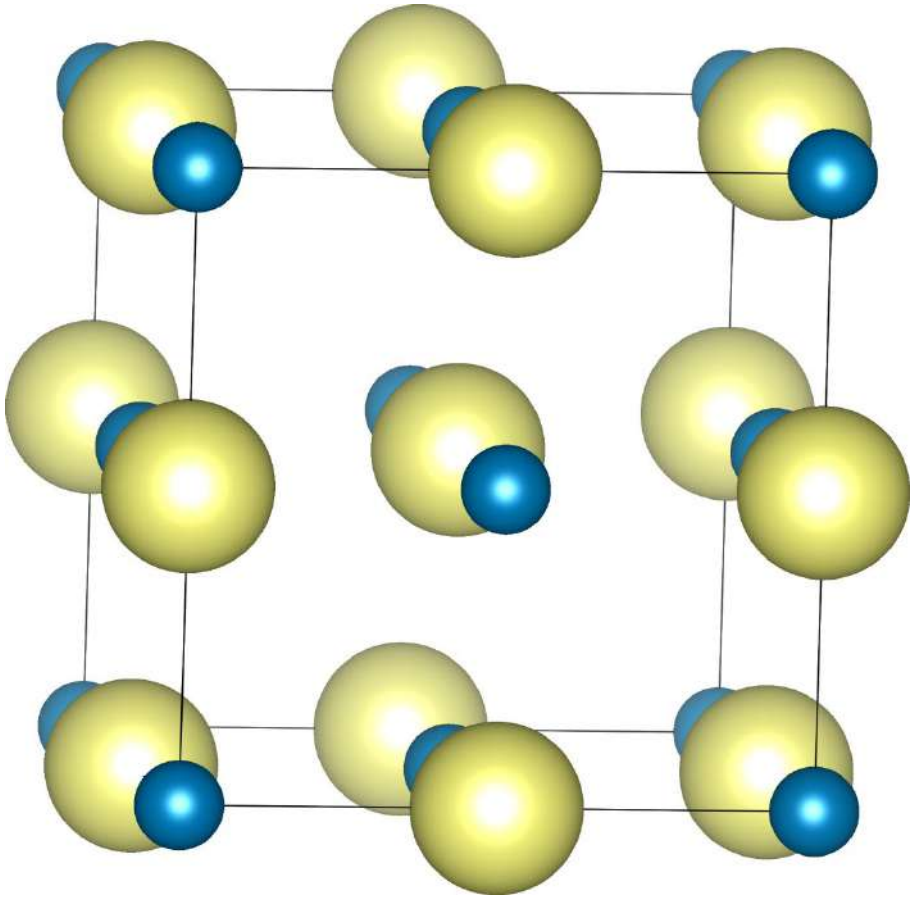
Chemistry 524
Inorganic Materials Chemistry

Prototypical Structures

Rock Salt (NaCl) has two interpenetrated *fcc* lattices (AX)



$Fm\bar{3}m$, a = 5.6573Å

Atom	x	y	z
Na	0.00	0.00	0.00
Cl	0.50	0.50	0.50

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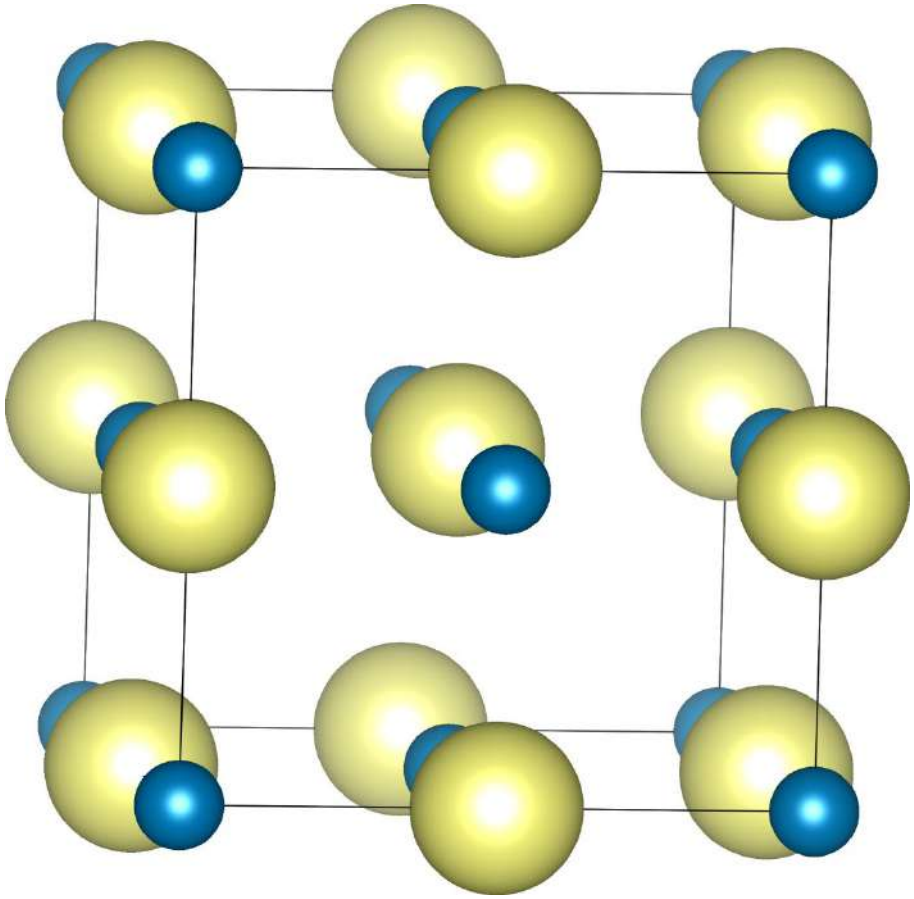
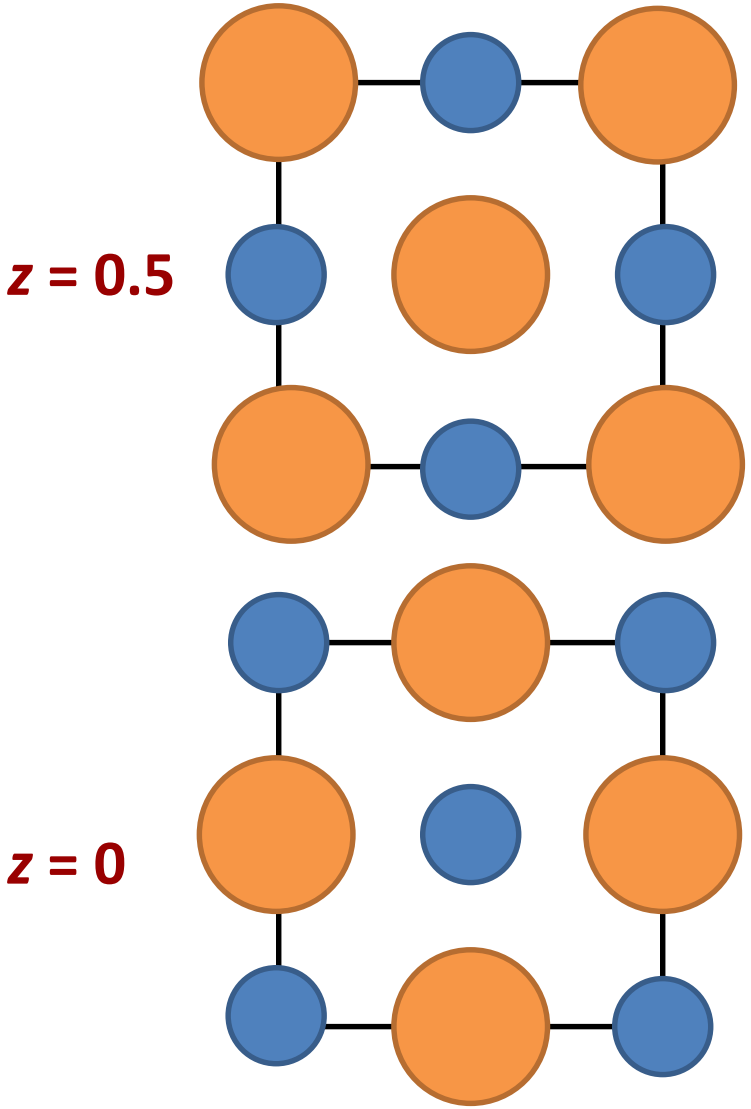
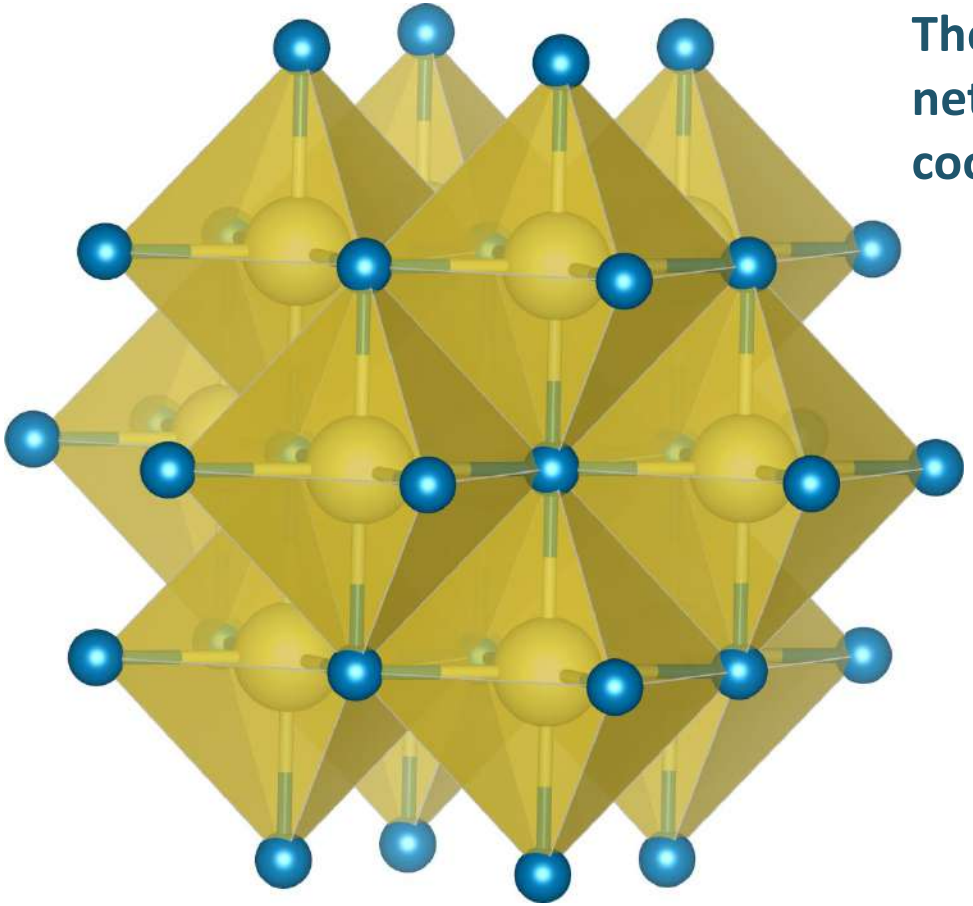




$LiCoO_2$ adopts an ordered rocksalt structure



The rock salt structure is a dense network of edge-sharing octahedrally coordinated cations

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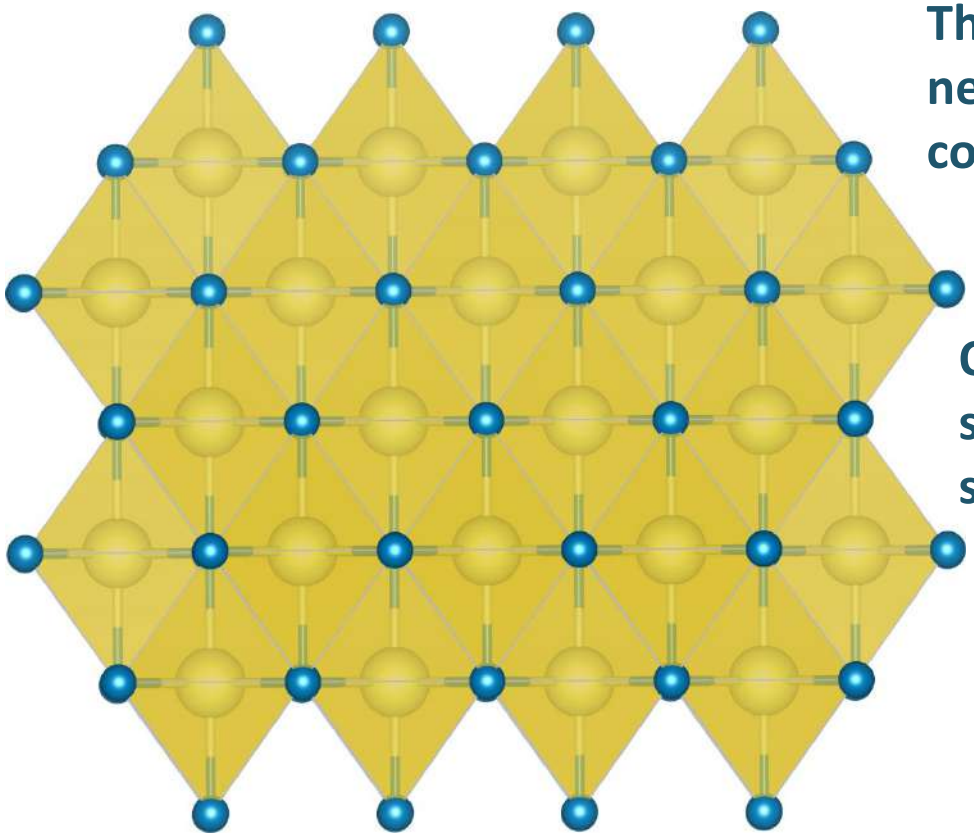

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Orienting in the correct fashion we can start to see the potential for a layered structure

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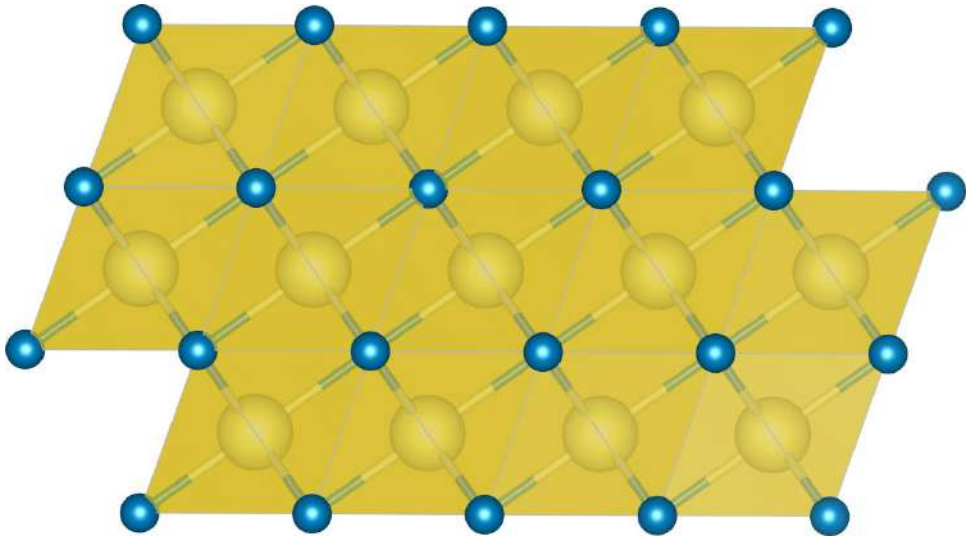

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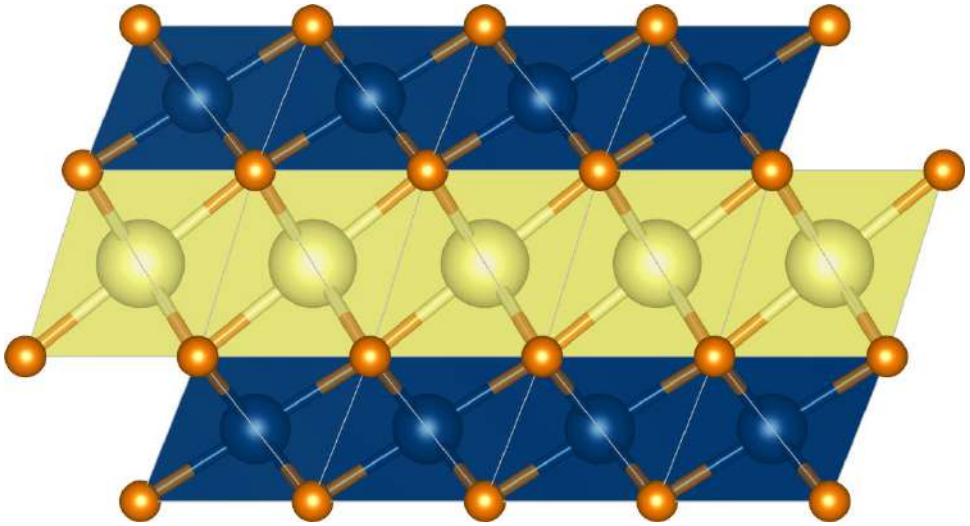

