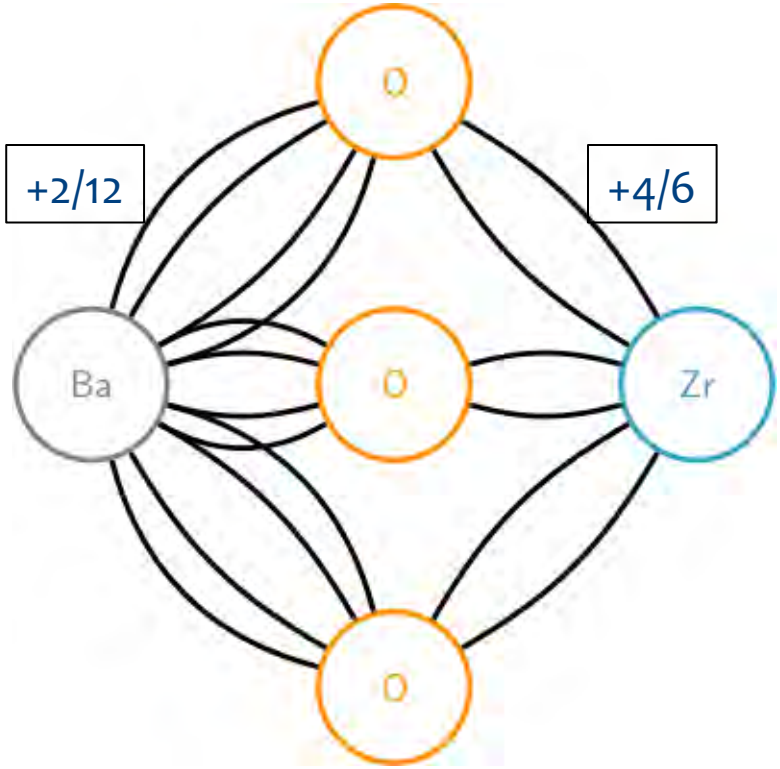
The ABO_3 structure-sorting field (from Muller and Roy)



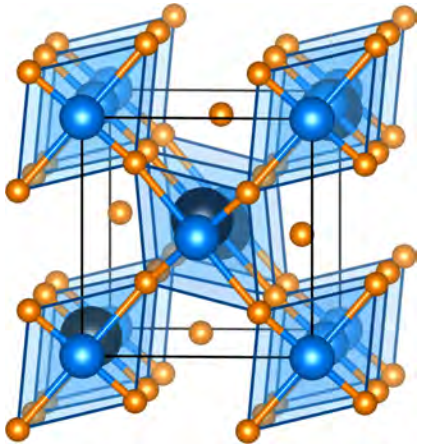
The superscripted roman numerals indicate coordination number.

$BaZrO_3$





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



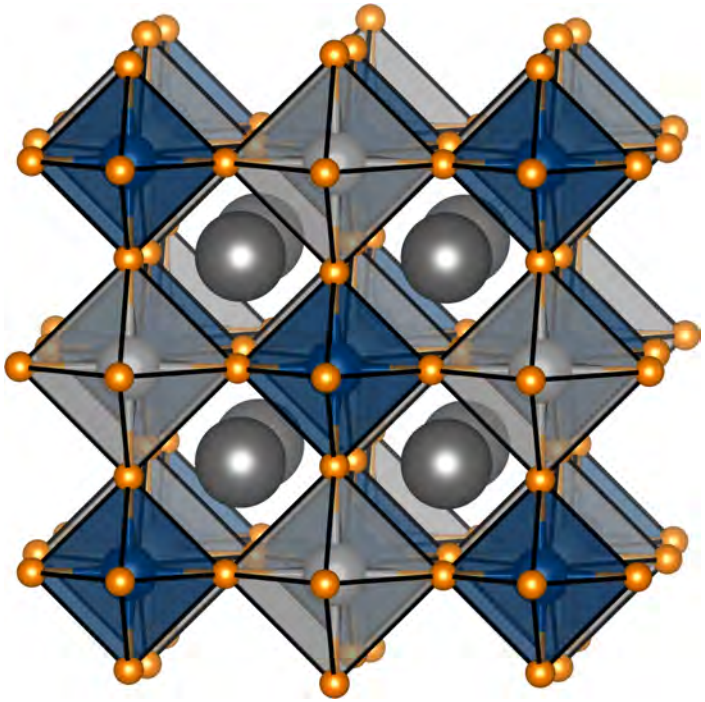
Note that the space group *Pnma* (#62) can be written in a variety of ways.

