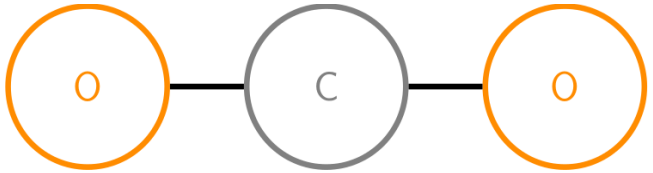
Refresher on oxide crystal structures

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

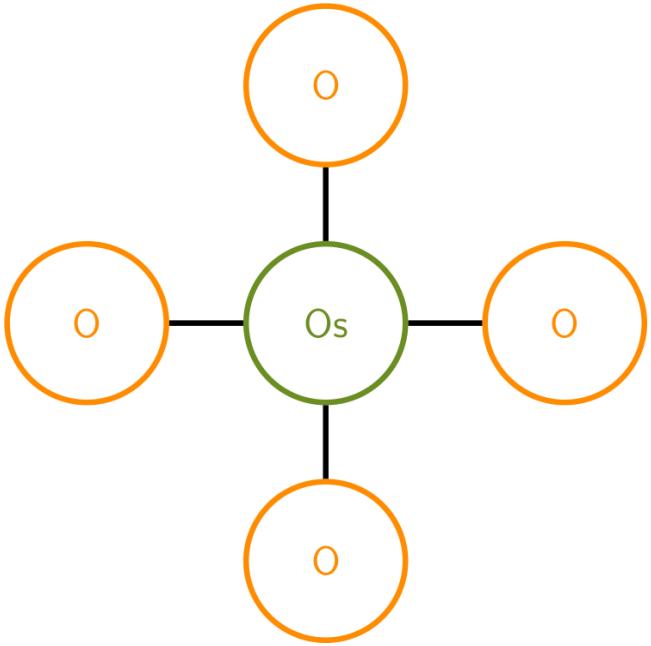
N.B.: CoO is simple, Co_3O_4 is not. $ZnCo_2O_4$ is certainly not !
Co_3O_4 and $ZnCo_2O_4$ are complex oxides.

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

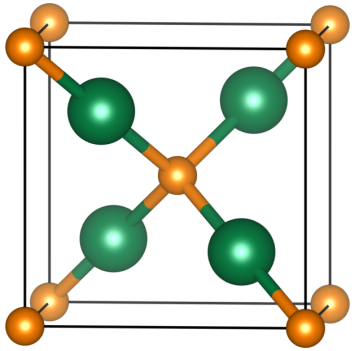


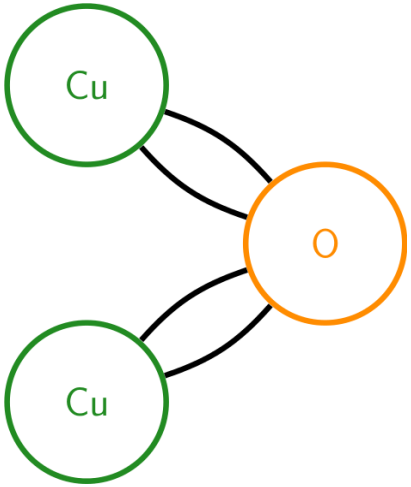
OsO_4: The structure comprises isolated tetrahedra (molecular). The graph is below:
Each Os connected to 4 O and each O to 1 Os



Crystal structures of simple oxides of monovalent ions: A_2O

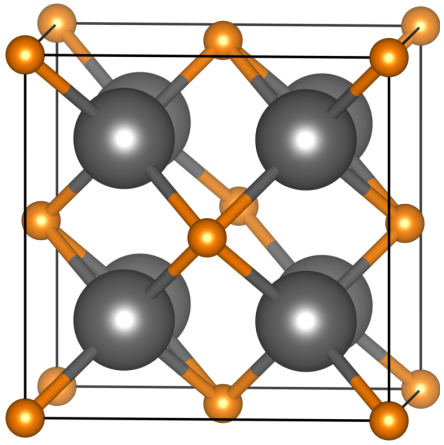
Cu_2O

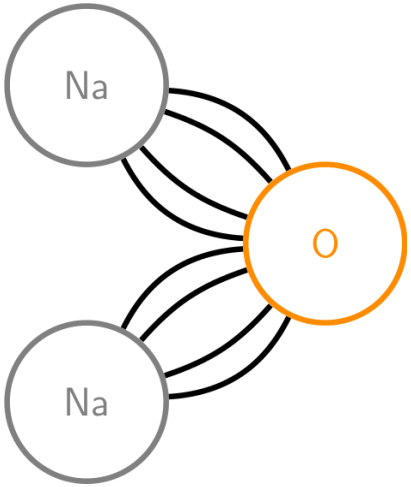




Linear coordination is unusual. Found usually in Cu^+ and Ag^+.

Na_2O (anti-fluorite)

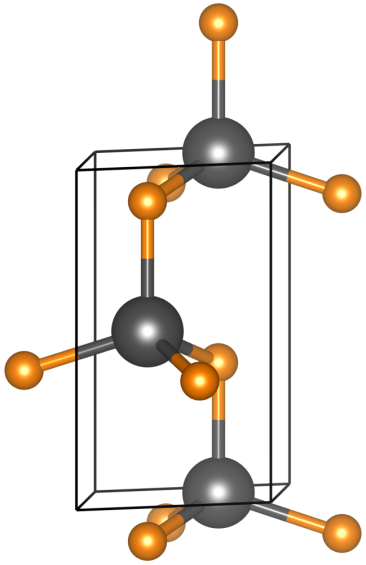


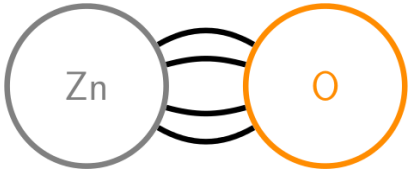


4-coordination for Na^+ and 8-coordination for O^{2-} are unusual.

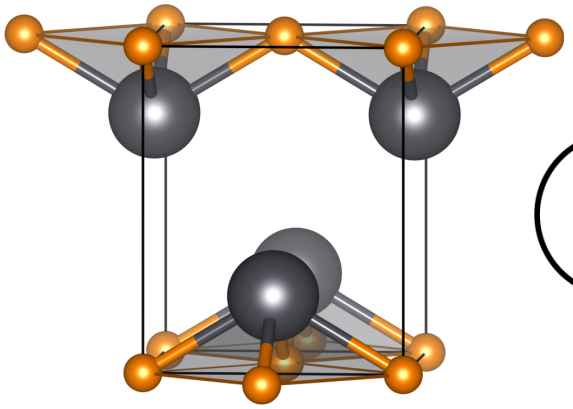
Crystal structures of simple oxides of divalent ions: AO