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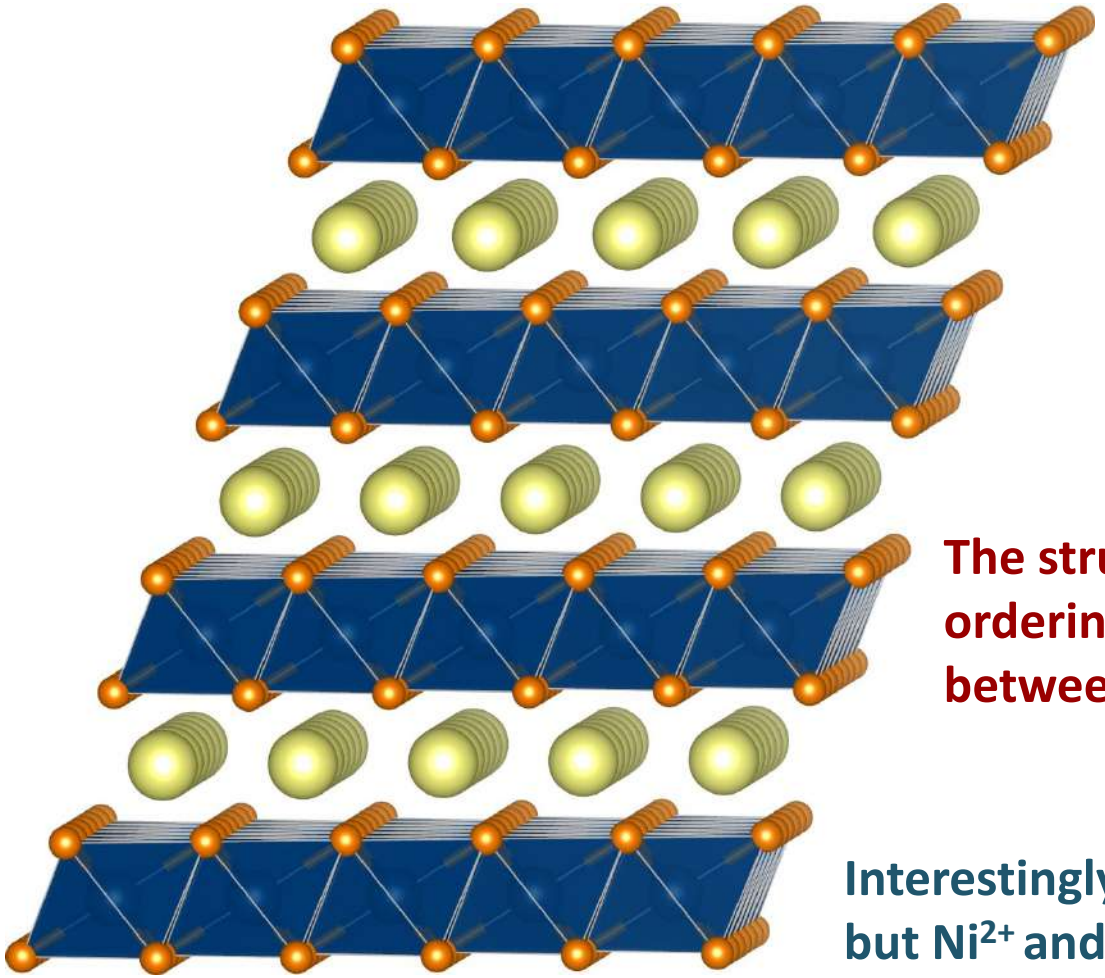
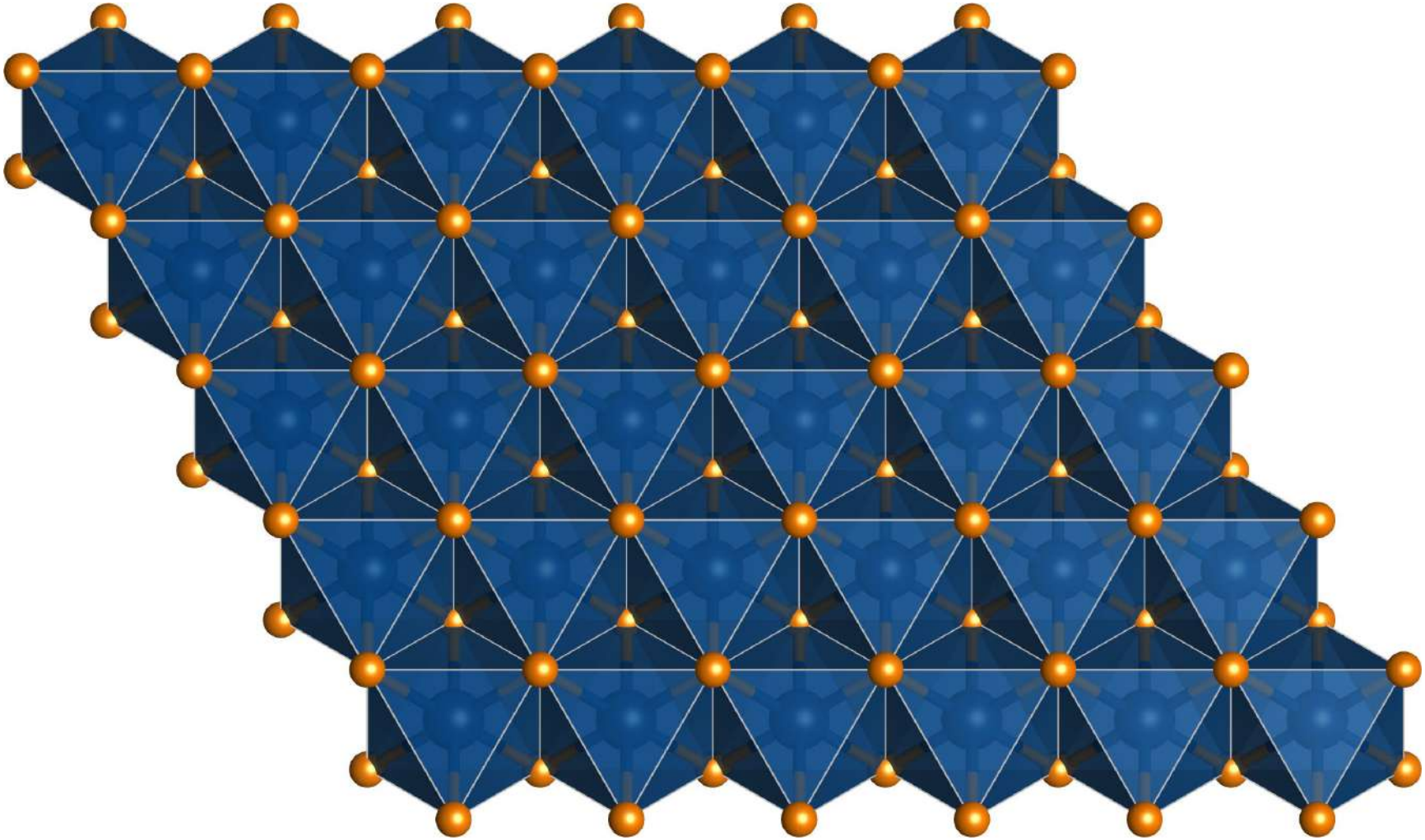


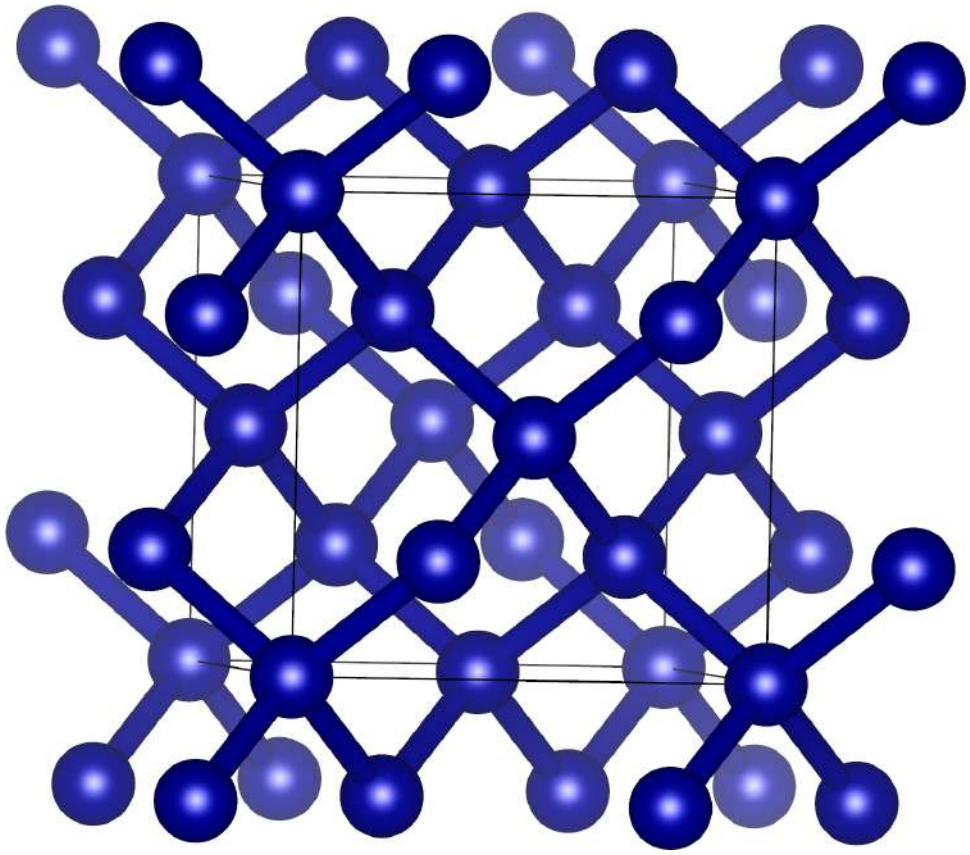
The structure of $LiCoO_2$ is formed by ordering the site occupancy of Li and Co between the layers

Interestingly, $LiNiO_2$ has a similar structure, but Ni^{2+} and Li^{+} have similar ionic radii, thus there is substantial mixing between the Li and Ni layers

$LiCoO_2$ has “brucite”-like layers of edge-sharing octahedra



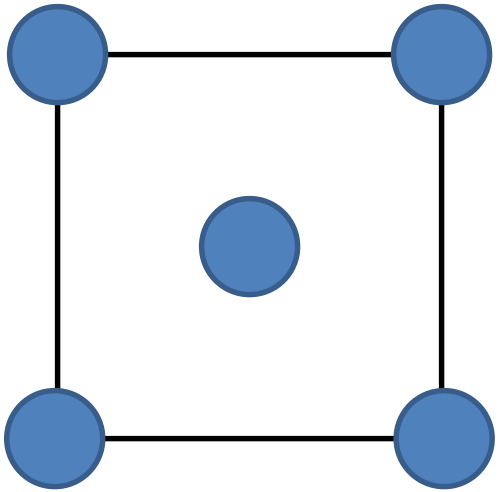
Carbon and Silicon both adopt the diamond structure



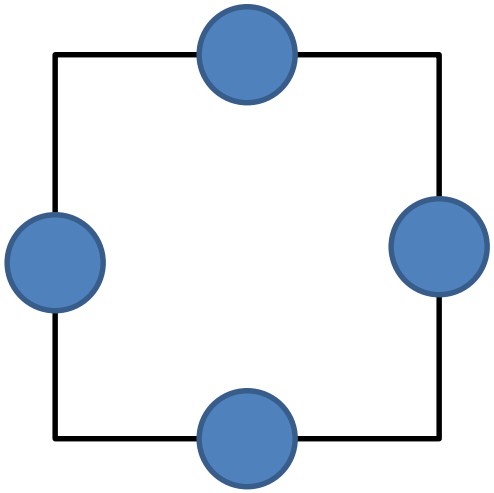
$Fd\bar{3}m$, a = 3.5667Å

Atom	x	y	z
C	0.00	0.00	0.00

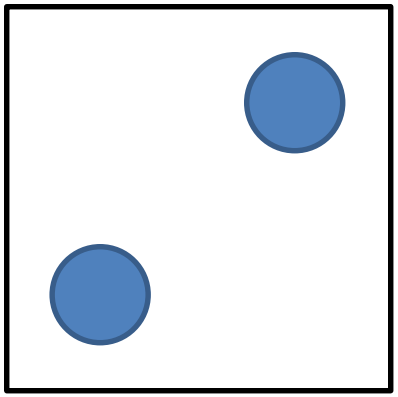
Carbon and Silicon both adopt the diamond structure



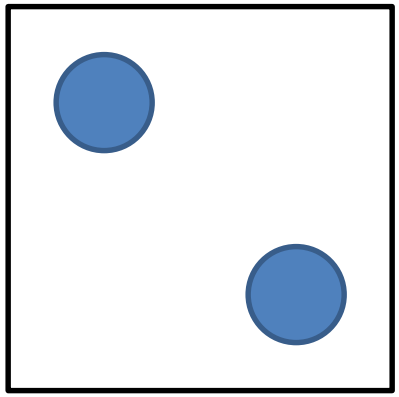
z = 0.00



z = 0.50

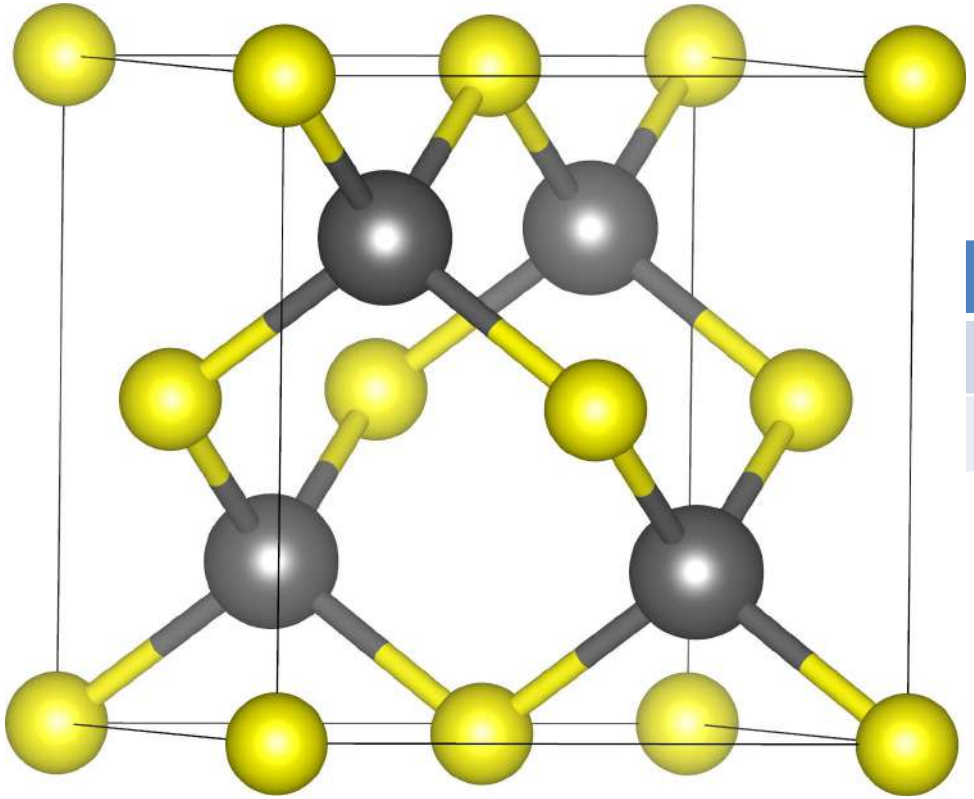


z = 0.25



z = 0.75

If there are different atoms, diamond becomes zinc blende

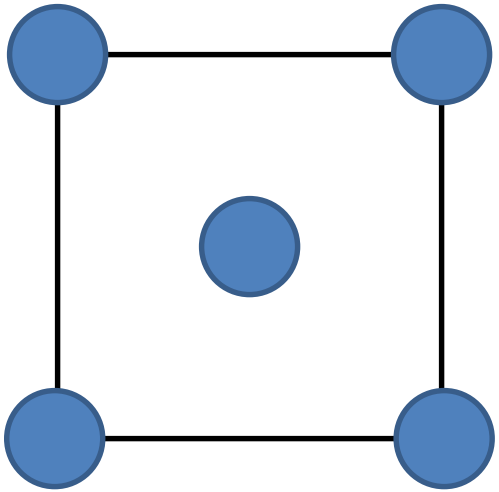


ZnS

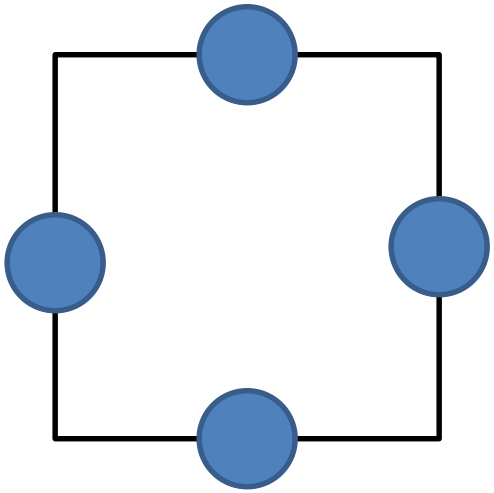
$F\bar{4}3m$, a = 5.4090Å

Atom	x	y	z
S	0.00	0.00	0.00
Zn	0.25	0.25	0.25

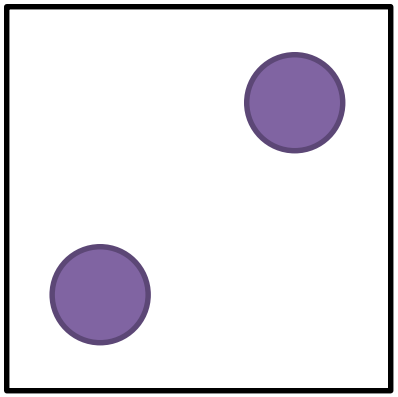
Stereographic projection of zinc blende



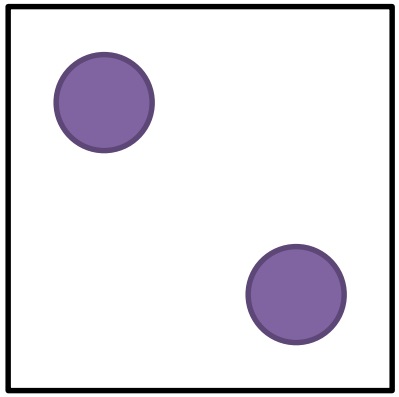
$z = 0.00$



$z = 0.50$

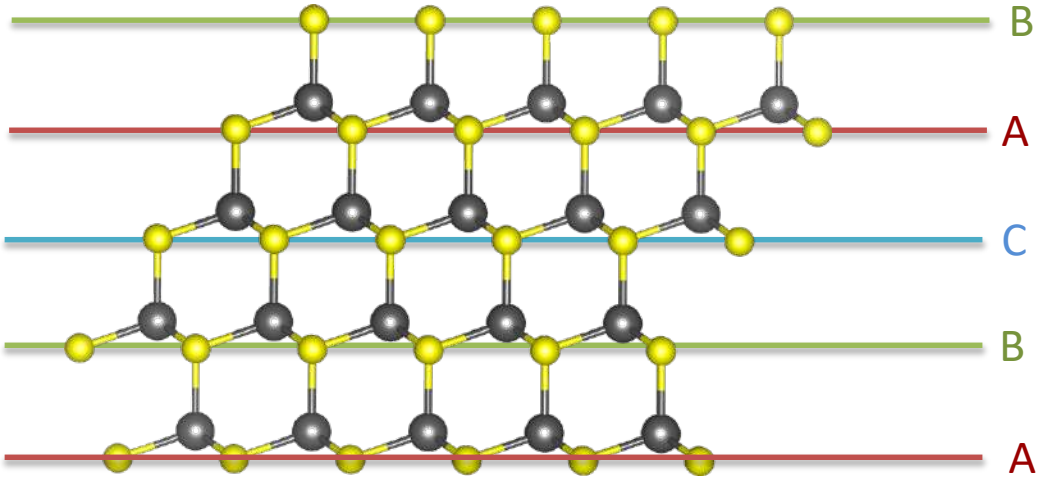


$z = 0.25$



$z = 0.75$

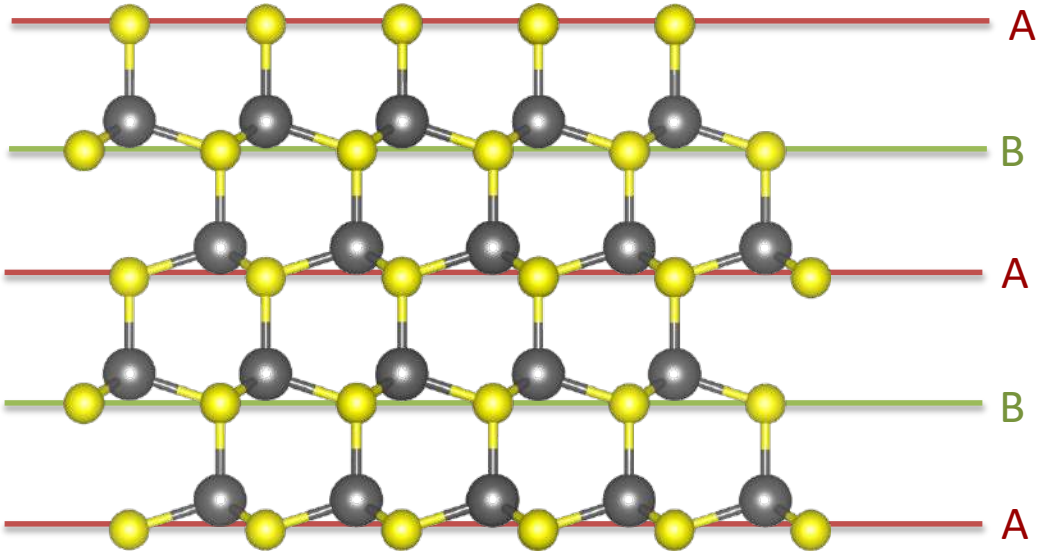
Wurtzite and Zinc Blende differ in stacking sequence