This is the most common perovskite space group.

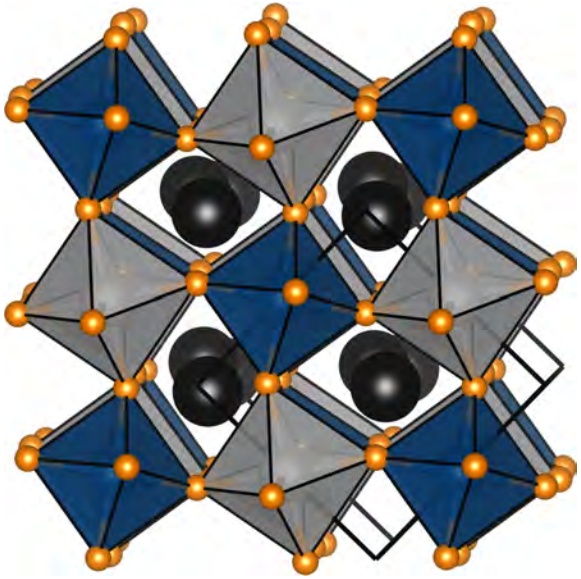
In the next so many structures, BO_6-polyhedra are depicted.

Ordered double perovskites (elpasolites)

Ba_2MgWO_6



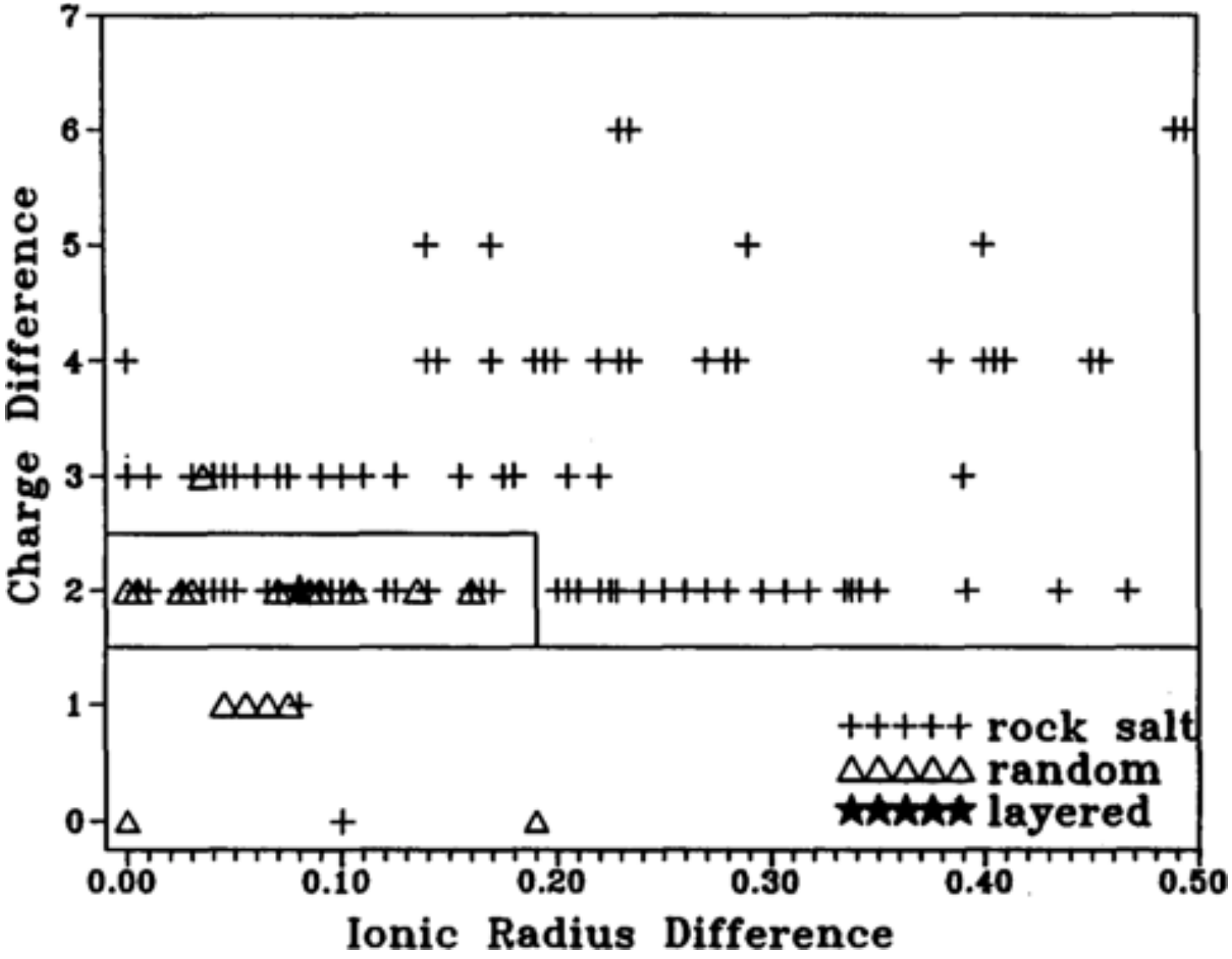
Ca_2MgWO_6



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

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

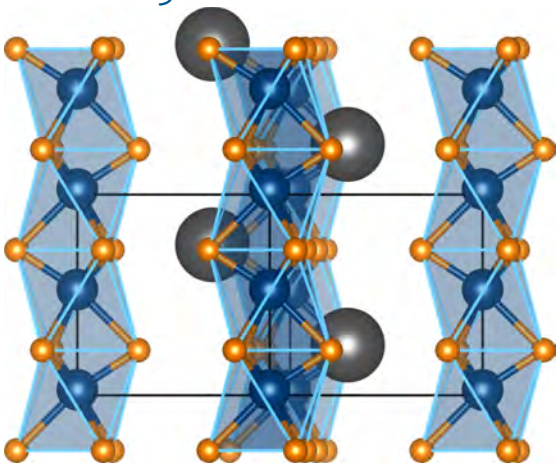