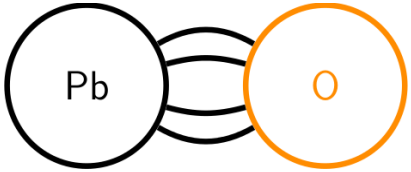
ZnO (wurtzite), sp^3



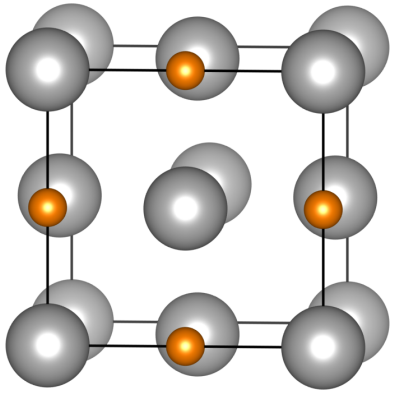


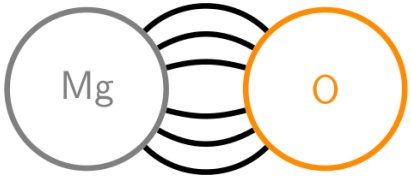
PbO (litharge), lone pairs





MgO (rock-salt)



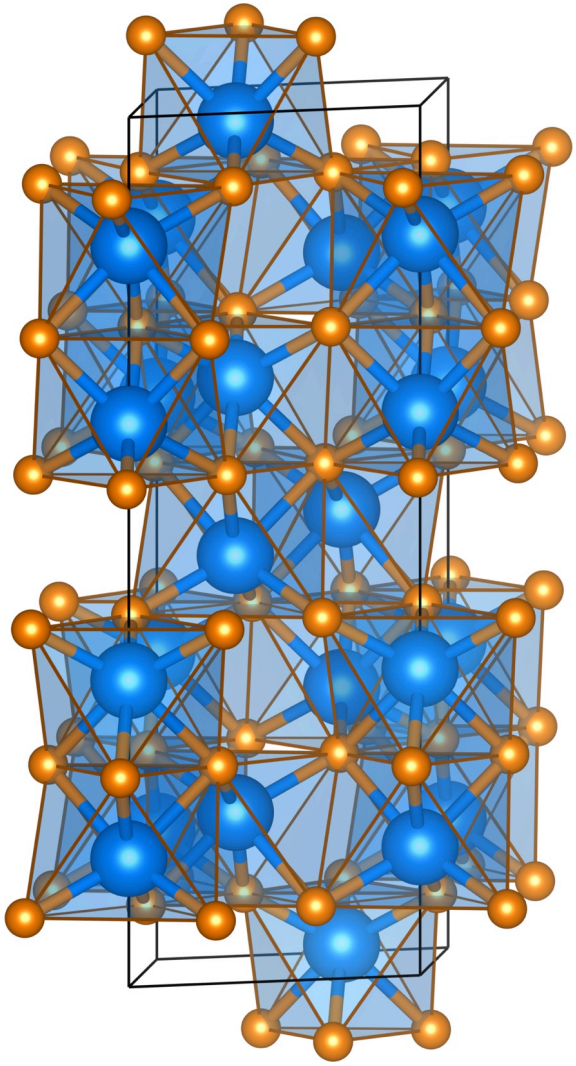


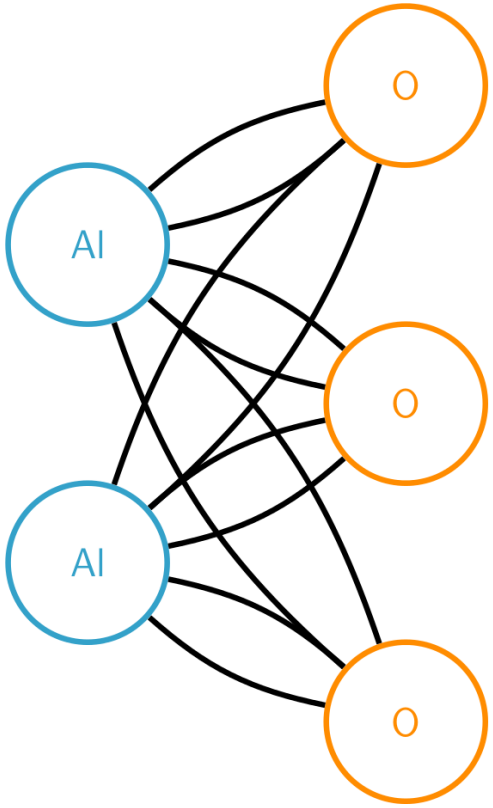
Ubiquitous for AO oxides including transition metals (distorted for CuO and NbO).

Insulators, metals (TiO), magnetic, …

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

α-Al_2O_3 (corundum)





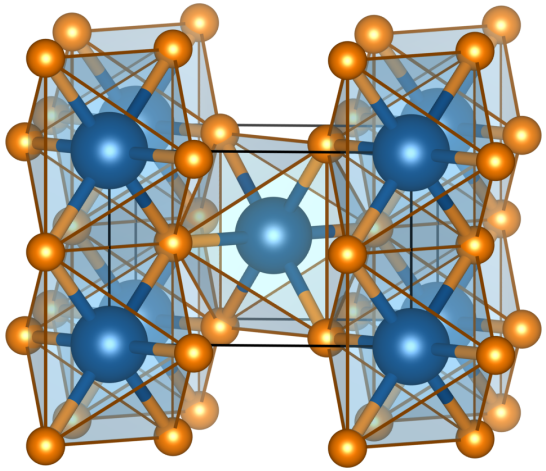
Also the structure of Cr_2O_3 and Fe_2O_3.

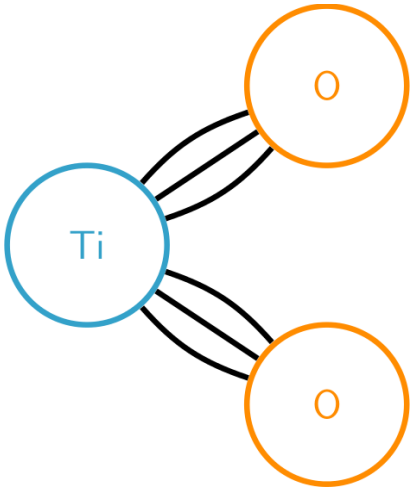
Ga_2O_3 does funny things.

In_2O_3 is different (bixbyite).

Crystal structures of simple oxides of tetravalent ions: AO_2

TiO_2 (rutile)

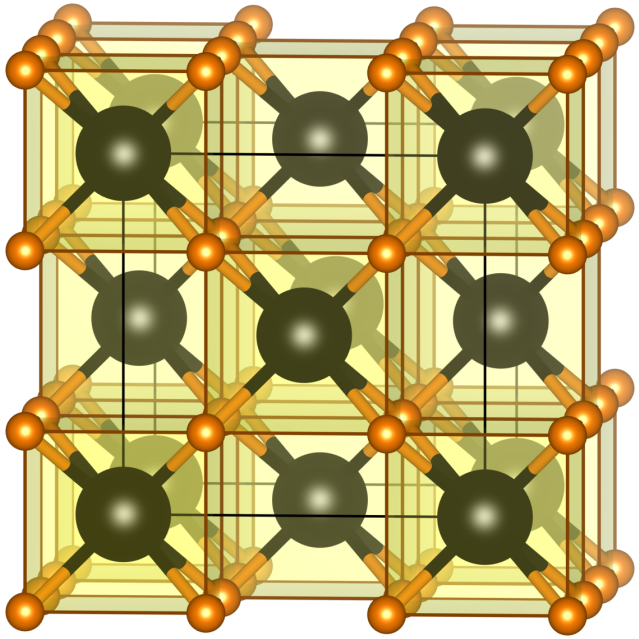


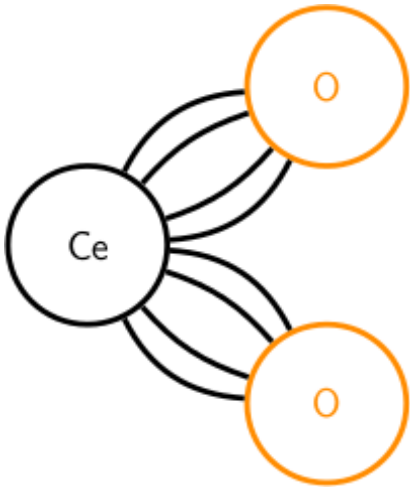


TiO_2 also crystallizes as anatase and brookite.