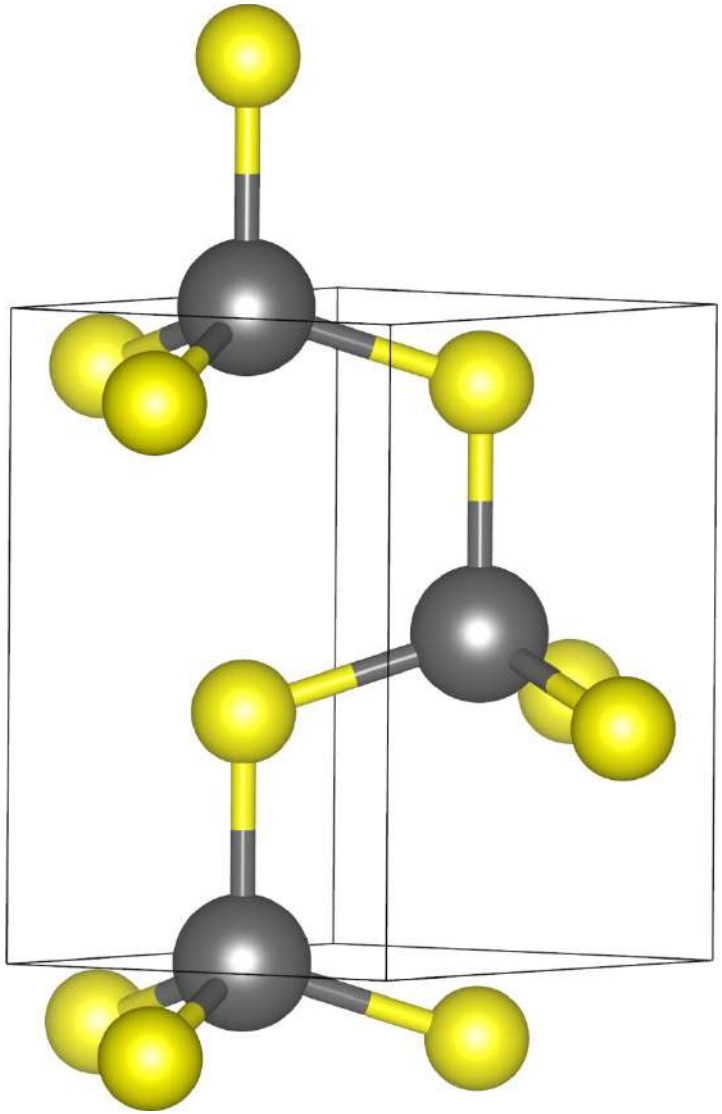
Zinc blende has a cubic unit cell with an fcc lattice of anions…

Thus the anions form a cubically close packed network with half of the tetrahedral interstitials containing a different cation

The principle difference in the wurtzite structure is that the anionic lattice is hexagonally close packed



The wurtzite unit cell is hexanal (hcp oxygen)

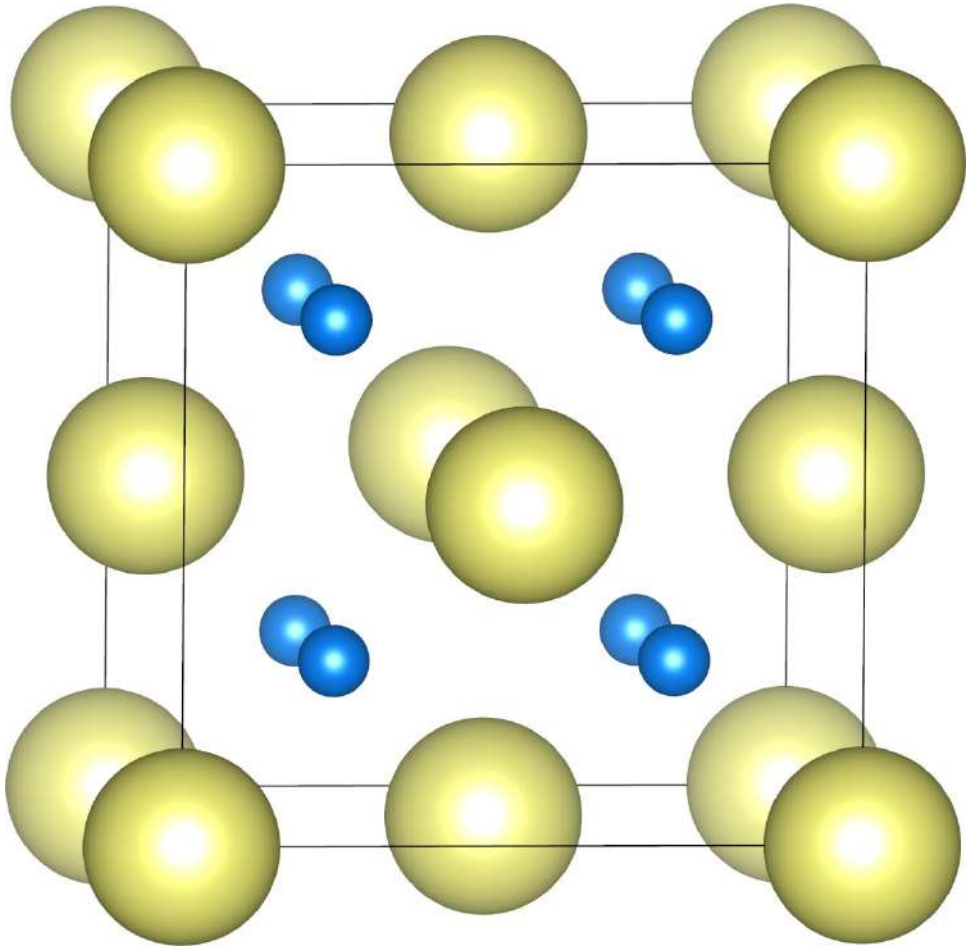


P63mc,

***a* = 3.2499, c = 5.2066**

Atom	*x*	*y*	*z*
S	0.3333	0.66667	0.00
Zn	0.3333	0.6667	0.3333+δ

The fluorite structure has general composition AX_2

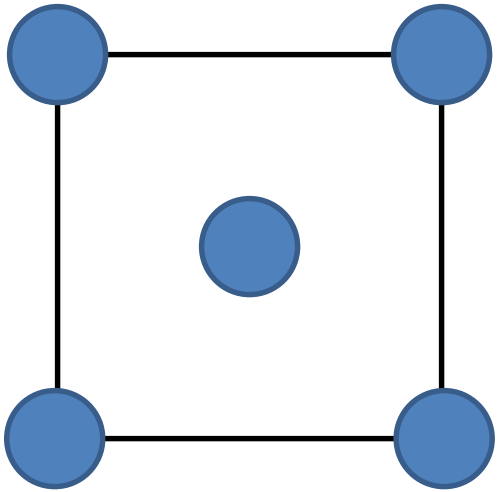


Many very important engineering materials adopt the fluorite structure – CeO_2, ZrO_2, UO_2

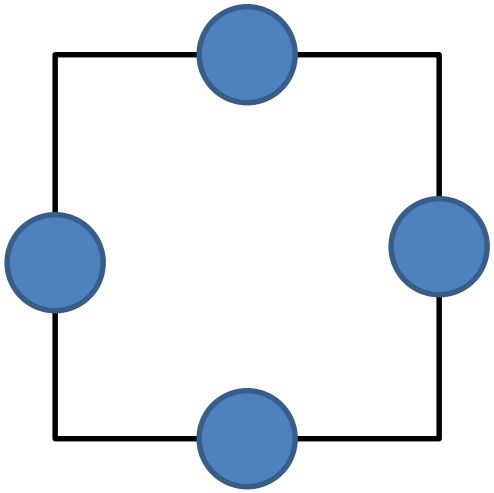
CeO_2 is an oxygen ion conductor commonly used in oxygen sensors and fuel cell membranes

$Y:ZrO_2$ (commonly called yttria stabilized zirconia) is a widely used structural material due to its exceptionally high hardness as well as a thermal barrier coating due to its low thermal conductivity

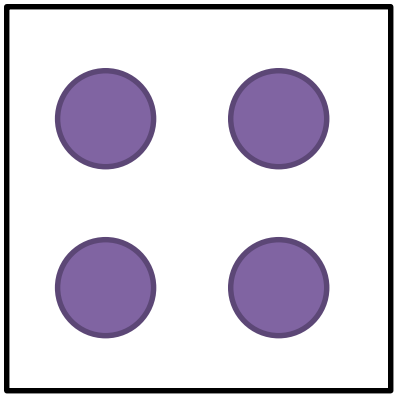
The fluorite has general composition AX_2



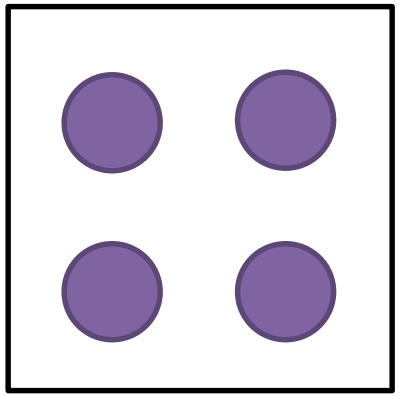
z = 0.00



z = 0.50



z = 0.25



z = 0.75

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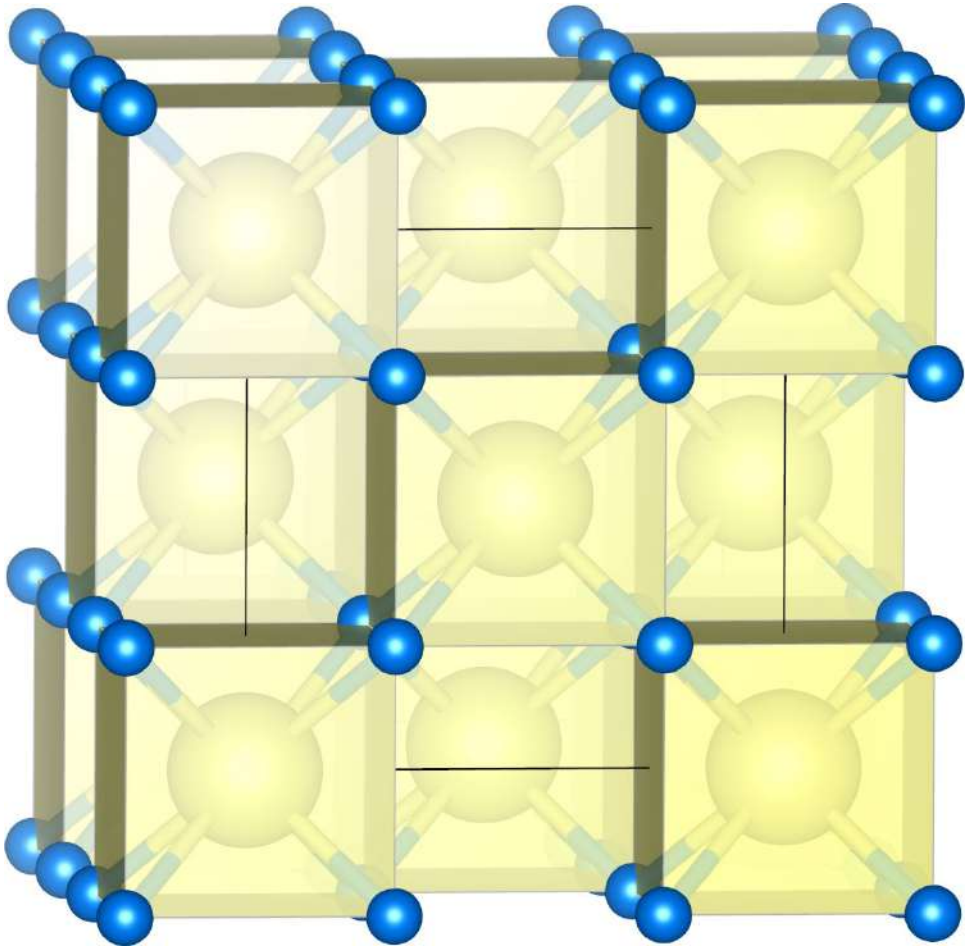

Looking at the polyhedral connectivity of the cations shows an unusual coordination environment compared to the octahedral and tetrahedral sites we have previously seen

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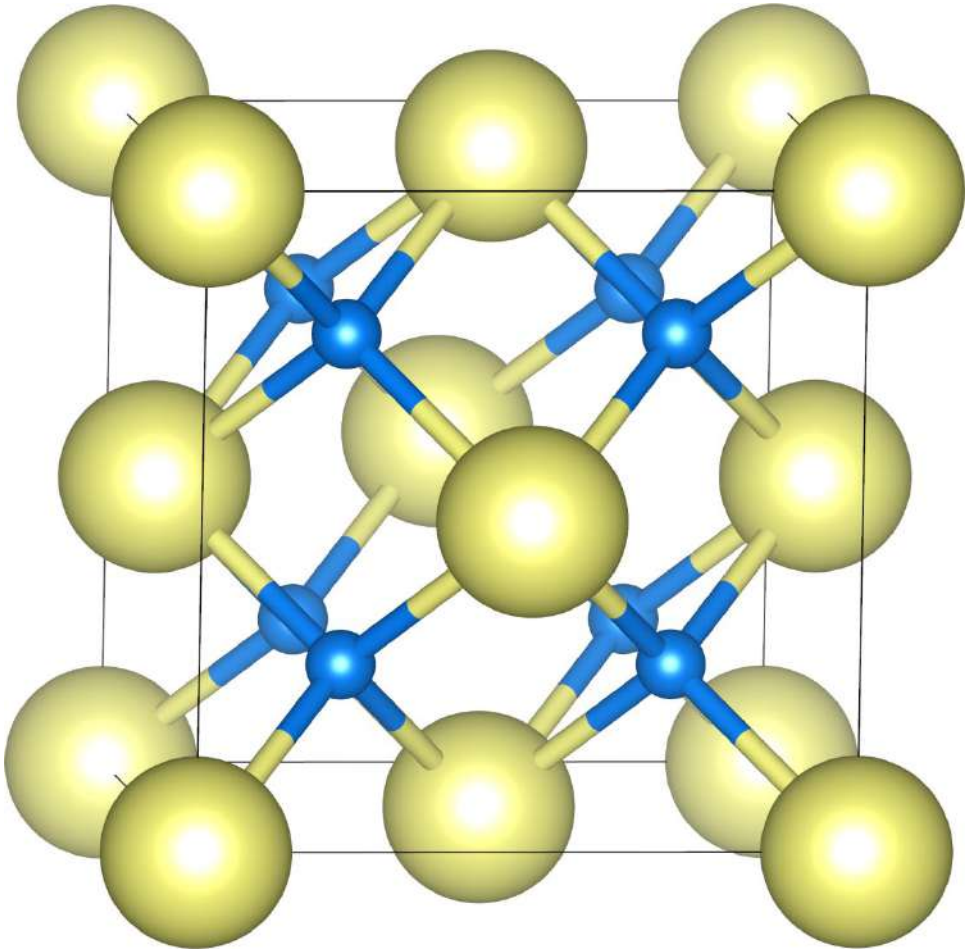
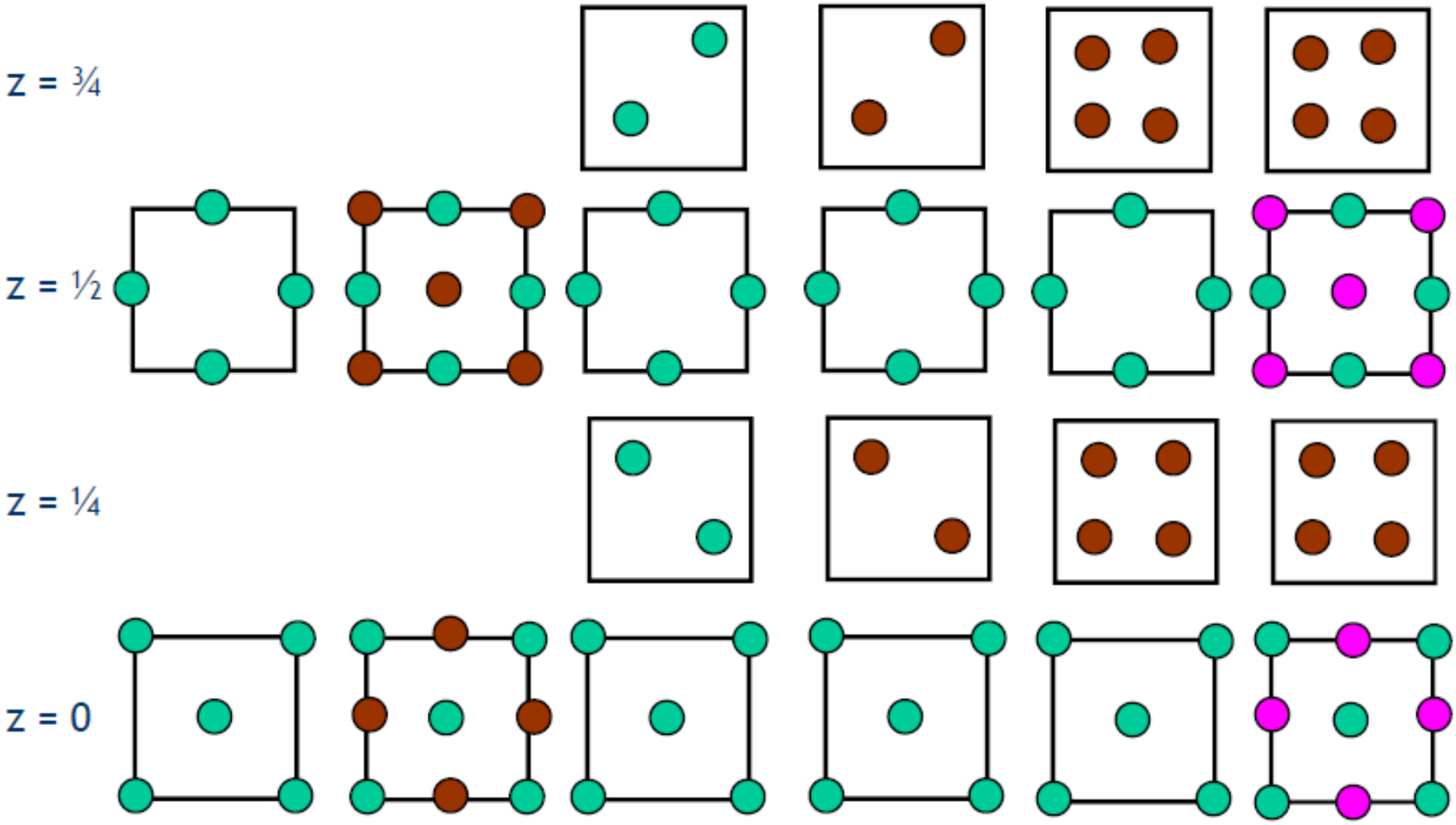