The double perovskite field: Charge and radius



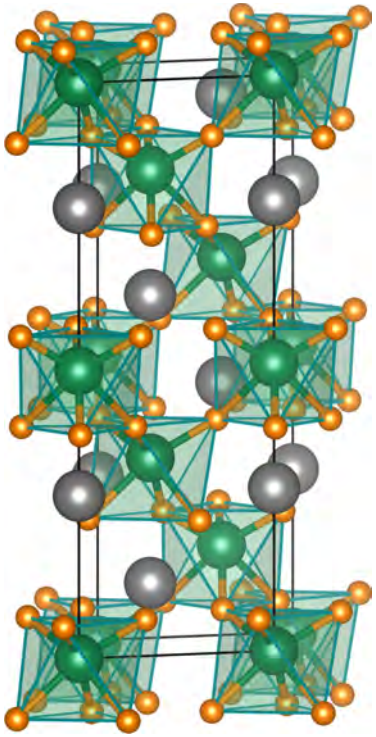
Anderson, Greenwood, and Poeppelmeier, *Prog. Solid State Chem.* **22** (1993) 197–233.

Hexagonal ABO_3 structures

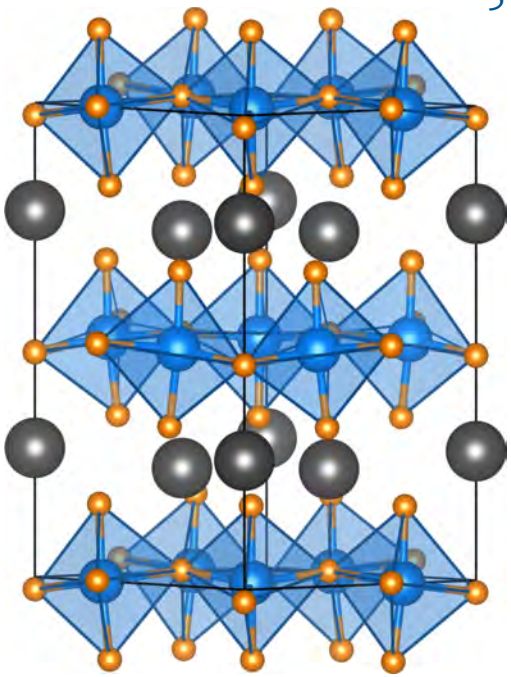
$BaNiO_3$



$LiNbO_3$ (ferroelectric *R*3*c*)



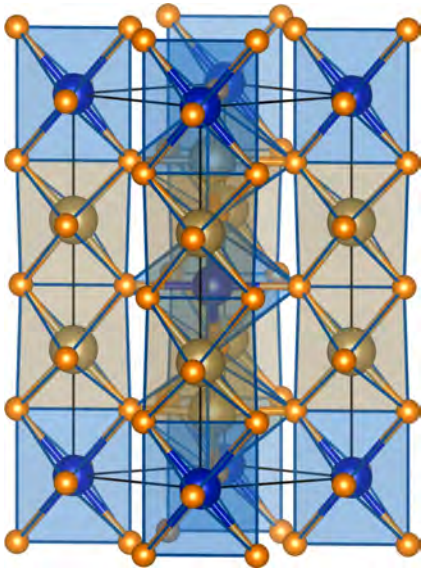
Ferroelectric $YMnO_3$ ("$YAlO_3$")