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

CeO_2 (fluorite)



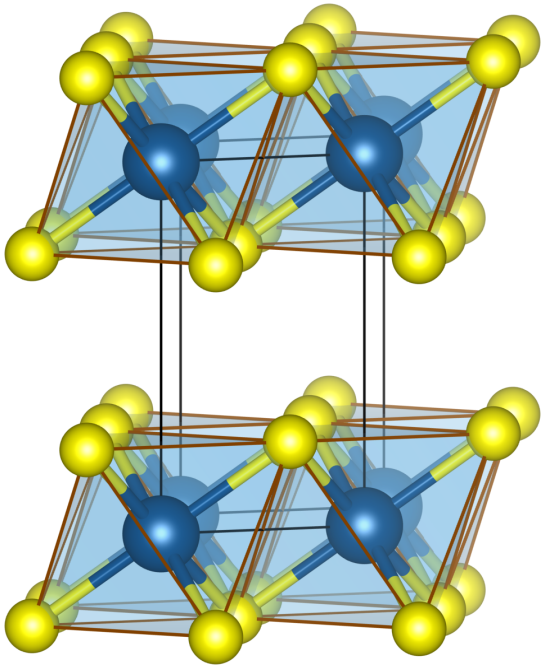


Also the structure of ThO_2, and of ZrO_2 and HfO_2 at elevated temperatures.

Ordered variants abound.

Oxides versus sulfides: TiS_2

$2H–TiS_2$

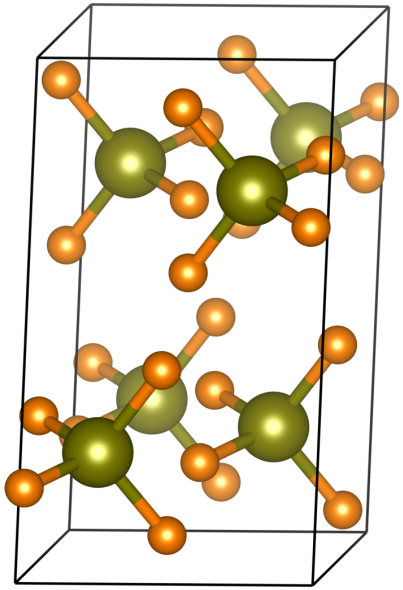


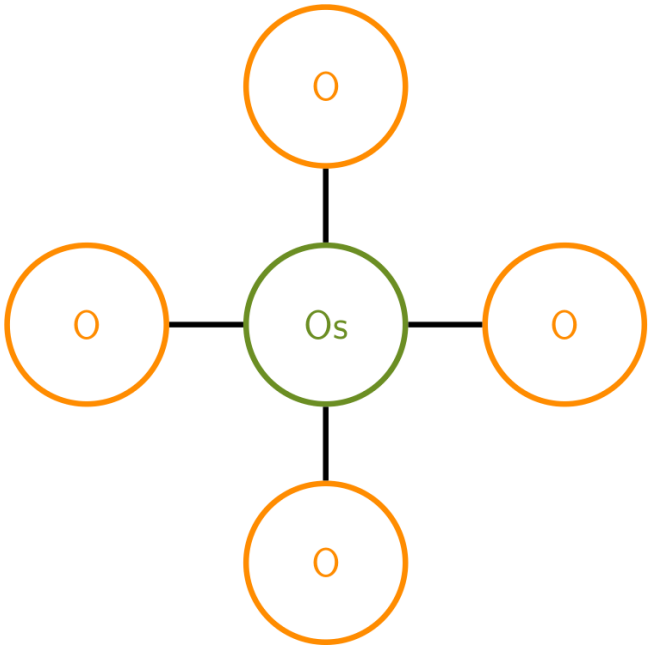
van der Waals gap (unlikely in oxides or fluorides, but occurs frequently in hydroxides)

This is the CdI_2 structure.

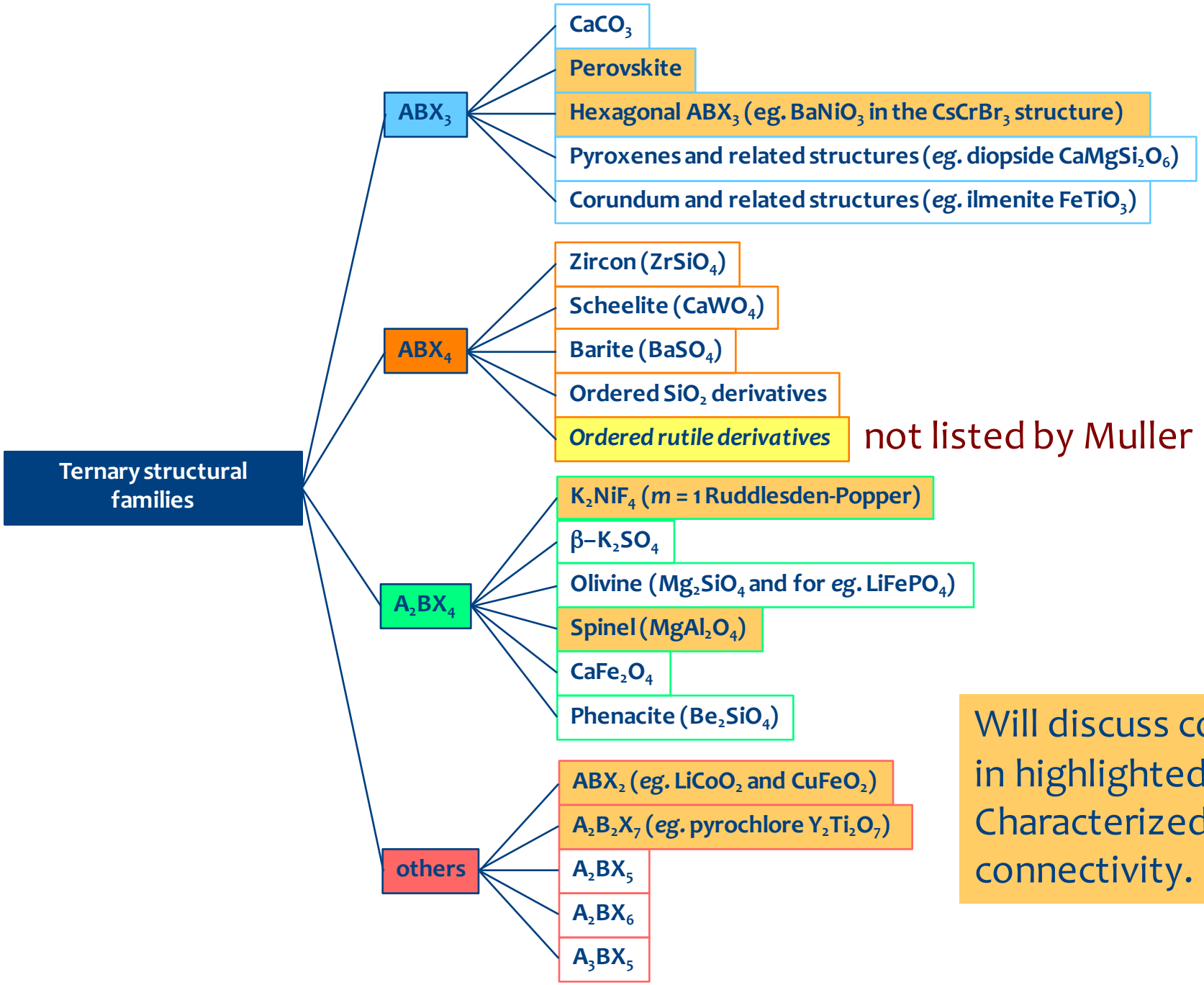
Crystal structures of an oxide with an octavalent ion: OsO_4