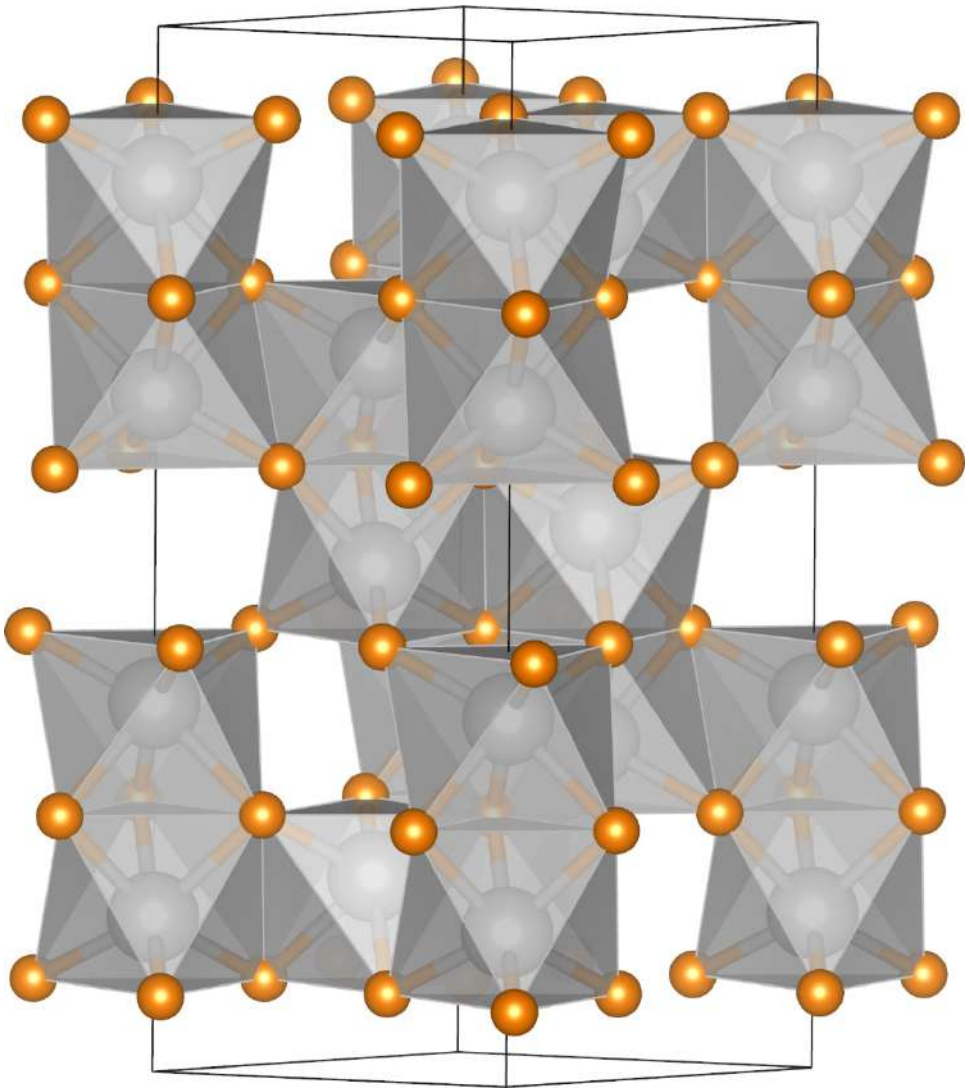
Looking at the polyhedral connectivity of the cations shows an unusual coordination environment compared to the octahedral and tetrahedral sites we have previously seen

Easier to understand the structure as a cubic close packing of the A cations with all of the tetrahedral interstitials occupied by the anions!

You should know how to draw these structures in projection



Al_2O_3, Cr_2O_3, and Fe_2O_3 adopt the corundum structure



The oxide ions in corundum form a hexagonal close packed lattice (along the *c*-direction). 2/3 of the octahedral sites are occupied

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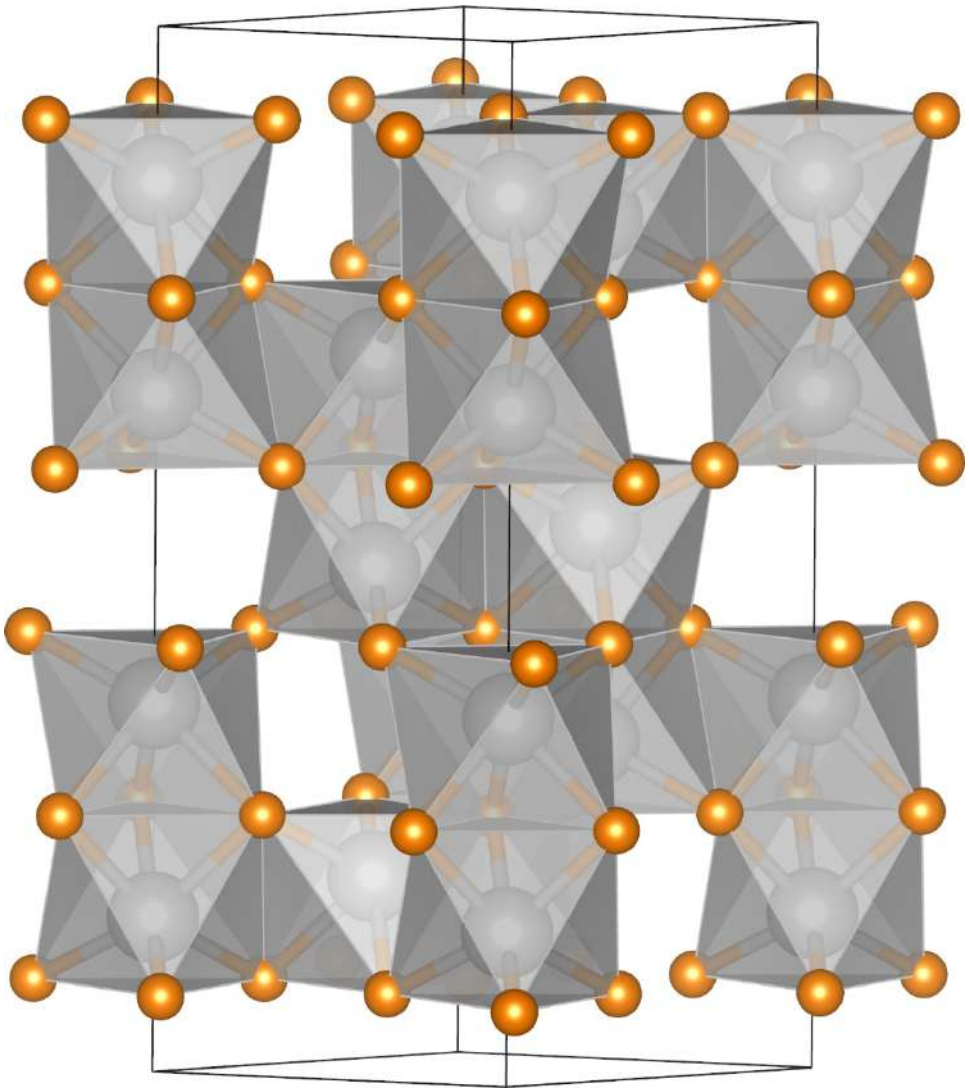

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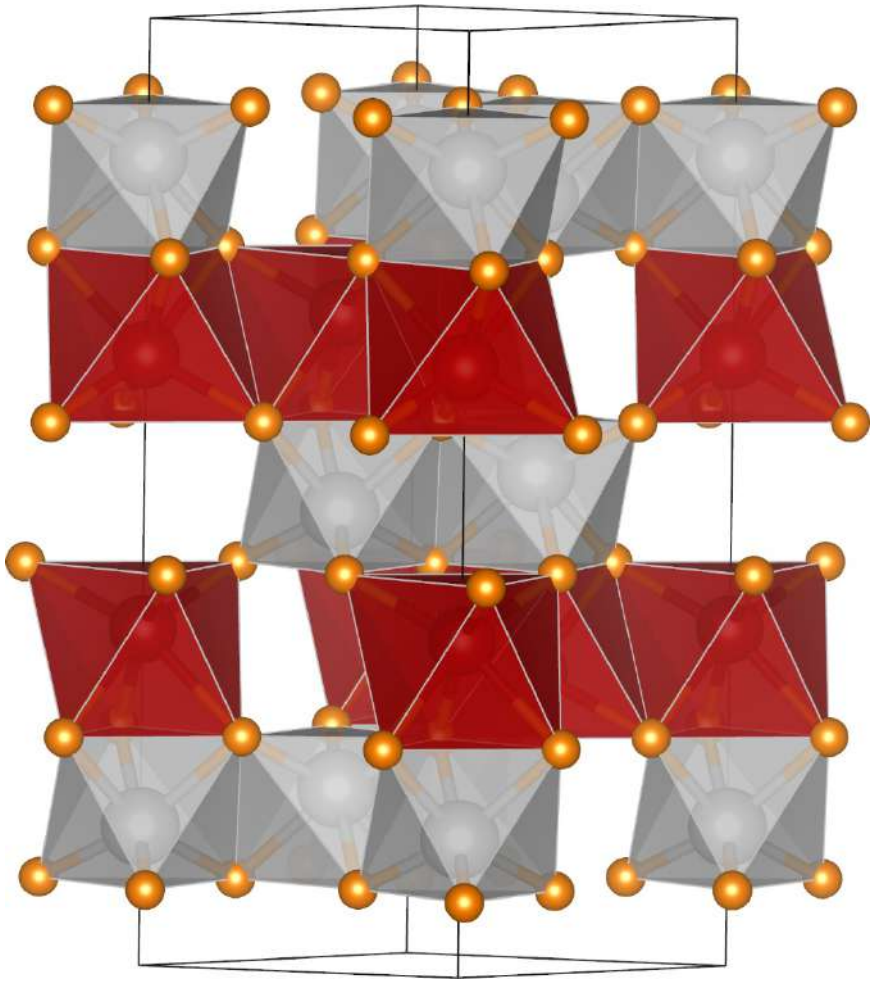
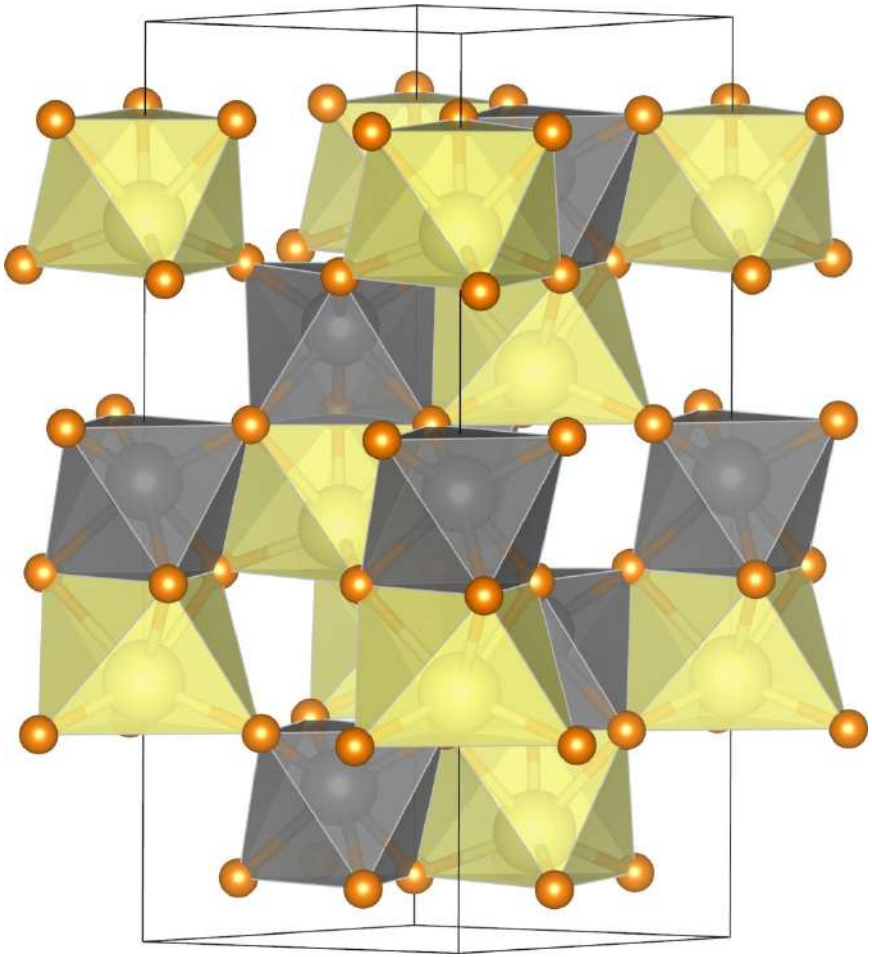
Small impurities of Cr in Al_2O_3 give ruby its brilliant red color

Two variants of ordered corundum exist



Fe and Ti form alternating layers along the *c*-axis to form ilmenite $FeTiO_3$

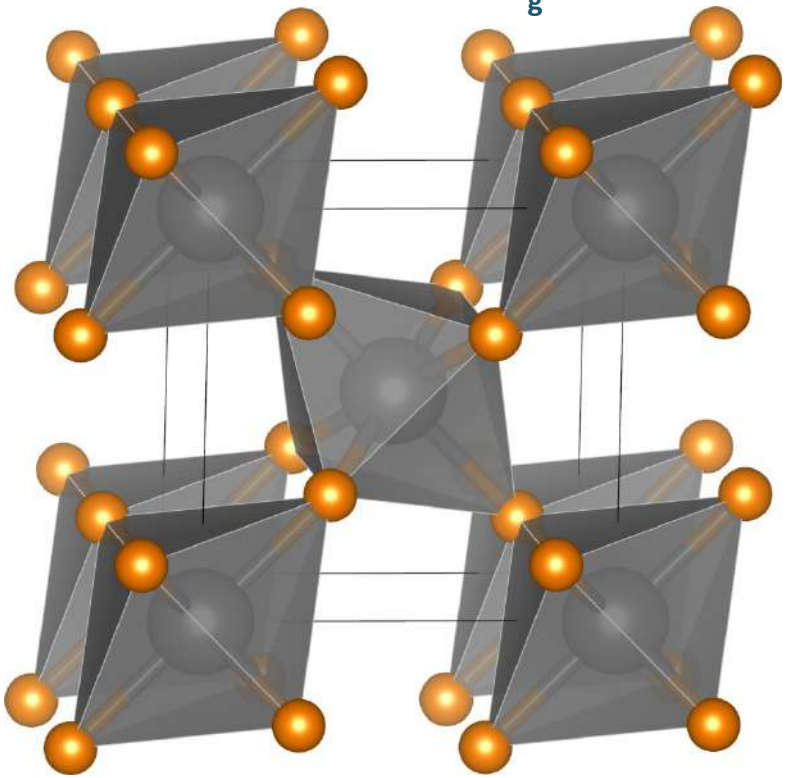
$LiNbO_3$ forms another ordered variant of corundum