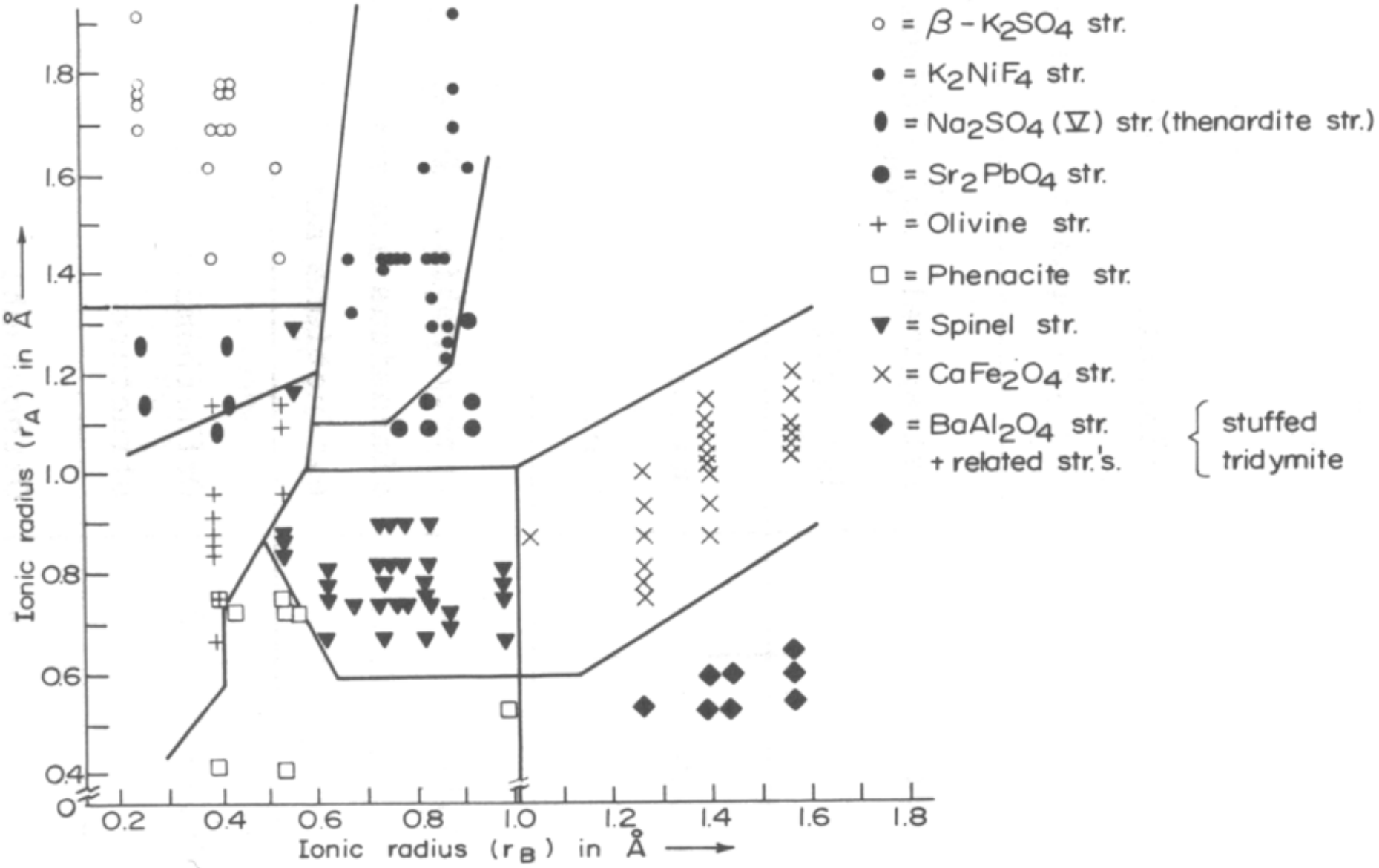
Unusual 5-fold coordination (trigonal bibyramid) of MnO_5

Ordered rutiles (the trirutile)