OsO_4





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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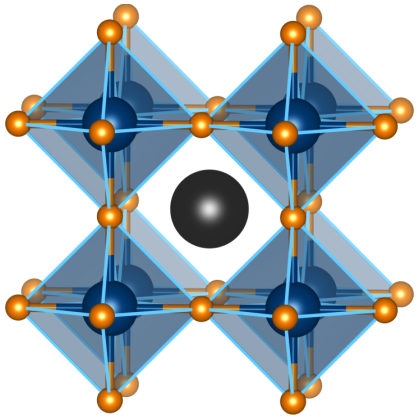
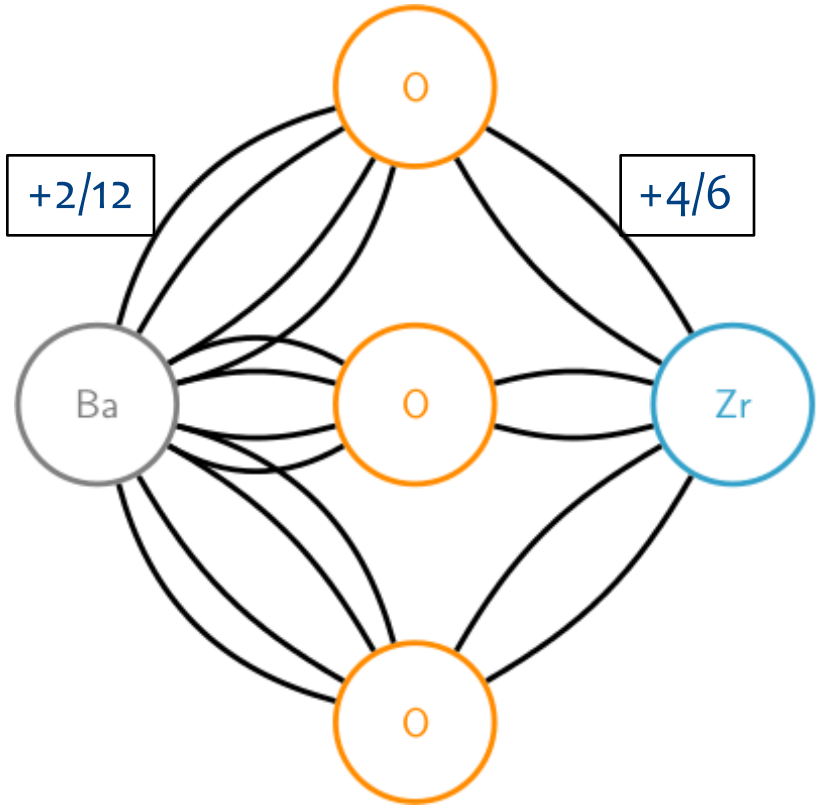
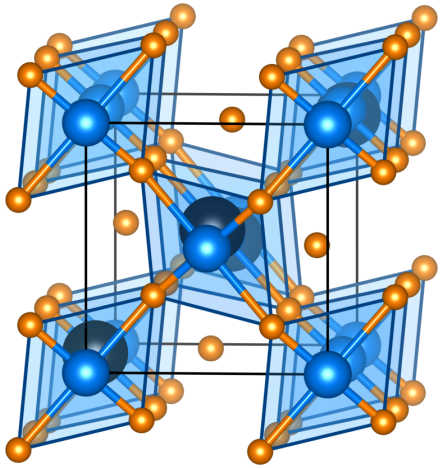
Perovskite

$BaZrO_3$





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



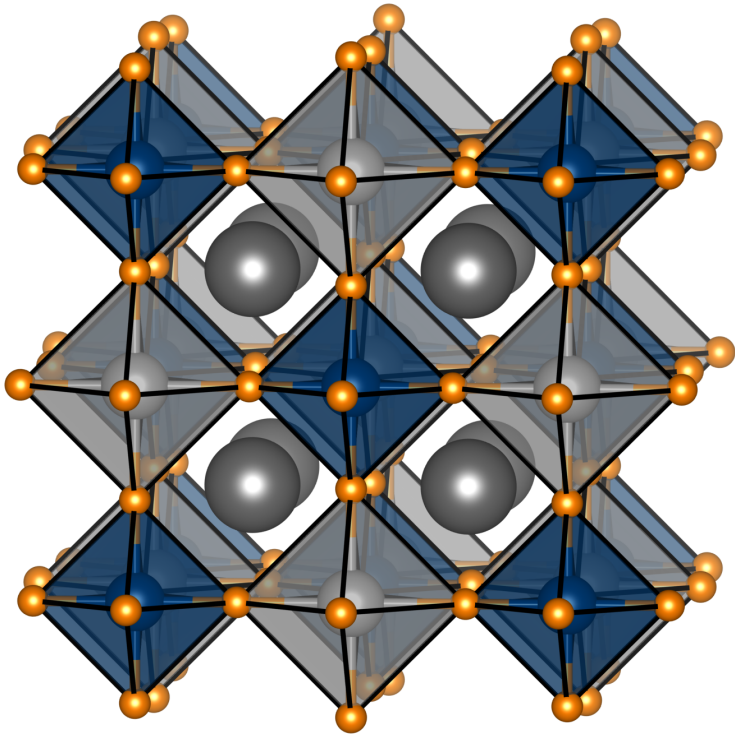
Note that the space group *Pnma* (#62) can be written in a variety of ways.

This is the most common perovskite space group.