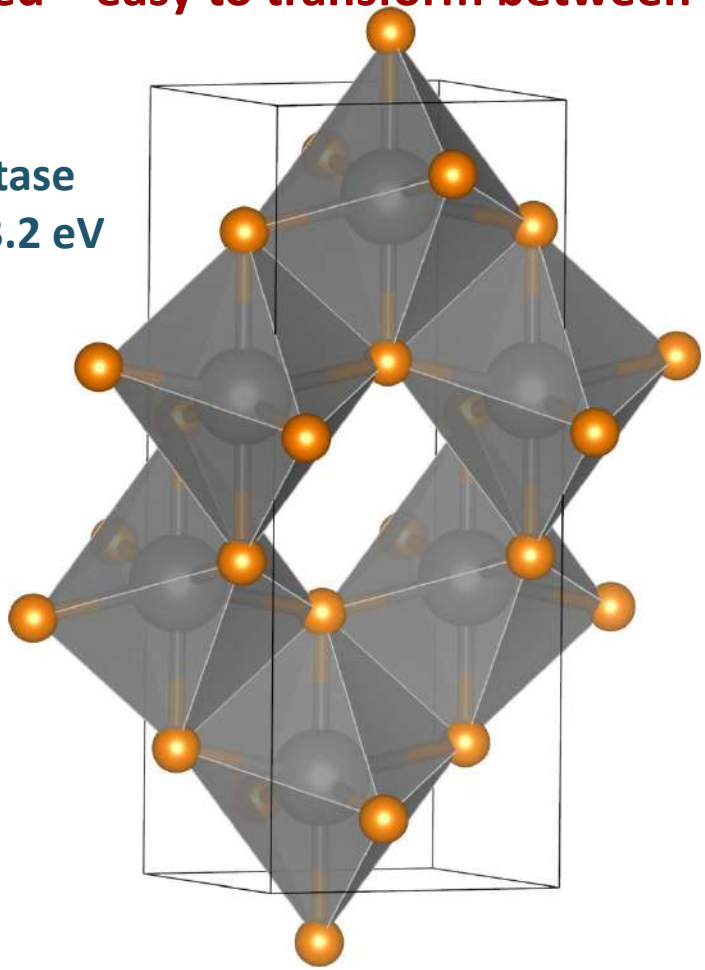
Both rutile and anatase have the composition AX_2

The ideal anion packing is hexagonally close-packed and the difference is principally in the interstitials which are occupied – easy to transform between the two

Rutile E_g = 3.0eV



Anatase
E_g = 3.2 eV

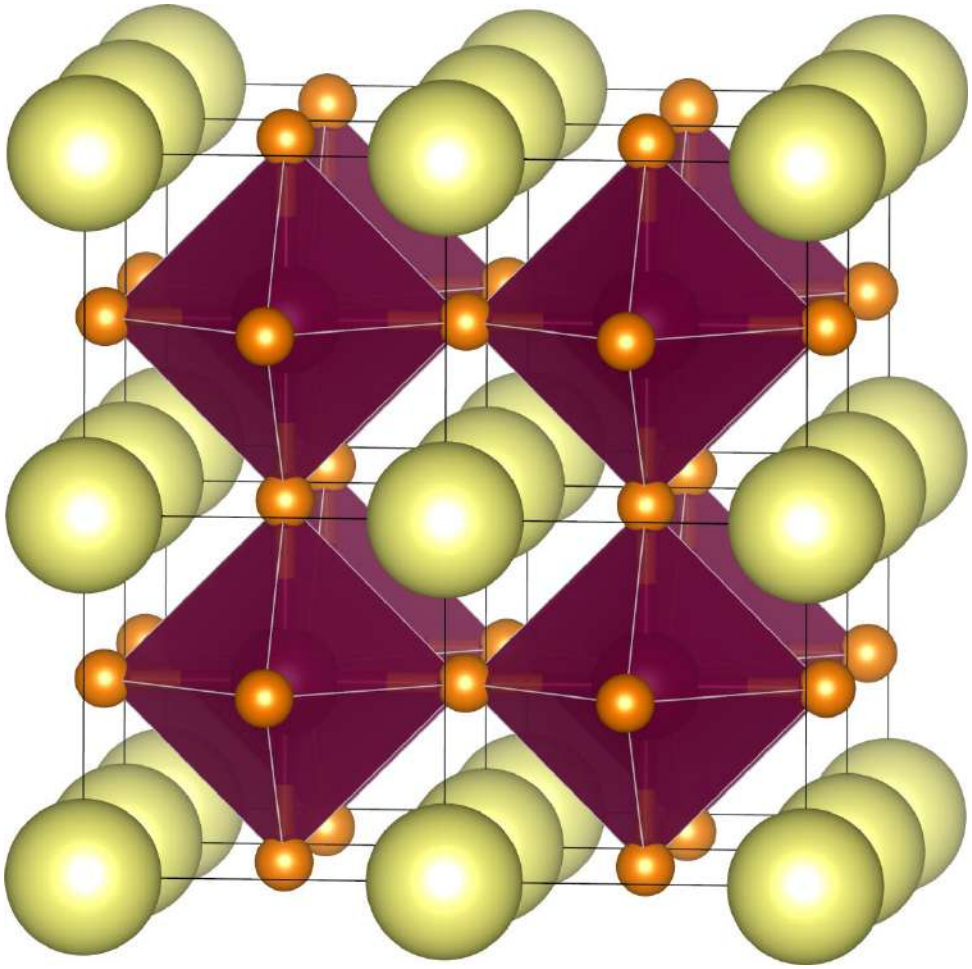


Anatase proves more efficient at hydrogen production, but both structures are very important in the physics and chemistry of TiO_2

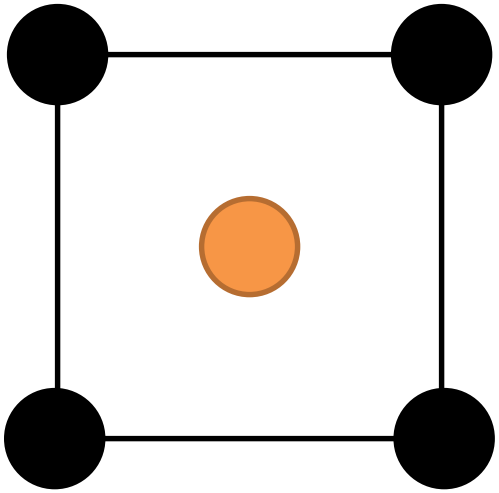
The perovskite structure has the formula ABX_3

Functional properties include:

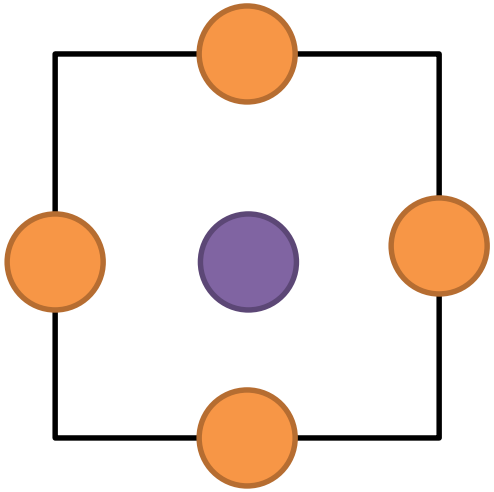
- High-T_c cuprate superconductors
- Colossal Magneto-Resistance ($La,SrMnO_3$)
- Fast ion conduction (Li^+, O^{2-}), batteries, fuel cells
- Mixed electronic/ionic conduction, fuel cells
- Oxidation/reduction catalysts
- Ferroelectric / piezoelectric ceramics ($BaTiO_3$, $Pb(ZrTi)O_3$)
- Important mineral structure in lower mantle ($MgSiO_3$)
- Frequency filters for wireless communications : $Ba(Zn_{1/3}Ta_{2/3})O_3$



Perovskite in stereographic projection



z = 0.00

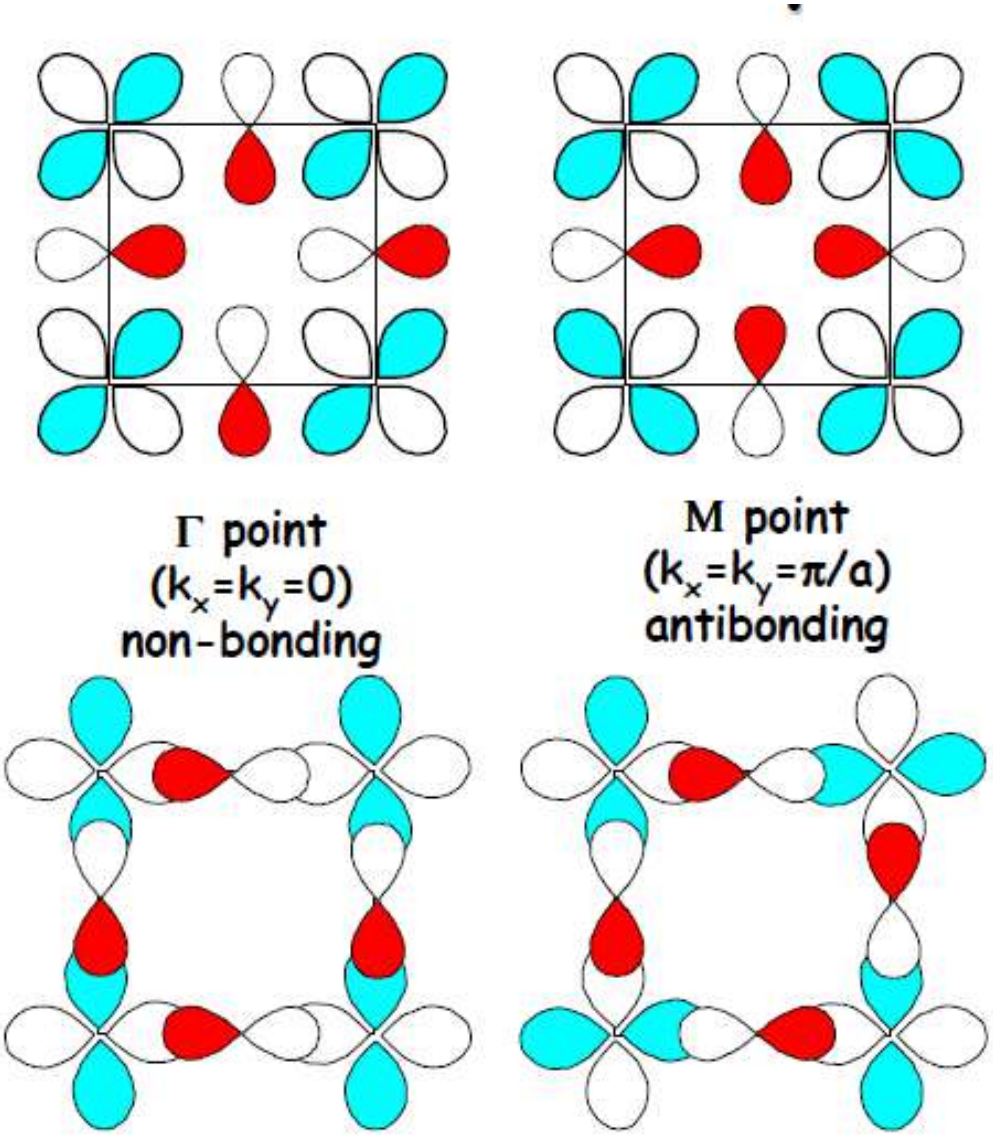


z = 0.50

Bear in mind this is the projection for a perfectly symmetric and undistorted perovksite!

The precise details of the structural distortions are extremely rich and continue to be studied quite actively

Perovskites allow for extremely good orbital overlap



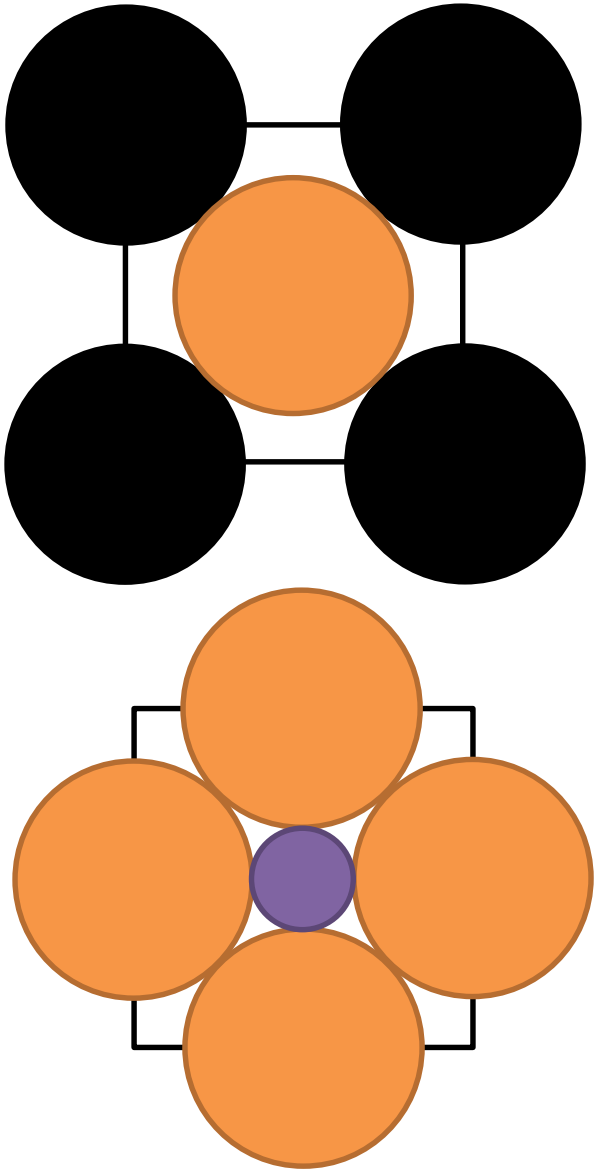
The Goldschmidt Tolerance factor predicts distortion

Goldschmidt Tolerance Factor:

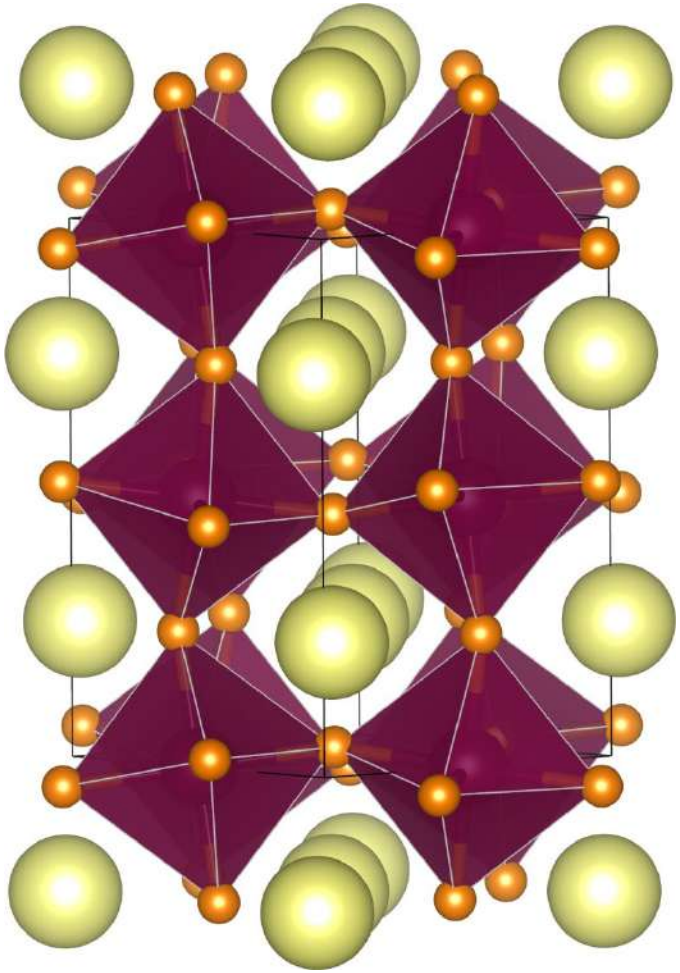
$$a = 2(r_B + r_X) = \sqrt{2}(r_A + r_X)$$

$$t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)}$$

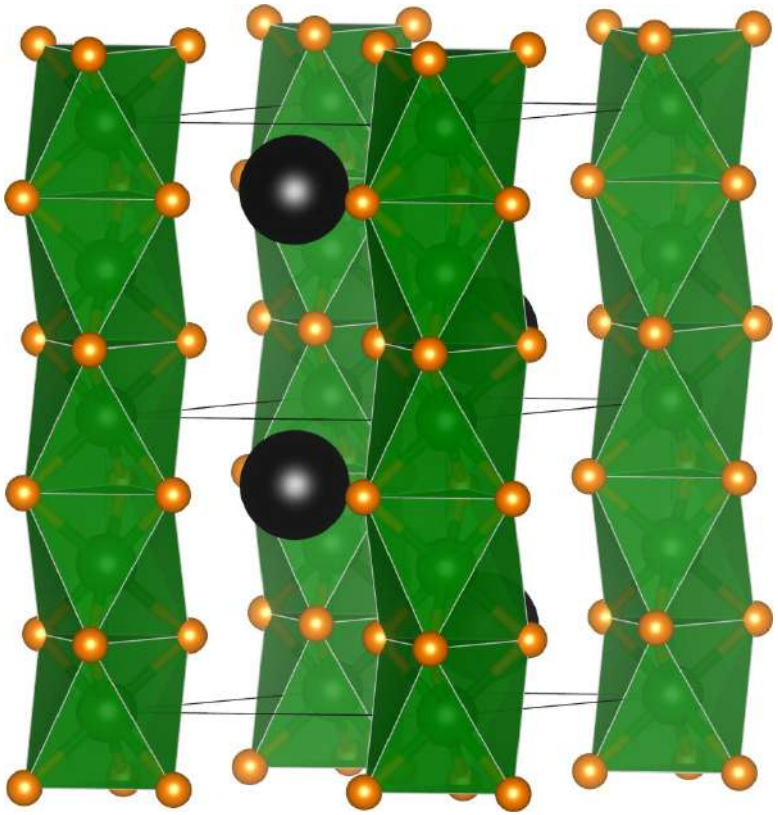
Goldschmidt tolerance factor (t)	Structure	Explanation	Example
>1	Hexagonal	A ion too big or B ion too small.	•$BaNiO_3$
0.9-1	Cubic	A and B ions have ideal size.	•$SrTiO_3$ •$BaTiO_3$
0.71 - 0.9	Orthorhombic/ Rhombohedral	A ions too small to fit into B ion interstices.	•$GdFeO_3$ •$CaTiO_3$
<0.71	Different structures	A ions and B have similar ionic radii.	•Ilmenite