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

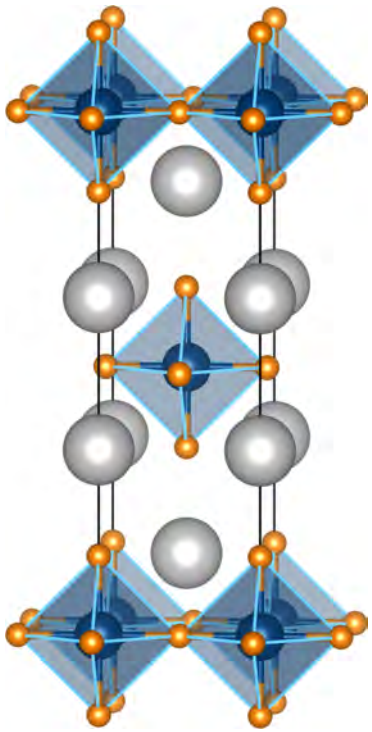


The A_2BO_4 structure-sorting field (from Muller and Roy)

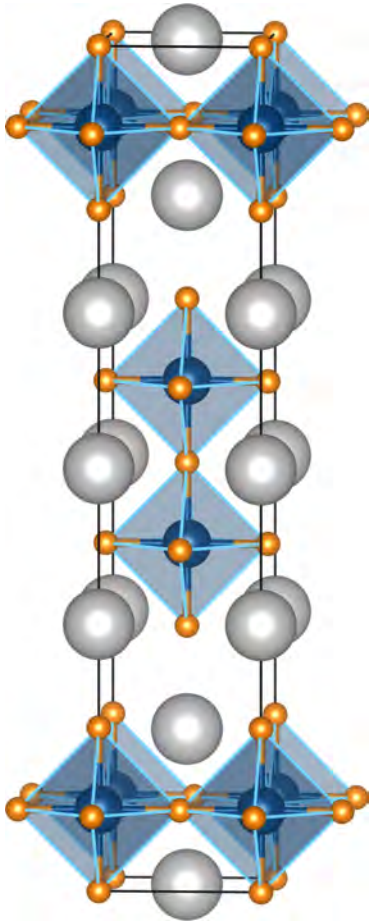


The superscripted roman numerals indicate coordination number.

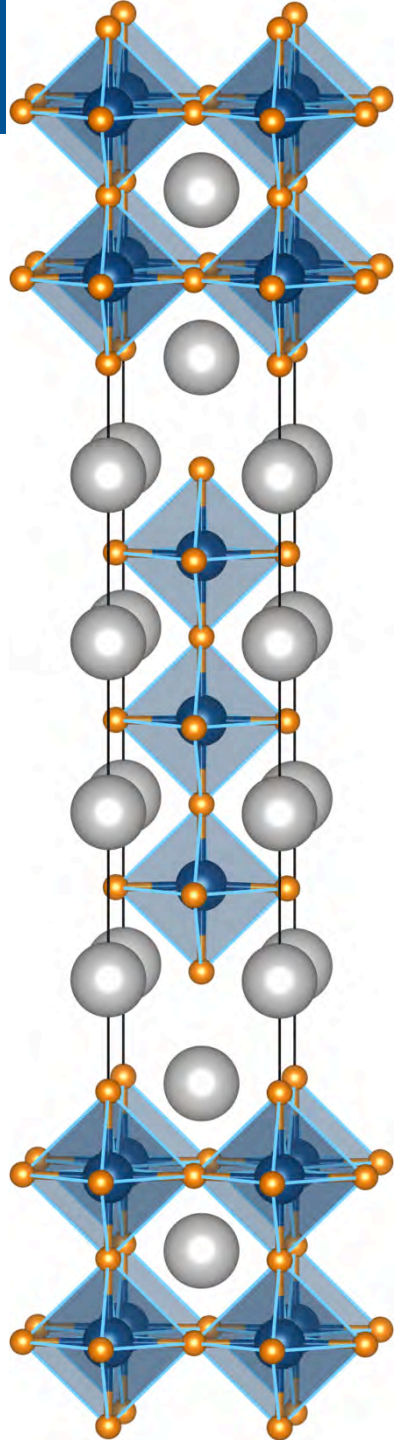
K_2NiF_4 and Ruddlesden-Popper (m = 1, 2, 3)
General formula $[SrO][SrTiO_3]_m$