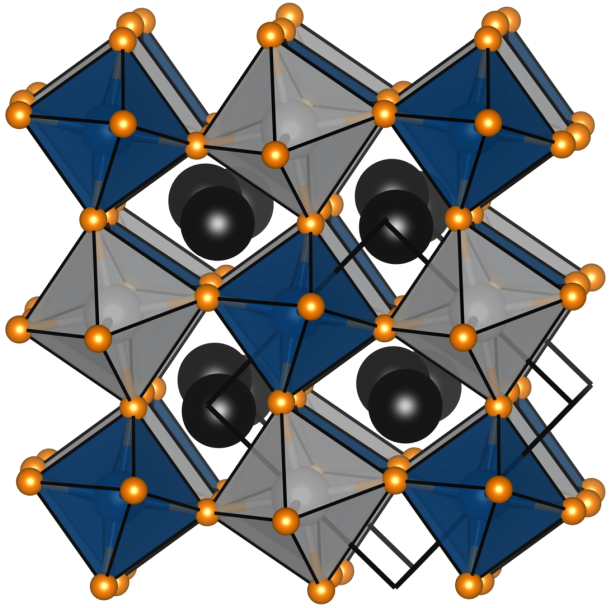
In the next so many structures, BO_6-polyhedra are depicted.

Ordered double perovskites (elpasolites)

Ba_2MgWO_6



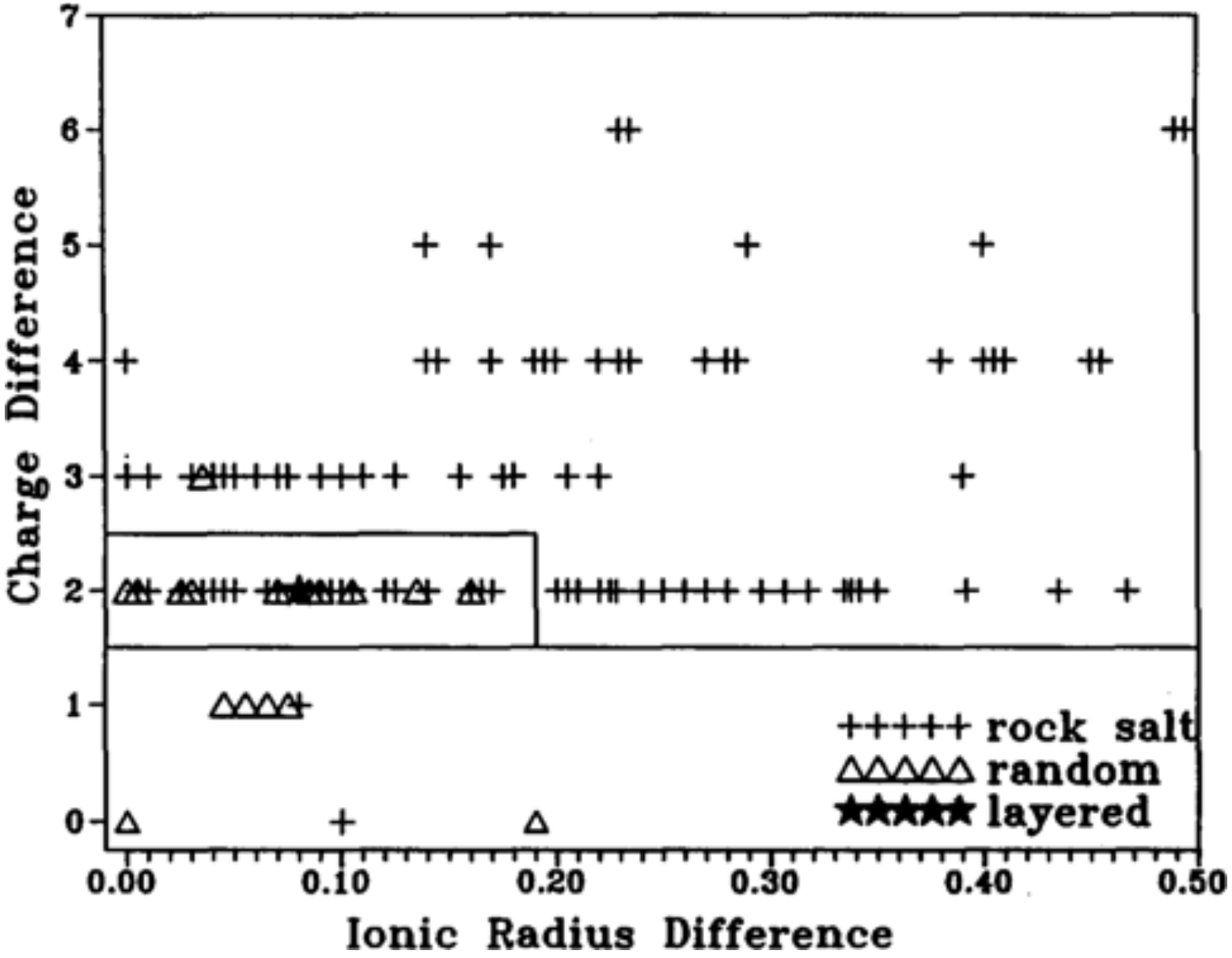
Ca_2MgWO_6



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.

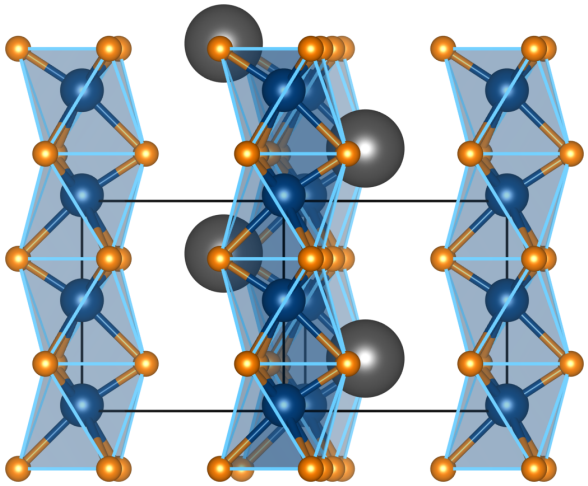
The double perovskite field: Charge and radius



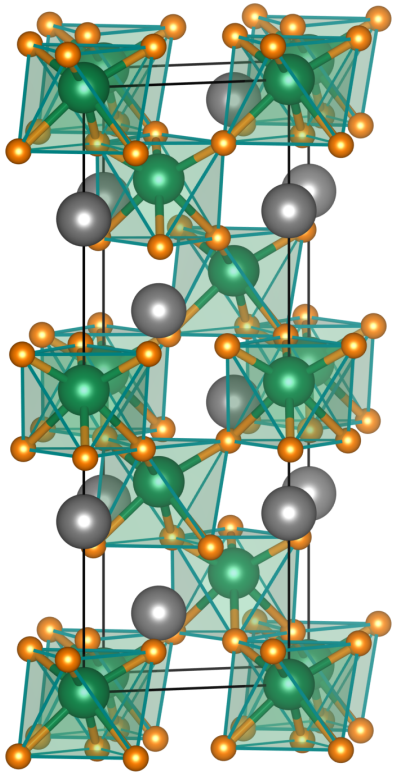
Anderson, Greenwood, and Poeppelmeier, *Prog. Solid State Chem.* **22** (1993) 197–233.