If the radii are not well matched, perovskites distort!



ortho-$CaMnO_3$



$BaNiO_3$

Glazer notation is shorthand to describe octahedral tilting

The tilt system is described by specifying the rotation about each of the cartesian axes

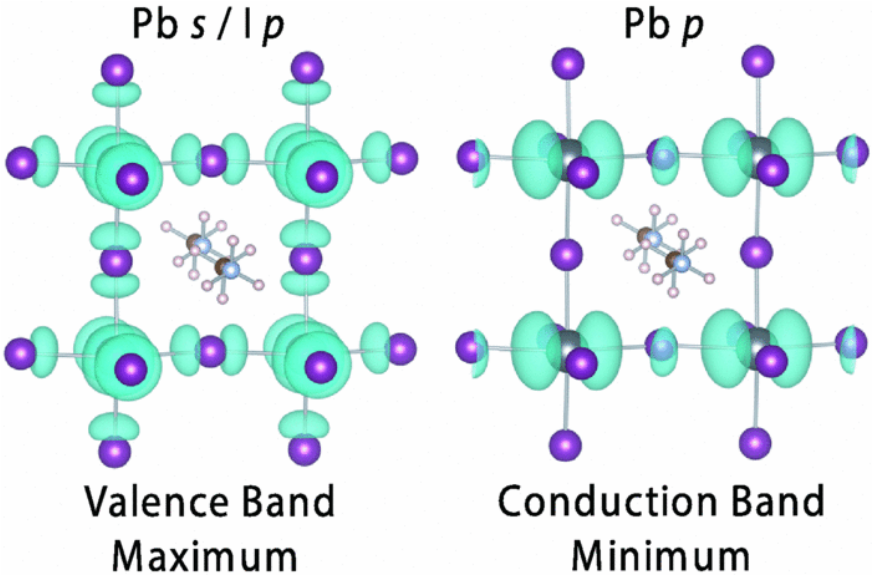
$a^0a^0a^0$	$a^+a^+a^+$	$a^+a^-c^+$
Undistorted system	Rotation is identical in all directions	Very complicated tilting pattern

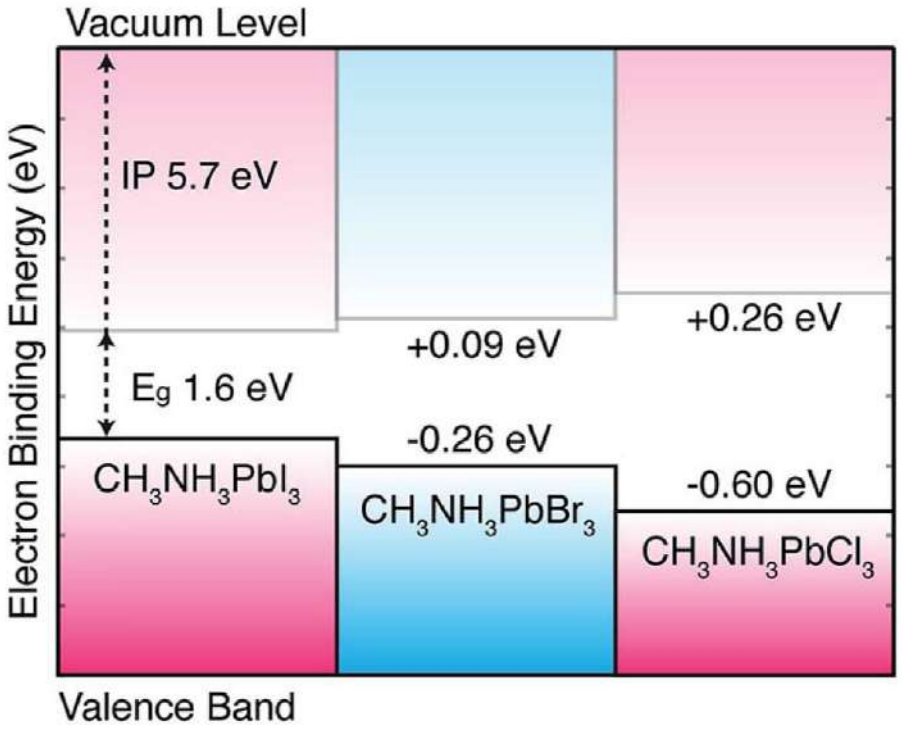
The letter denotes the RELATIVE magnitude of the rotation around the xyz axes

The superscript denotes the RELATIVE rotation with respect to other axes

Patrick Woodward (THE Ohio State) is the leading authority on all things perovskites

Perovskites allow us to tune properties through composition

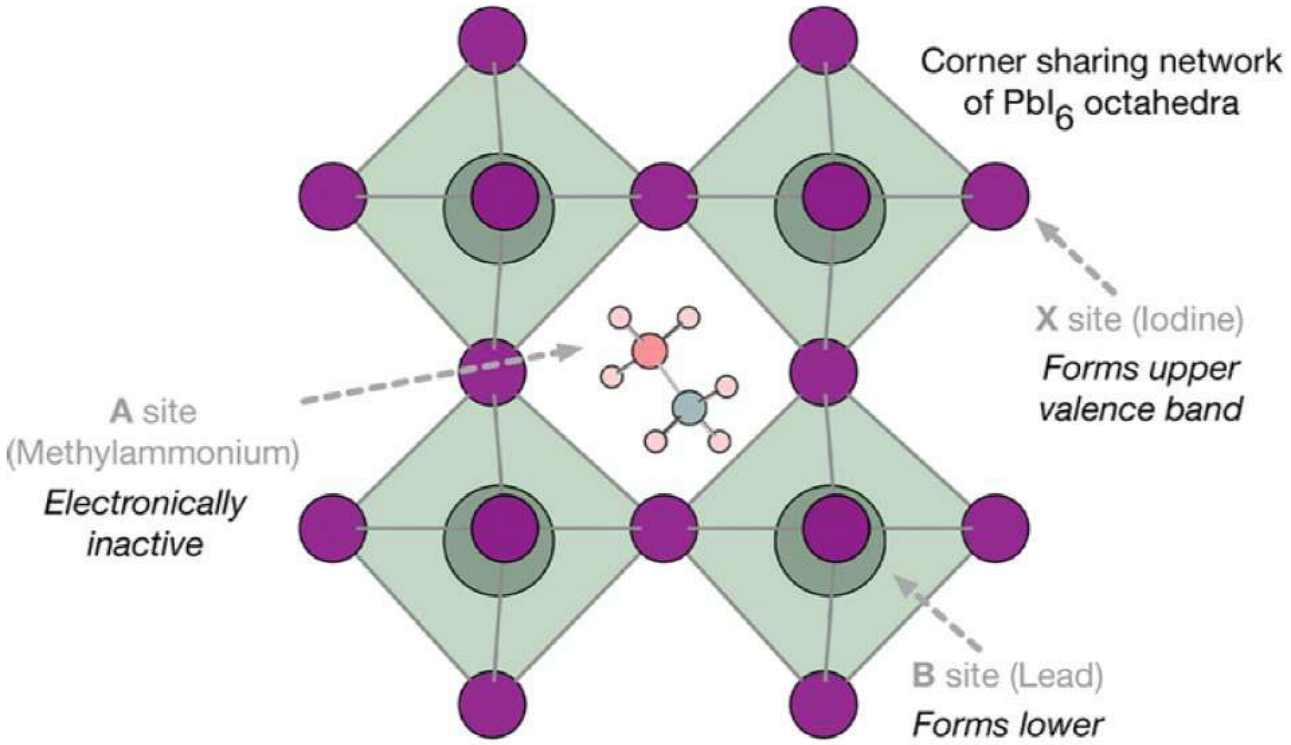




Careful! Cl doping in $CH_3NH_3PbI_{3-x}Cl_x$ is more about processing than bonding

Walsh *et al* APL Mat. 1, 042111 (2013); Walsh *et al*. Mater. Horiz., 2, 228 (2015)

ABX_3 composition gives us many knobs to turn



Perovskite-structured hybrid halide
$CH_3NH_3PbI_3$

Chemical flexibility of I-II-VI_3 perovskites

A site:
organic cation or inorganic cation

- *Size*
- *Shape*
- *Polarisation*

B site:
inorganic cation

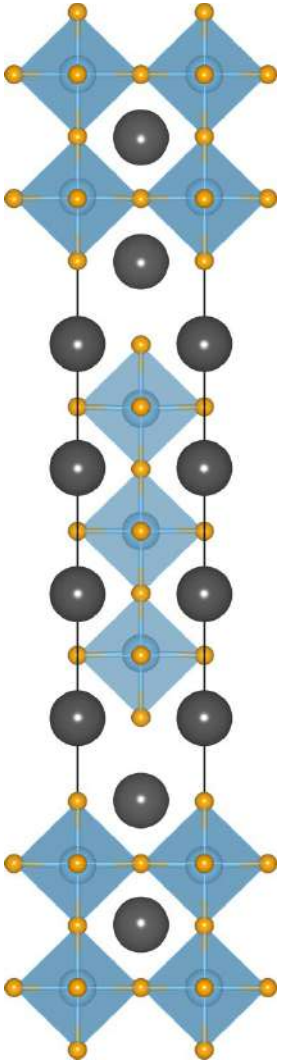
- *Size*
- *Redox*

X site:
inorganic anion or polyanion

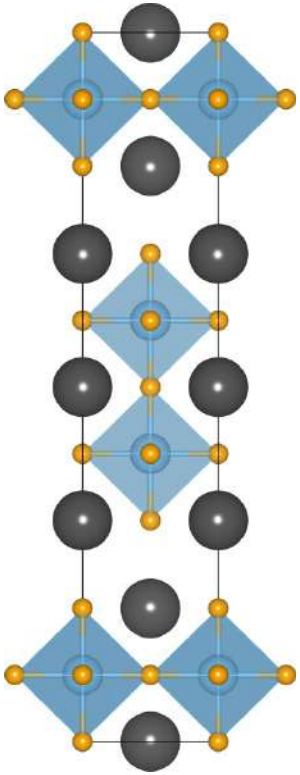
- *Size*
- *Shape*
- *Redox*

Walsh *et al.* J. Phys. Chem. C 2015, 119, 5755–5760

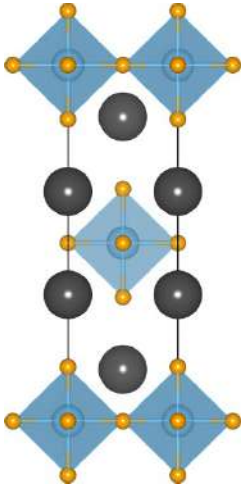
Ruddleson-Popper phases – $(AO)(ABX_3)_n$



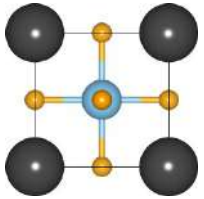
$n = 3$



$n = 2$

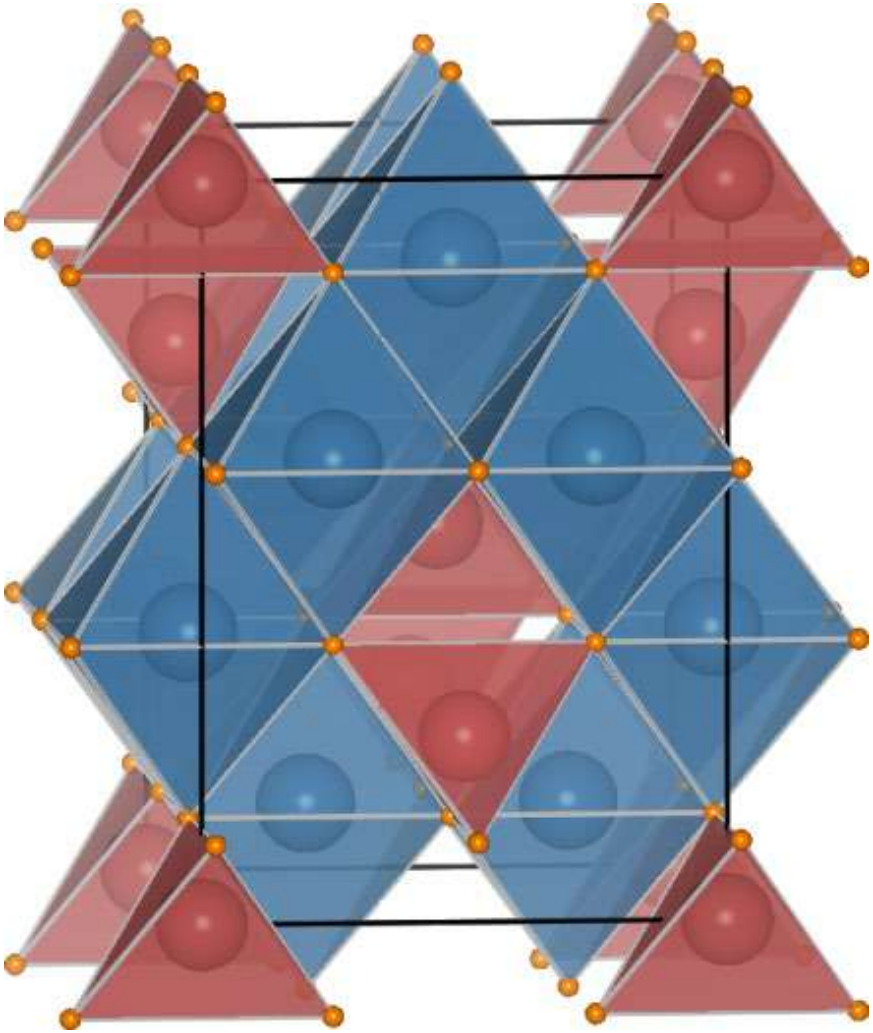


$n = 1$



$n = \infty$

Many useful materials adopt the spinel structure!

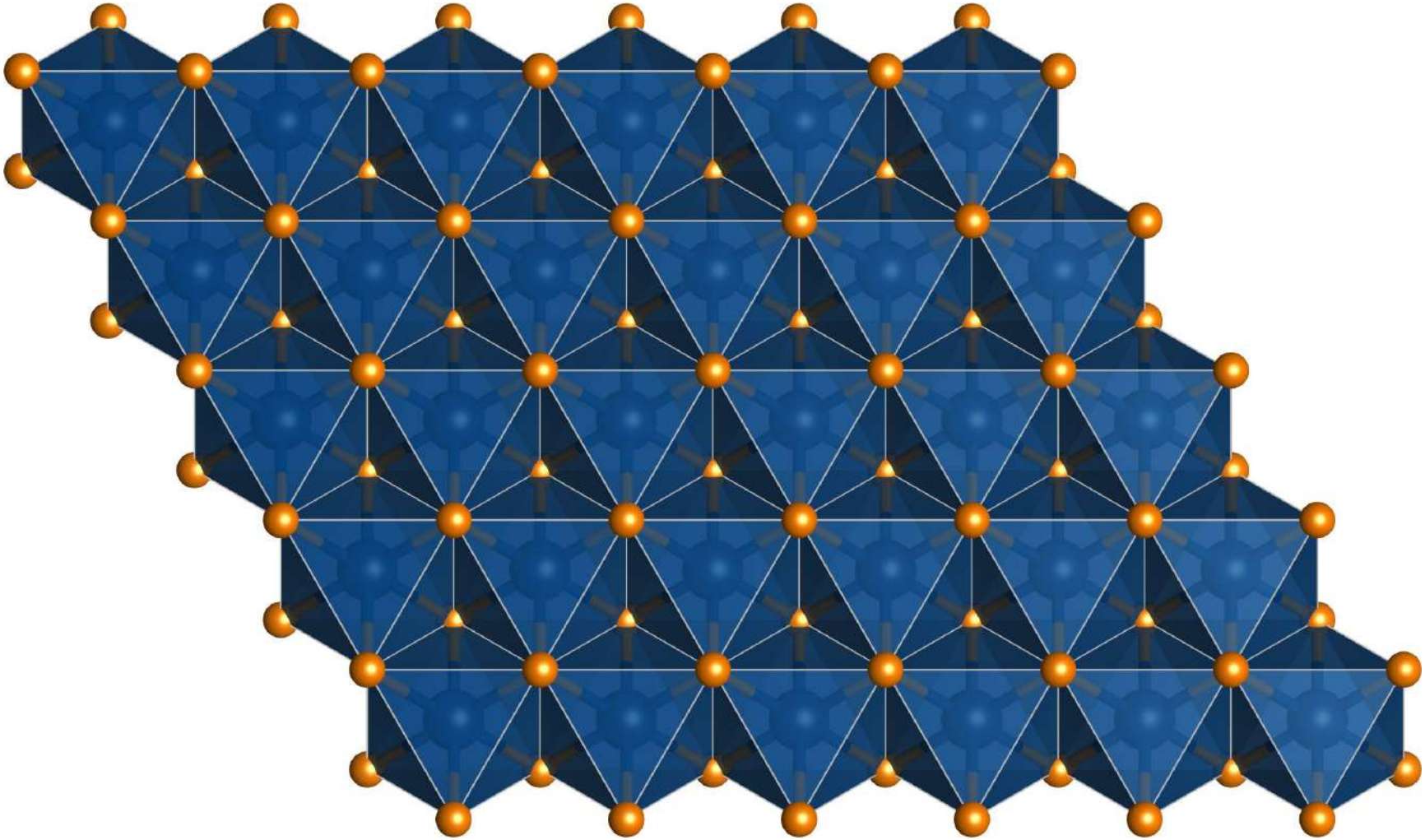


The spinel structure contains a cubically close packed layer of oxygen anions.