Sr_2TiO_4



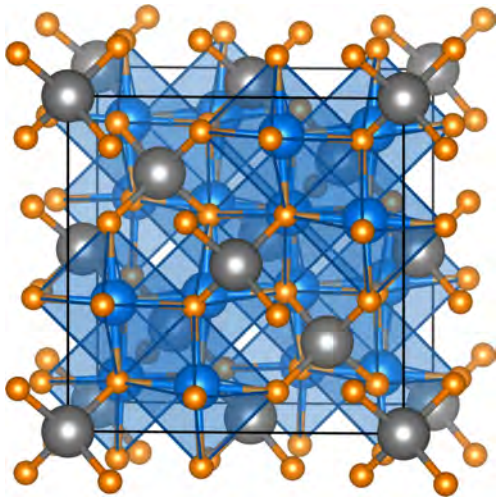
$Sr_3Ti_2O_7$

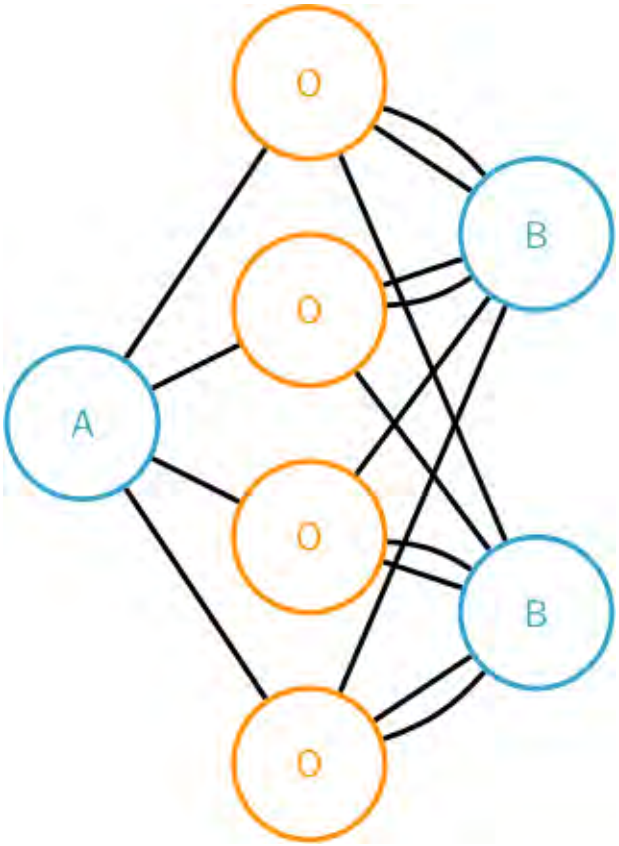


$Sr_4Ti_3O_{10}$

$m = 3$

$MgAl_2O_4$



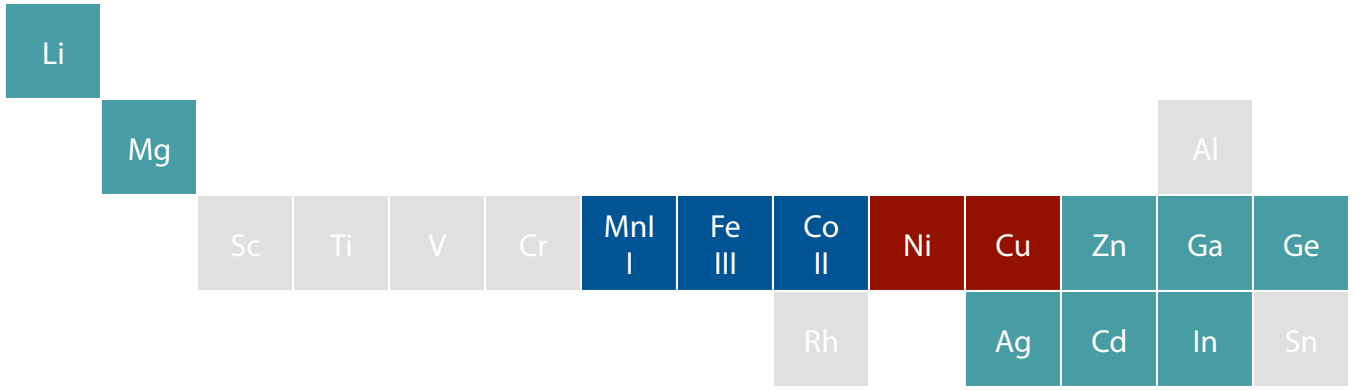


Ubiquitous structure when ions have similar sizes, around 0.6 Å.
A is tetrahedrally coordinated, and *B* octahedral (actually with a slight trigonal distortion).