Hexagonal ABO_3 structures

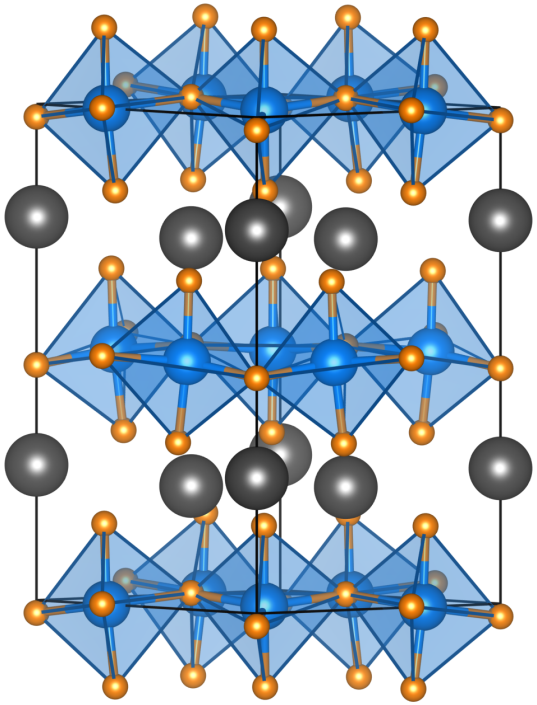
$BaNiO_3$



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



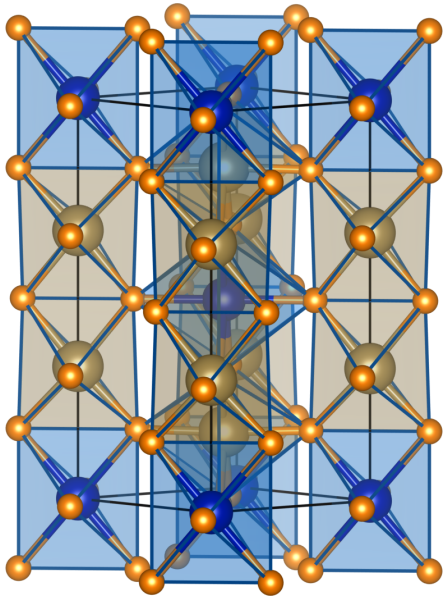
Ferroelectric $YMnO_3$ ("$YAlO_3$")



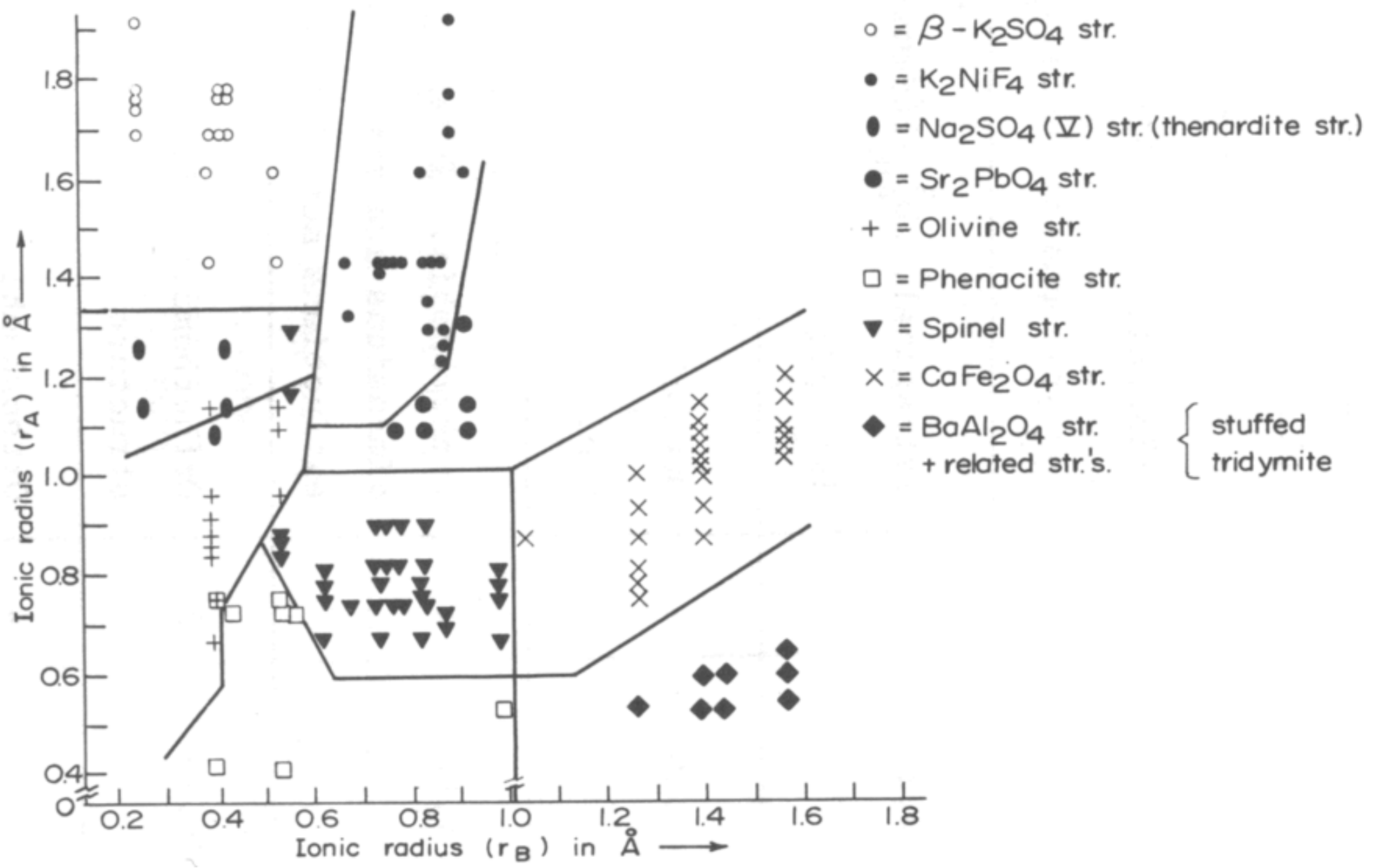
Unusual 5-fold coordination (trigonal bibyramid) of MnO_5

Ordered rutiles (the trirutile)