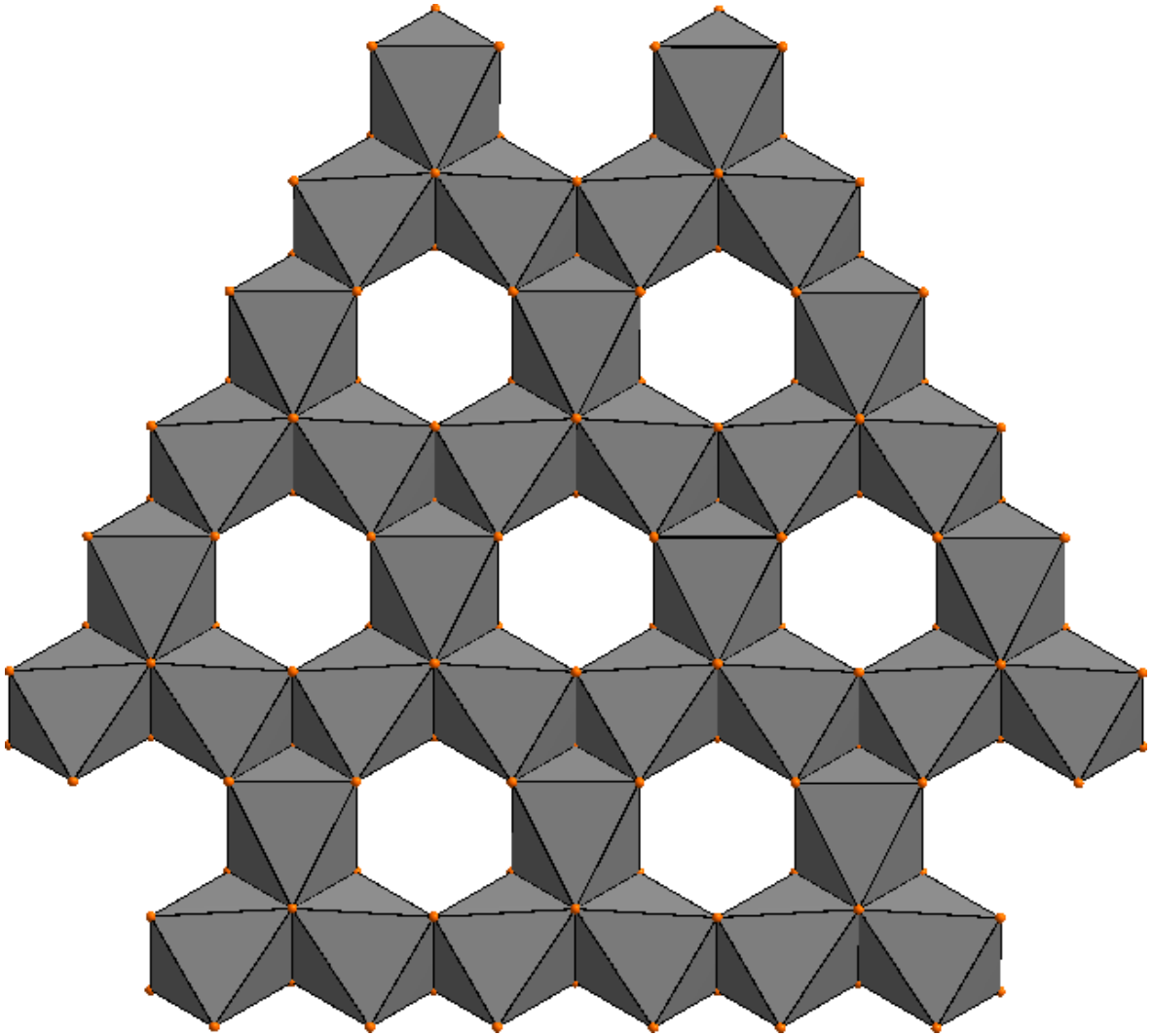
Only half of the octahedral sites and one eigth of the tetrahedral sites are fully occupied

The A and B sites can both accommodate transition metals

The connectivity of spinels is very complex



The connectivity of spinels is very complex



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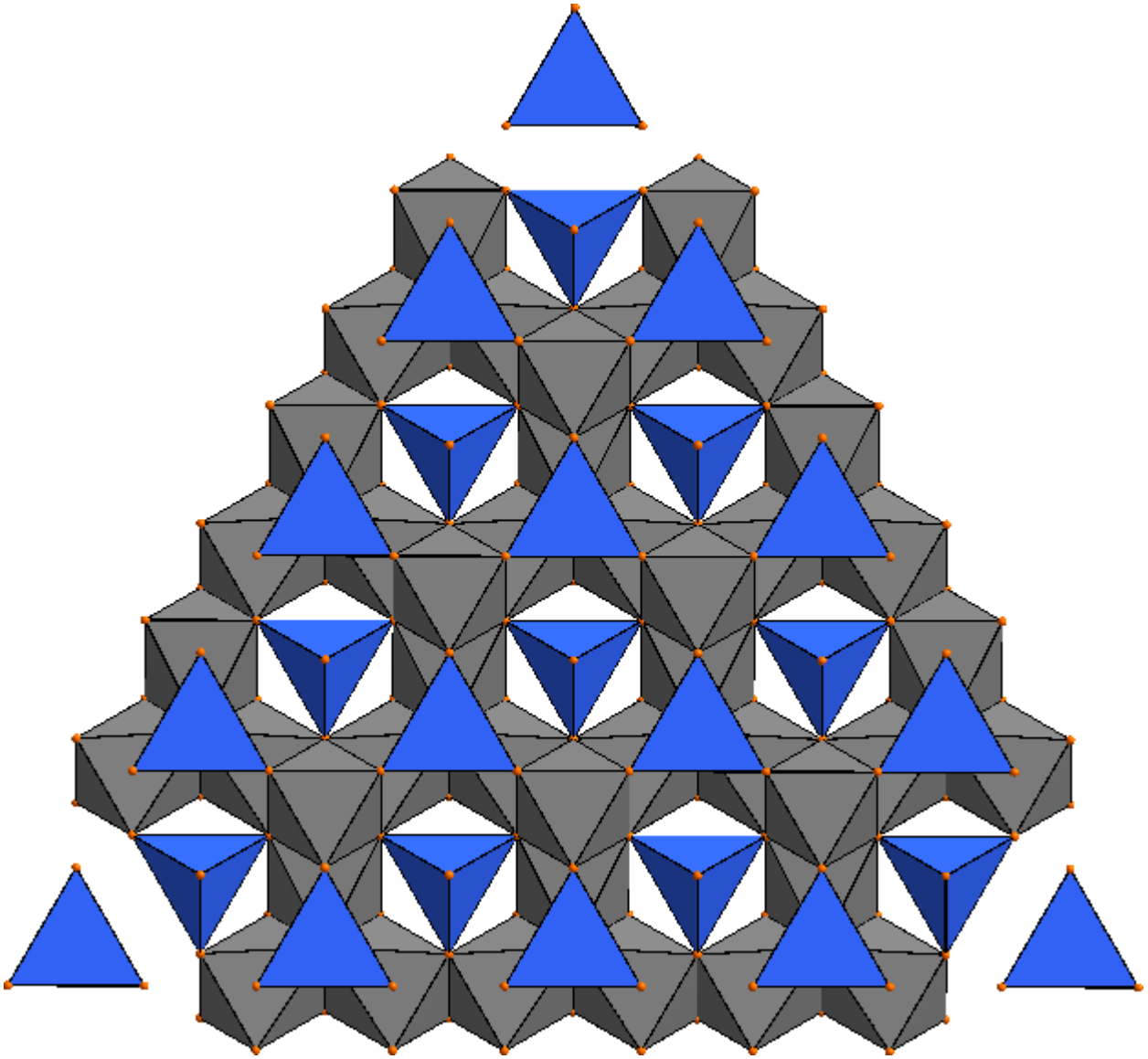
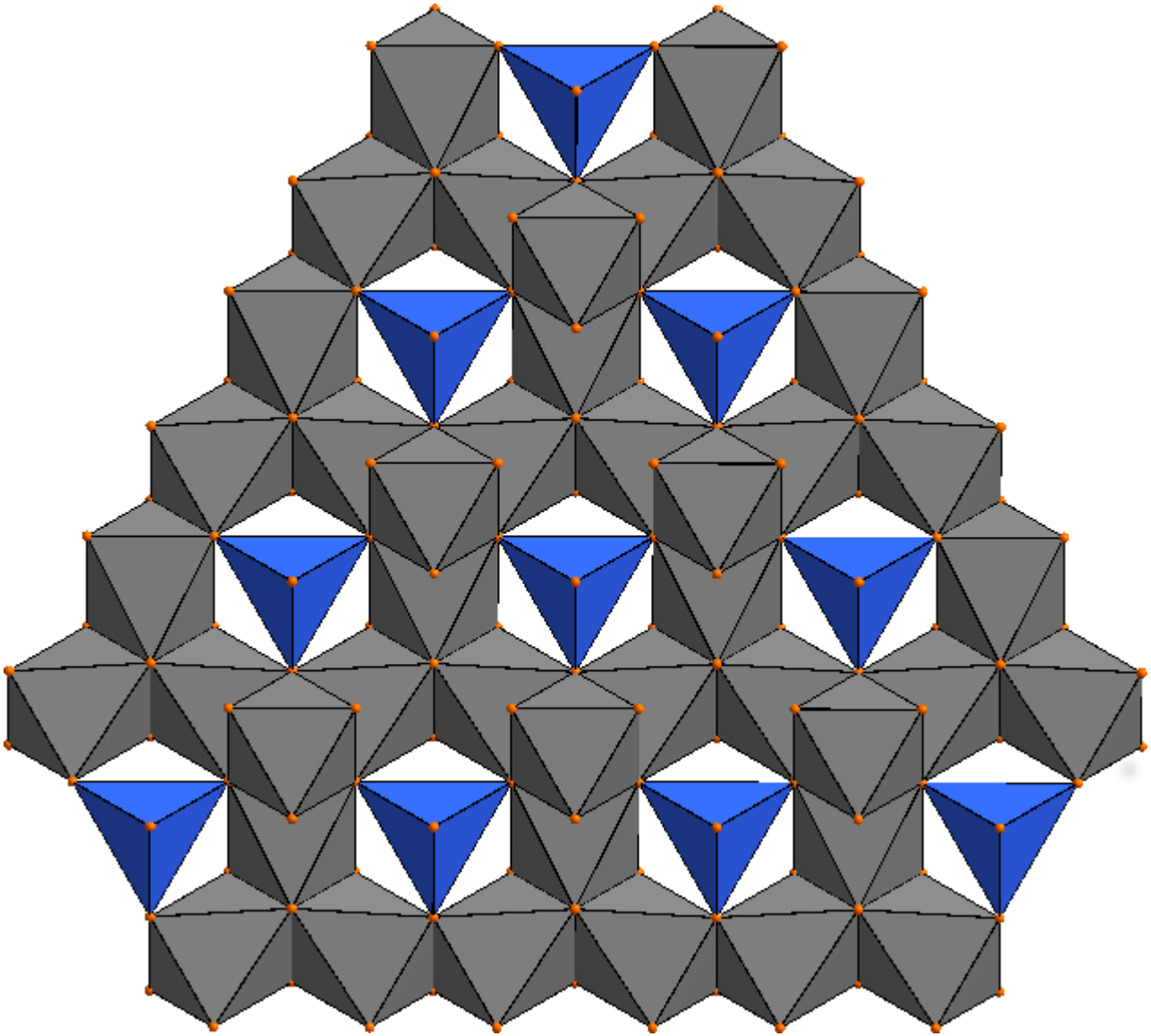


The connectivity of spinels is very complex



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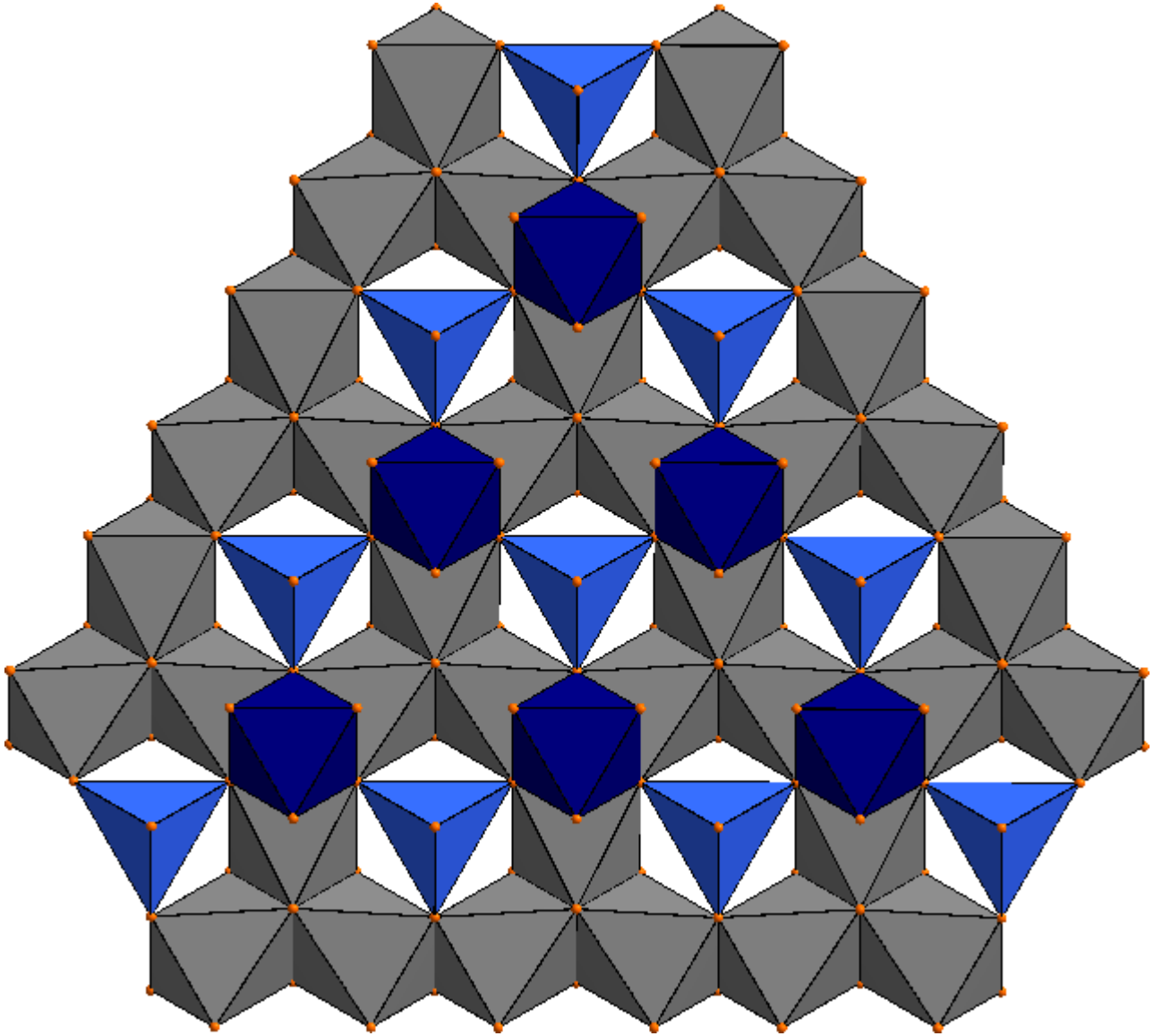
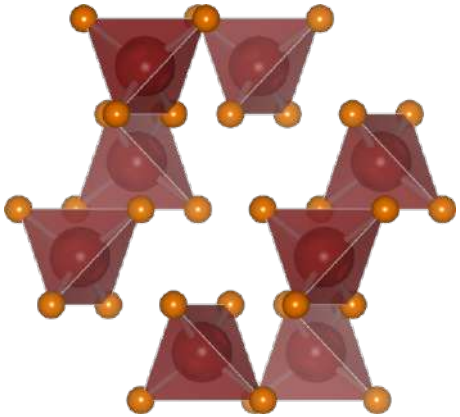


Spinel structure – AB_2X_4

A-sublattice



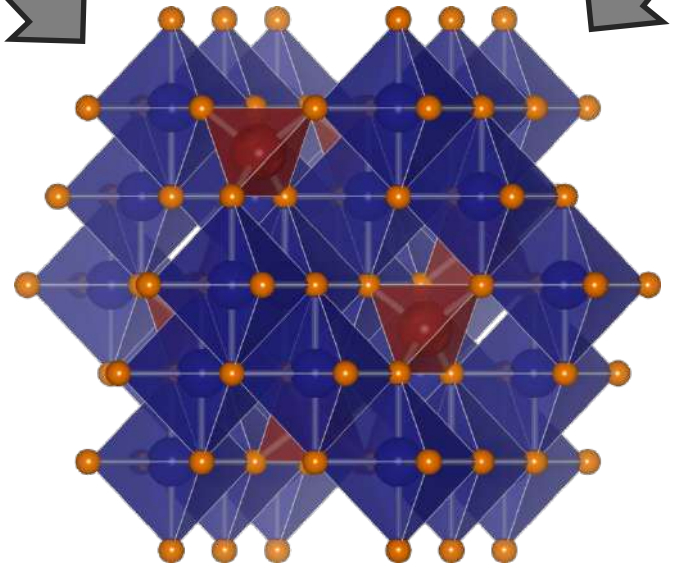
Isolated tetrahedra (diamond)

$Fd\bar{3}m$,

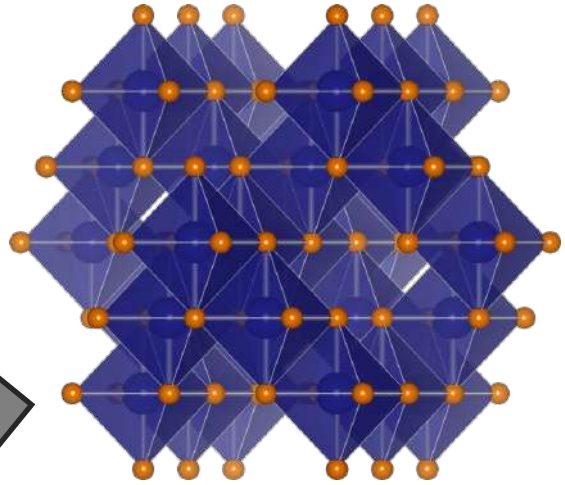
a = 8.3346Å

Atom	x	y	z
Co	0.00	0.00	0.00
Cr	0.625	0.625	0.625
O	u	u	u

Both sites can accommodate most 3*d* transition metals: versatility and substitutional control