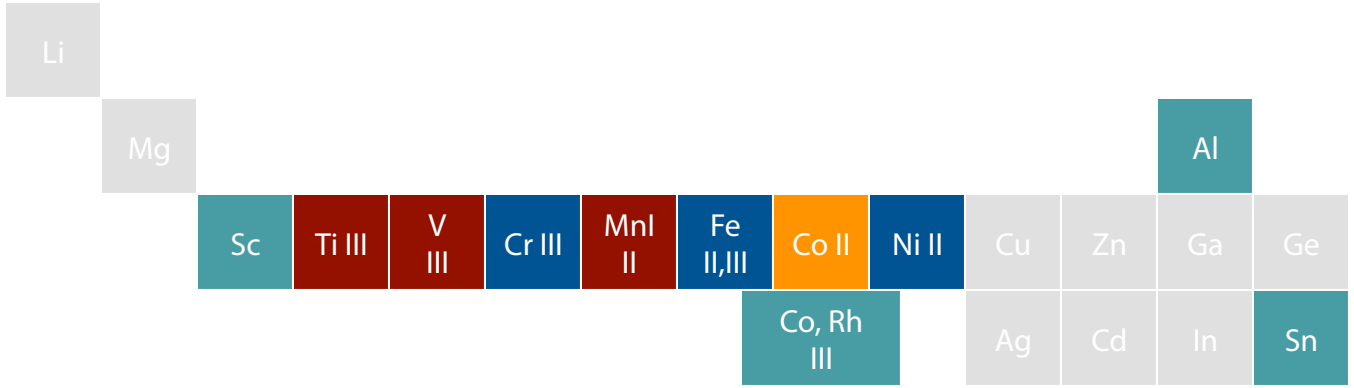
In general, lower oxidation states and smaller bandwidths than in perovskites.

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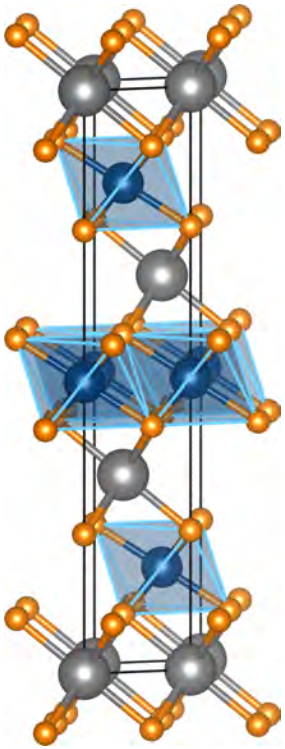
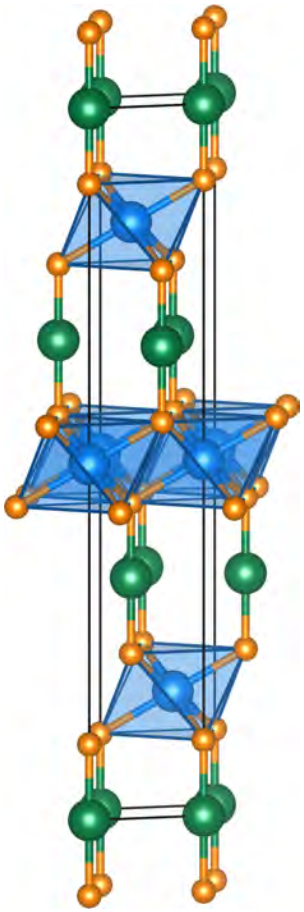
Some ABO_2 structures: Highly dense in-plane, and frequently metallic

$LiCoO_2$ (ordered rock-salt)



111-ordered with alternating octahedral LiO_6 and CoO_6 stacking

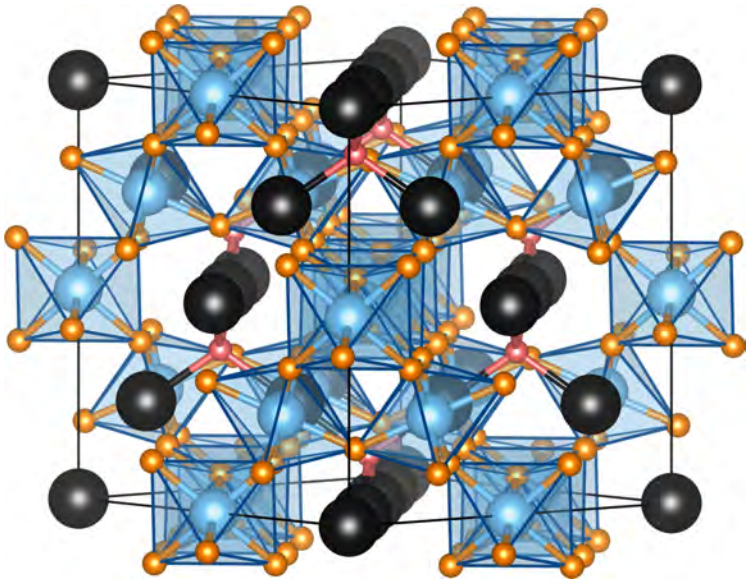
$3R$–$CuFeO_2$ (delafossite)