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

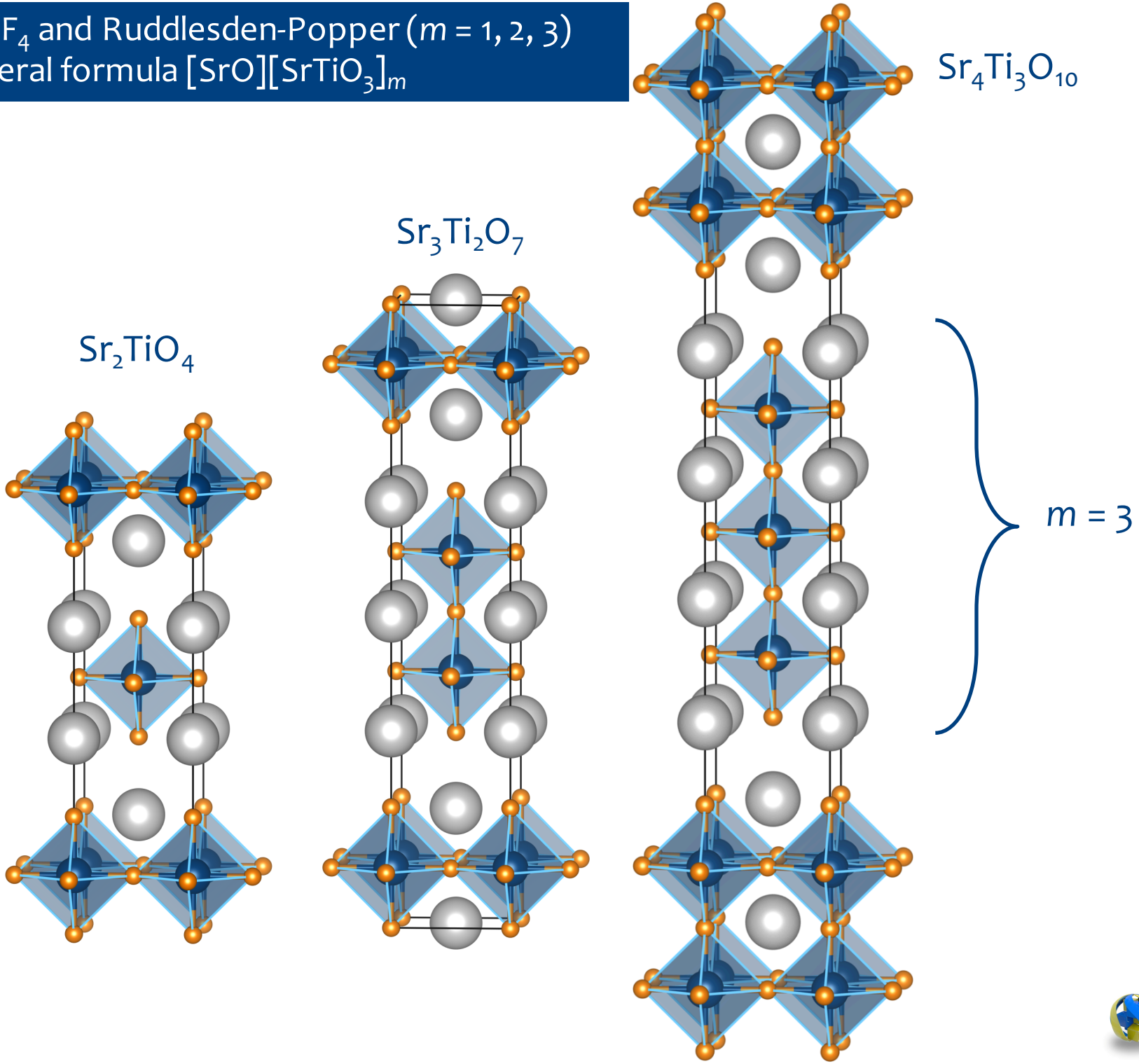


The A_2BO_4 structure-sorting field (from Muller and Roy)



The superscripted roman numerals indicate coordination number.

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



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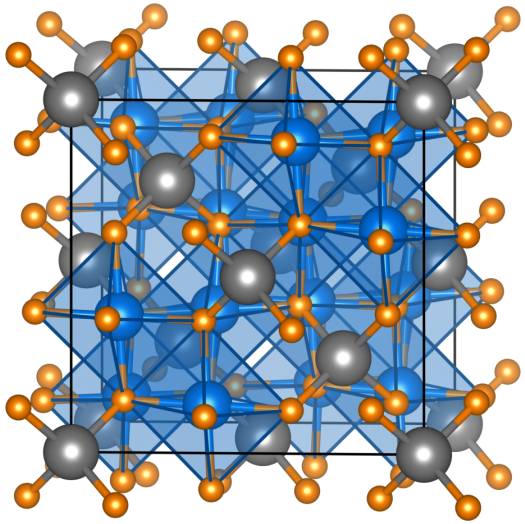
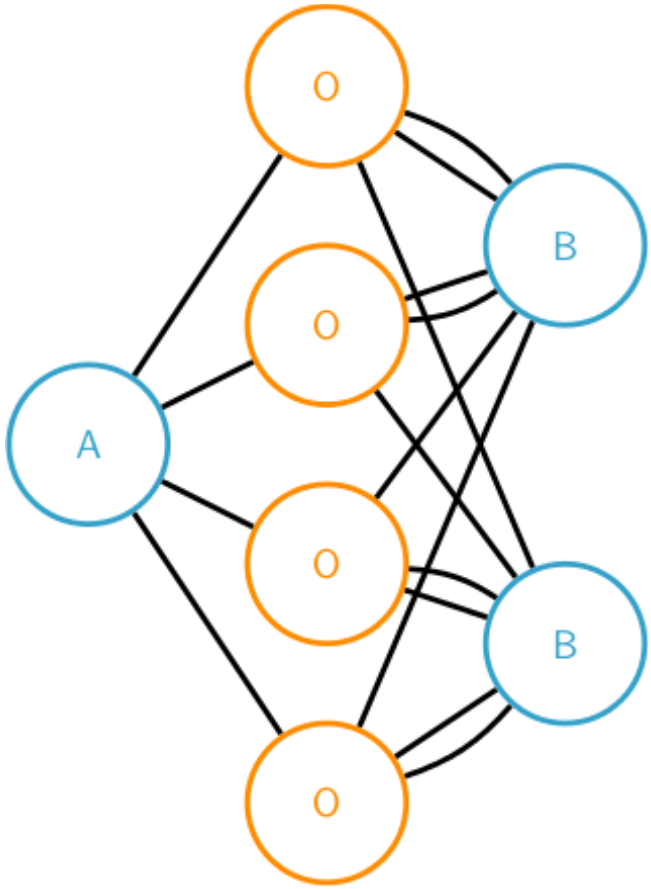
Spinel AB_2O_4

$MgAl_2O_4$



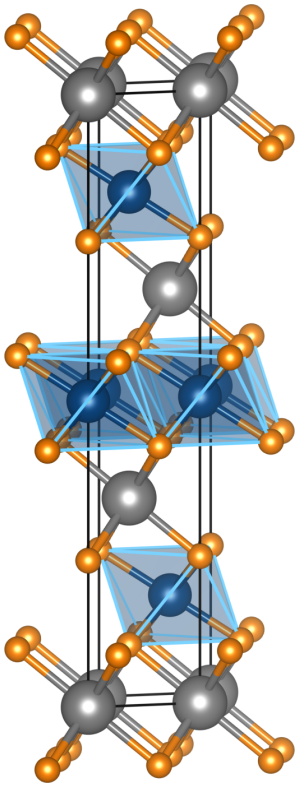


Ubiquitous structure when ions have similar sizes, around 0.6 Å.
A is tetrahedrally coordinated, and *B* octahedral (actually with a slight trigonal distortion).