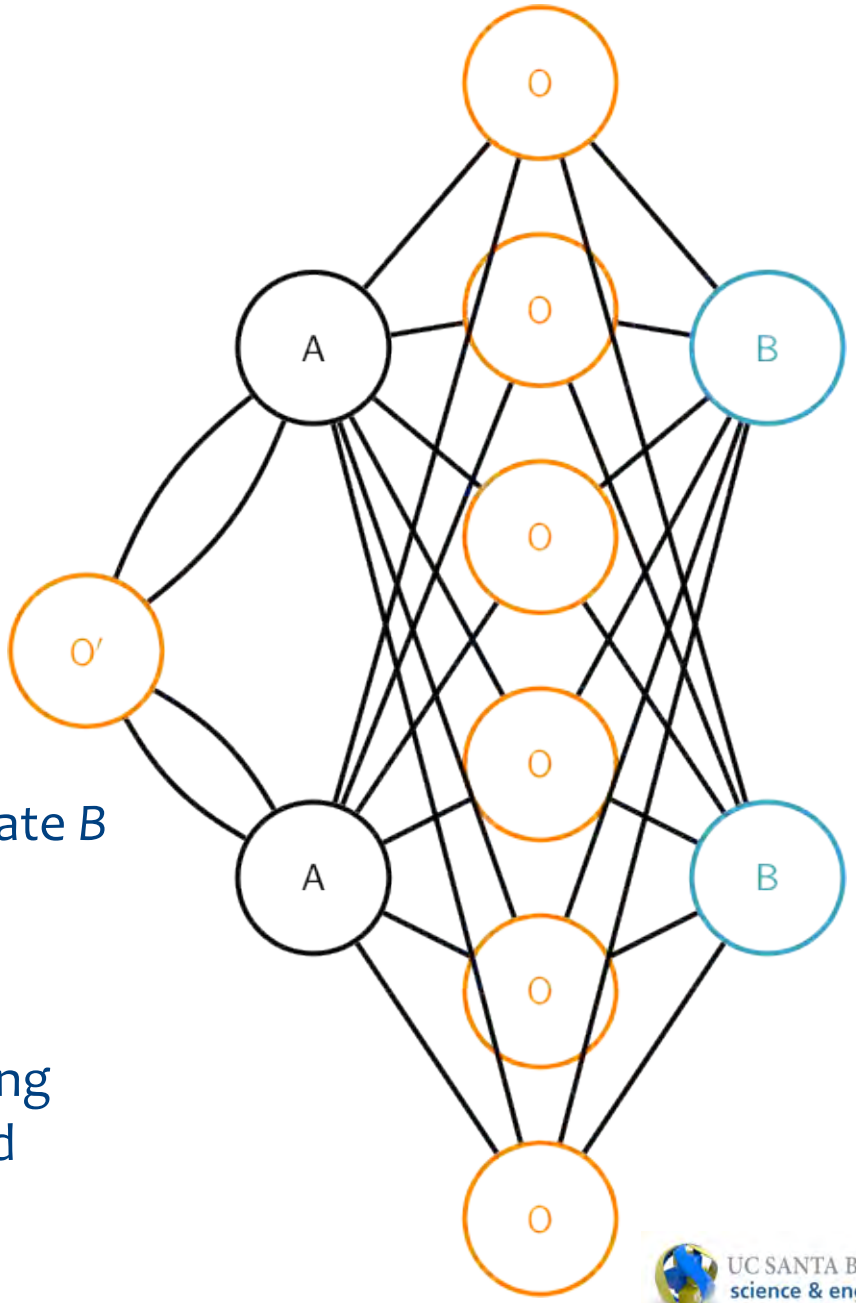


BO_2 (CdI_2) slabs separated by two-coordinate atoms, usually Cu^+ and Ag^+. Also unusually, Pd^{1+} and Pt^{1+}.

$A_2B_2O_7$ pyrochlore

$Y_2Ti_2O_7 = Y_2Ti_2O_6Ó$





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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