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

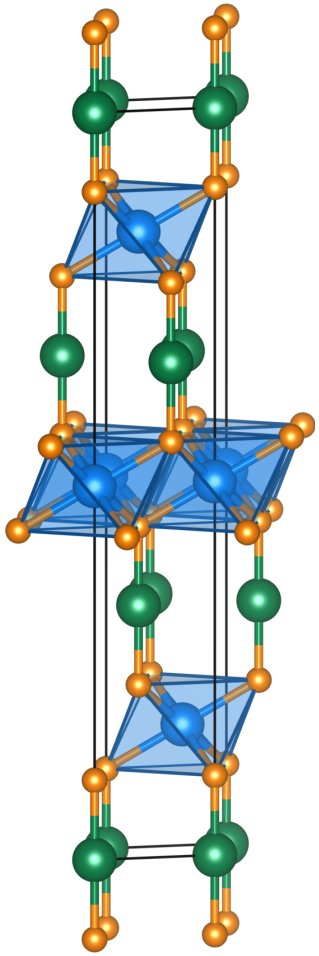
Some ABO_2 structures: Highly dense in-plane, and frequently metallic

$LiCoO_2$ (ordered rock-salt)



111-ordered with alternating octahedral LiO_6 and CoO_6 stacking

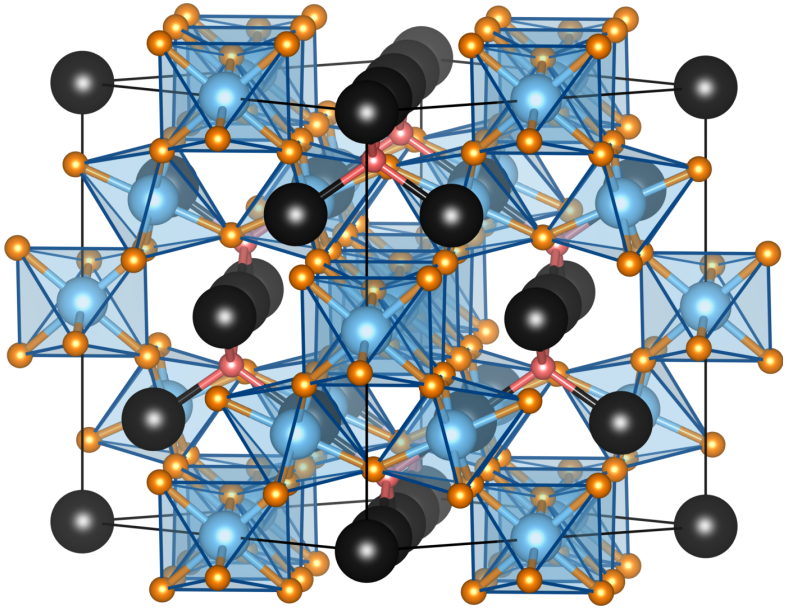
$3R$–$CuFeO_2$ (delafossite)

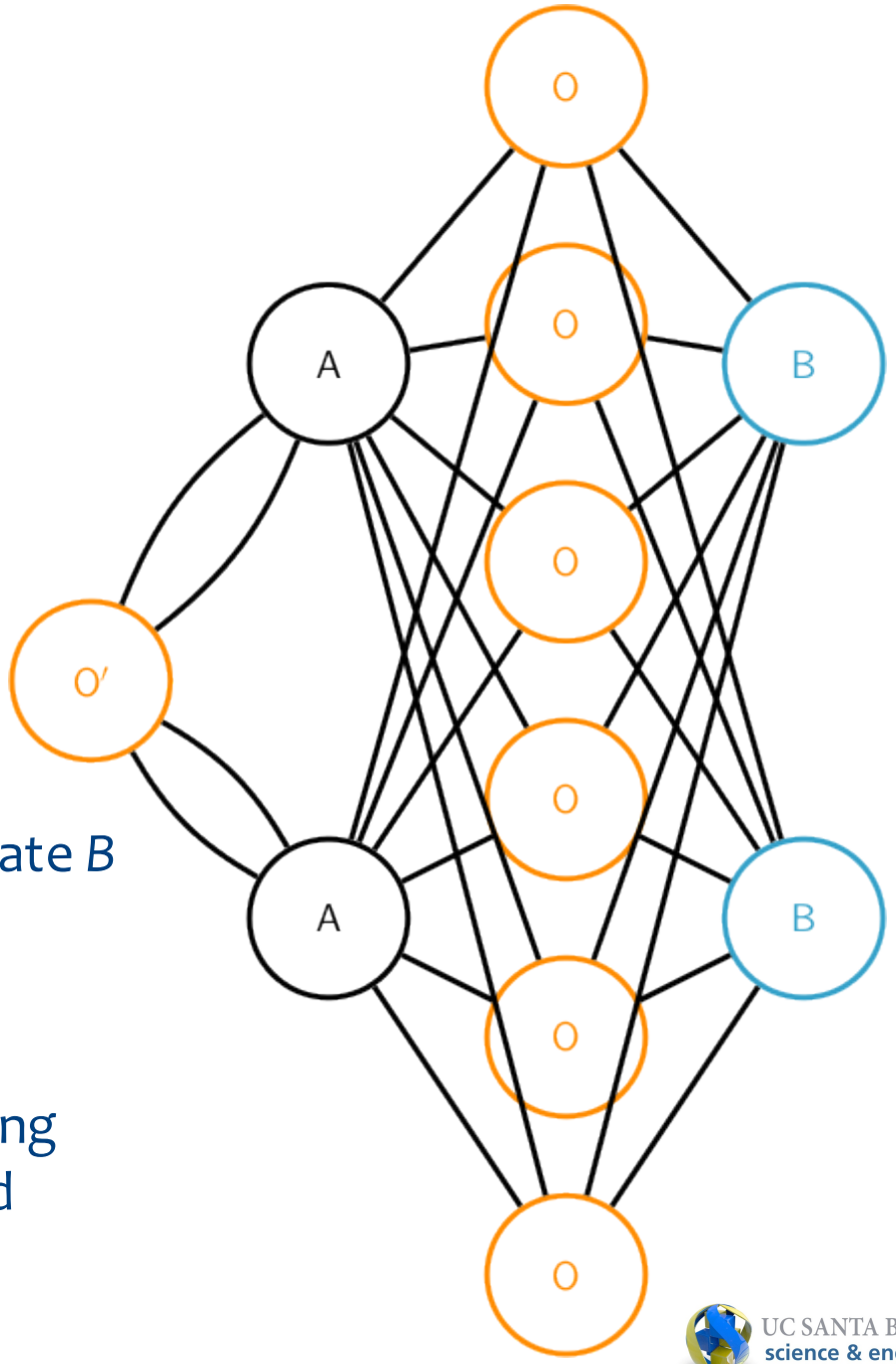


BO_2 (CdI_2) slabs separated by two-coordinate atoms, usually Cu^+ and Ag^+. Also unusually, Pd^{1+} and Pt^{1+}.

$A_2B_2O_7$ pyrochlore

$Y_2Ti_2O_7 = Y_2Ti_2O_6O'$





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.