B-sublattice

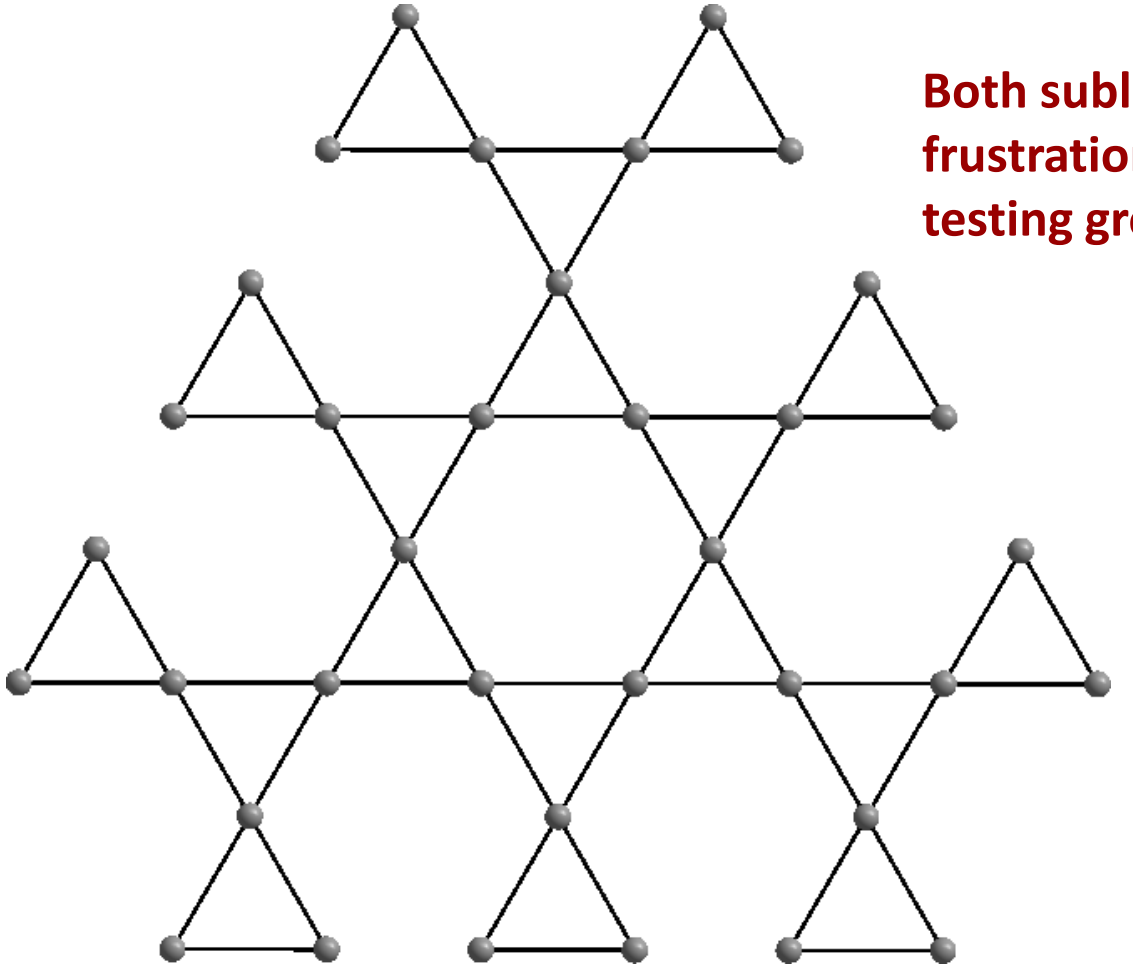


Edge sharing octahedra (pyrochlore)

u is typically near 0.25, as it gets larger the tetrahedral site gets larger and the octahedral site shrinks

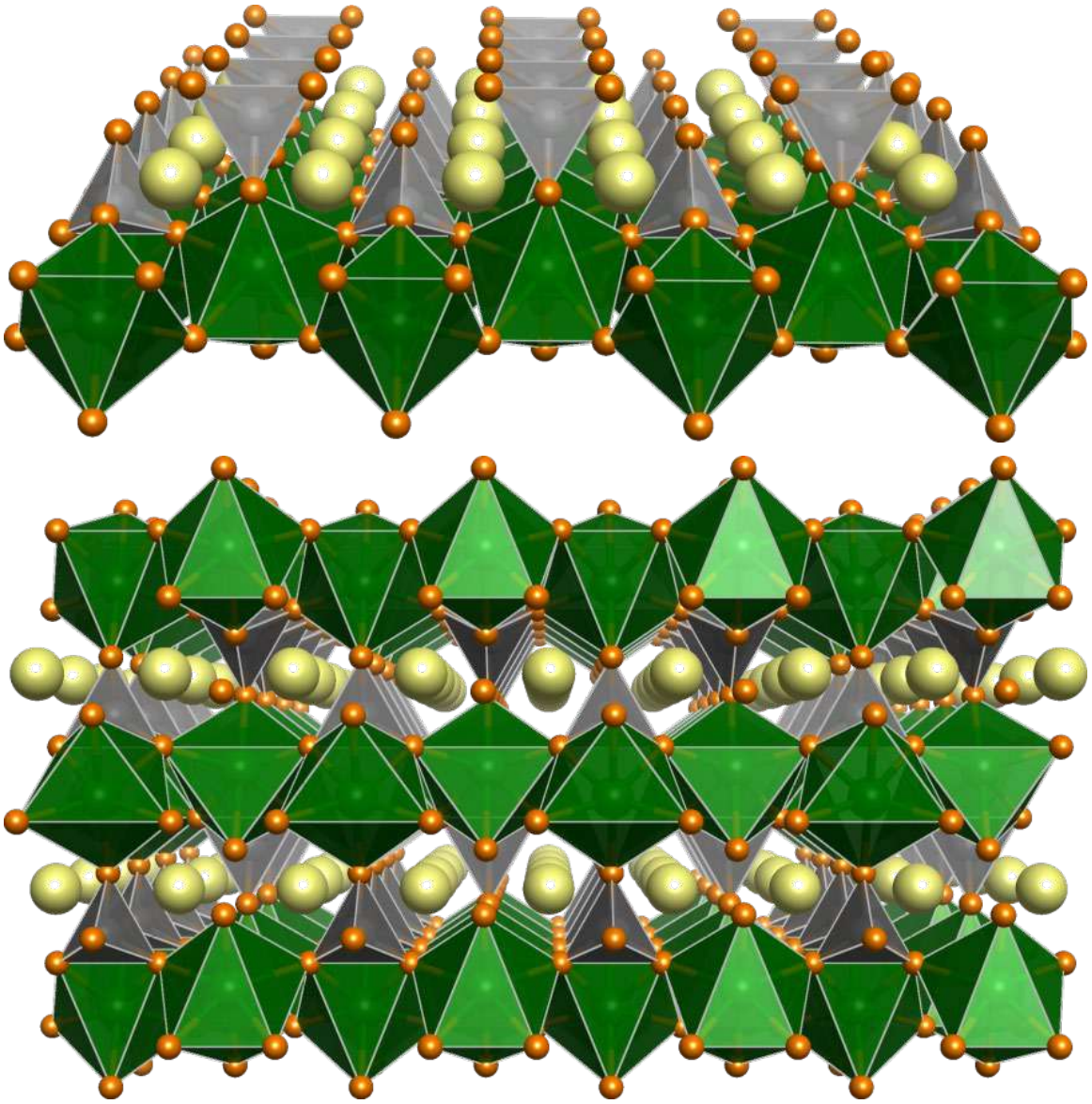
The B-sublattice contains a Kagome net – very frustrated

The *A*-sublattice is actually just a diamond net



Both sublattices exhibit lots of geometric frustration and are therefore a great testing ground for properties and physics

Olivine is directly analogous to spinels – B_2AO_4



Contains *hcp* layers of oxygen rather than *ccp*

Spinels contain two transition metals on the A or B site, whereas olivine usually contains a main group element like P, S, or Si on the A site.

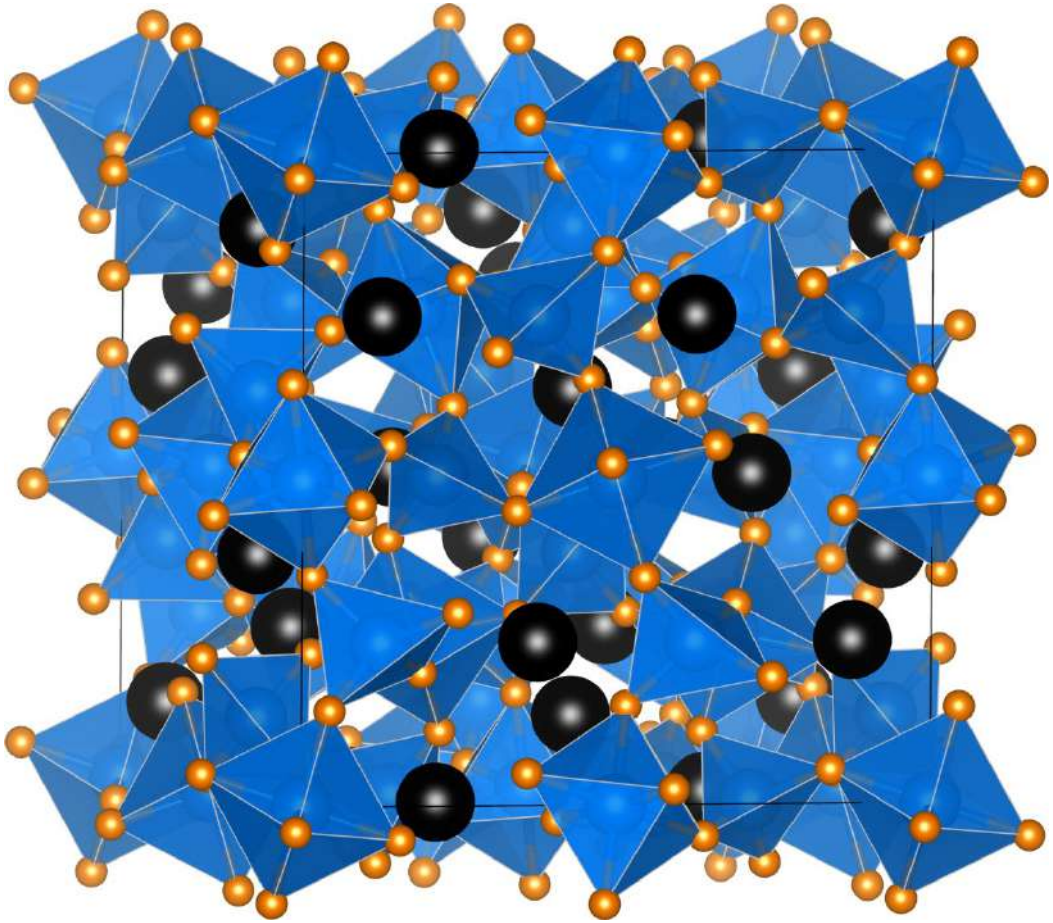
$LiFePO_4$ is the prototypical example of the olivine structure

The garnet structure is exceptionally rich – $\{R_3\}[M_2](XO_4)_3$

MO_6 octahedra share corners with XO_4 tetrahedra to form a 3D network

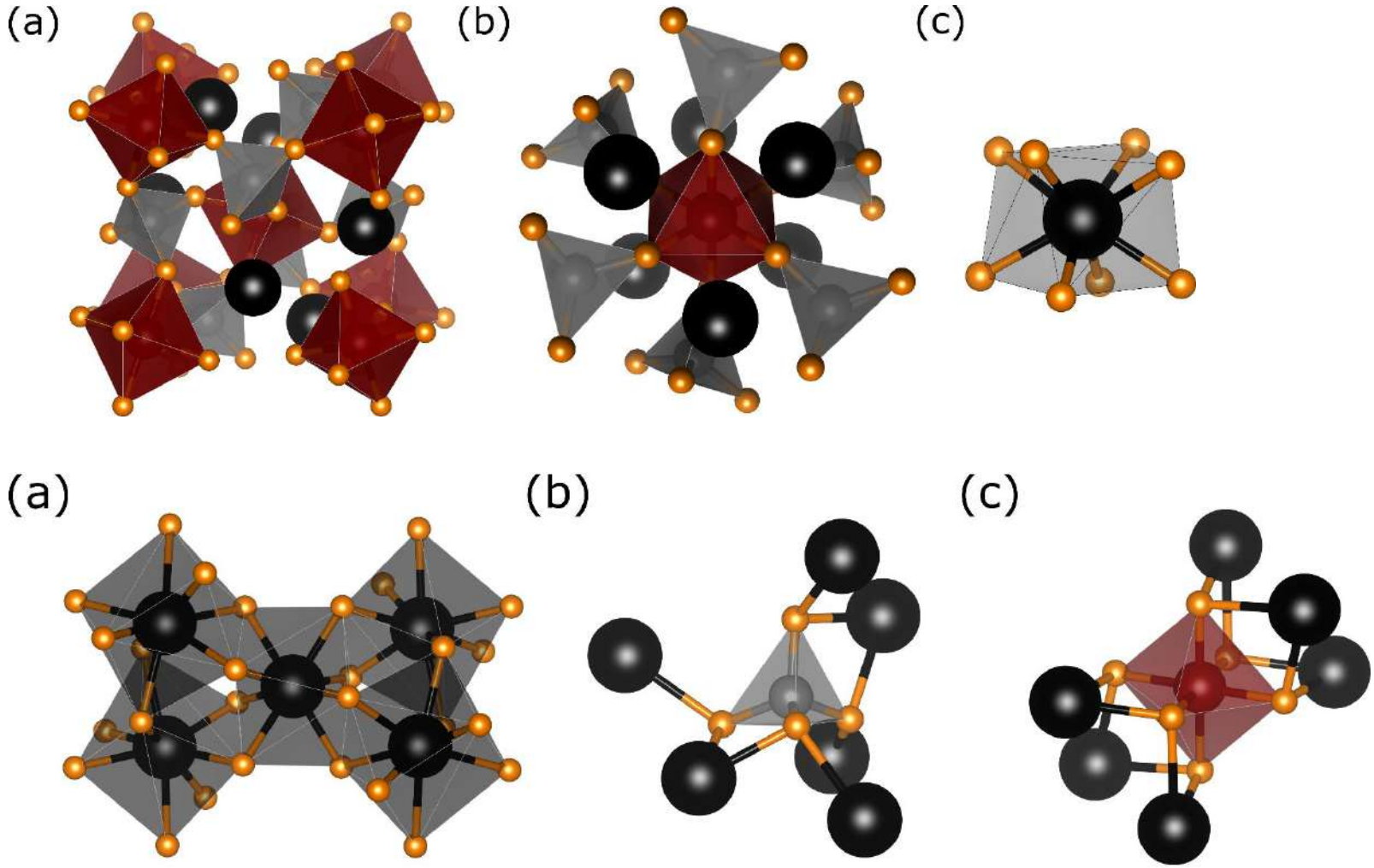
Larger R ions sit in an 8-coordinate position

Garnets – particularly $\{Y_3\}[Al_2](Al_3)O_{12}$ (YAG) – are extensively used in phosphors since the Y site can be substituted with other rare earth elements



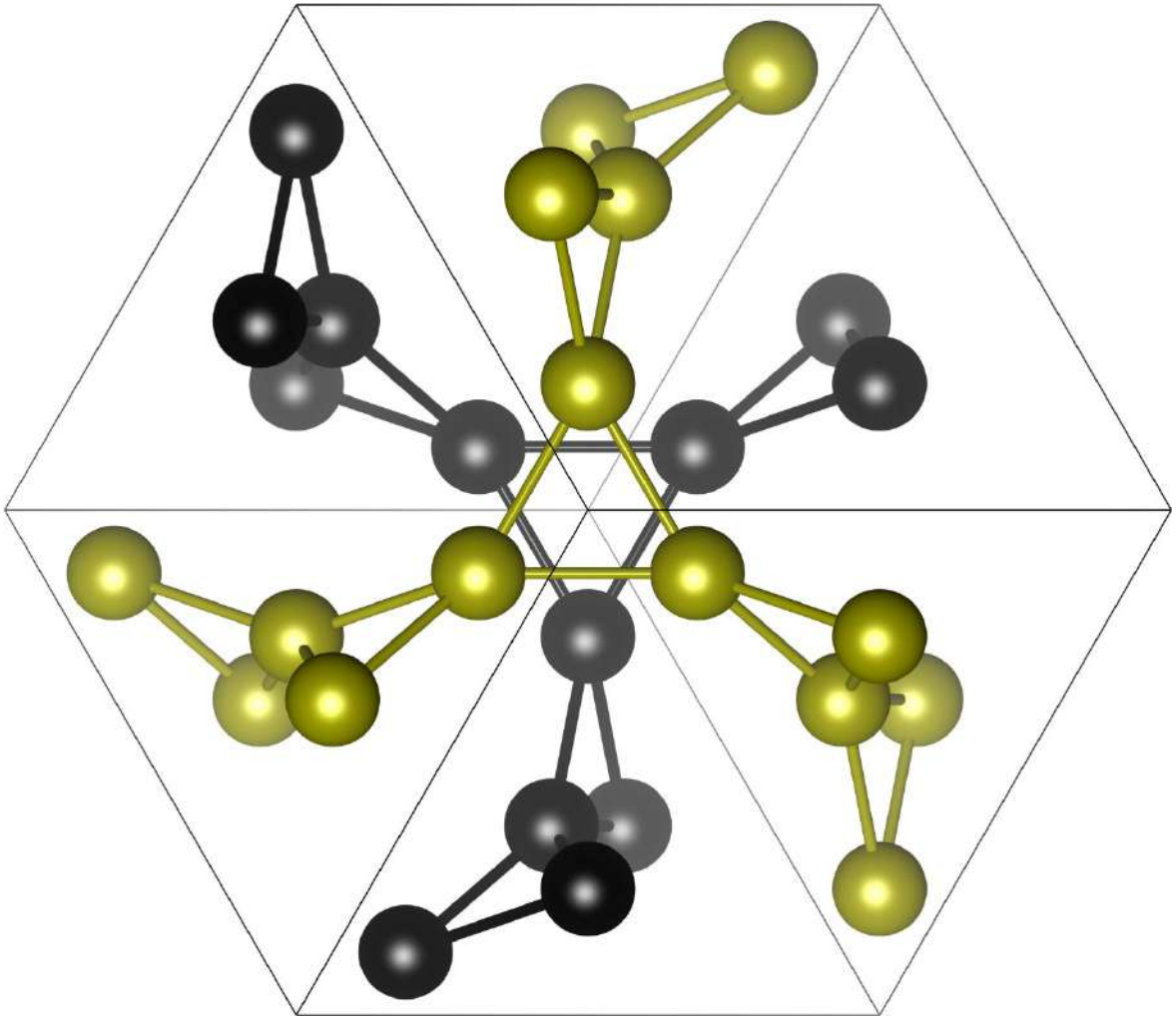
Garnets are a “fruit fly” for magnetism, complex structure

$$R_3B_2(AO_4)_3$$

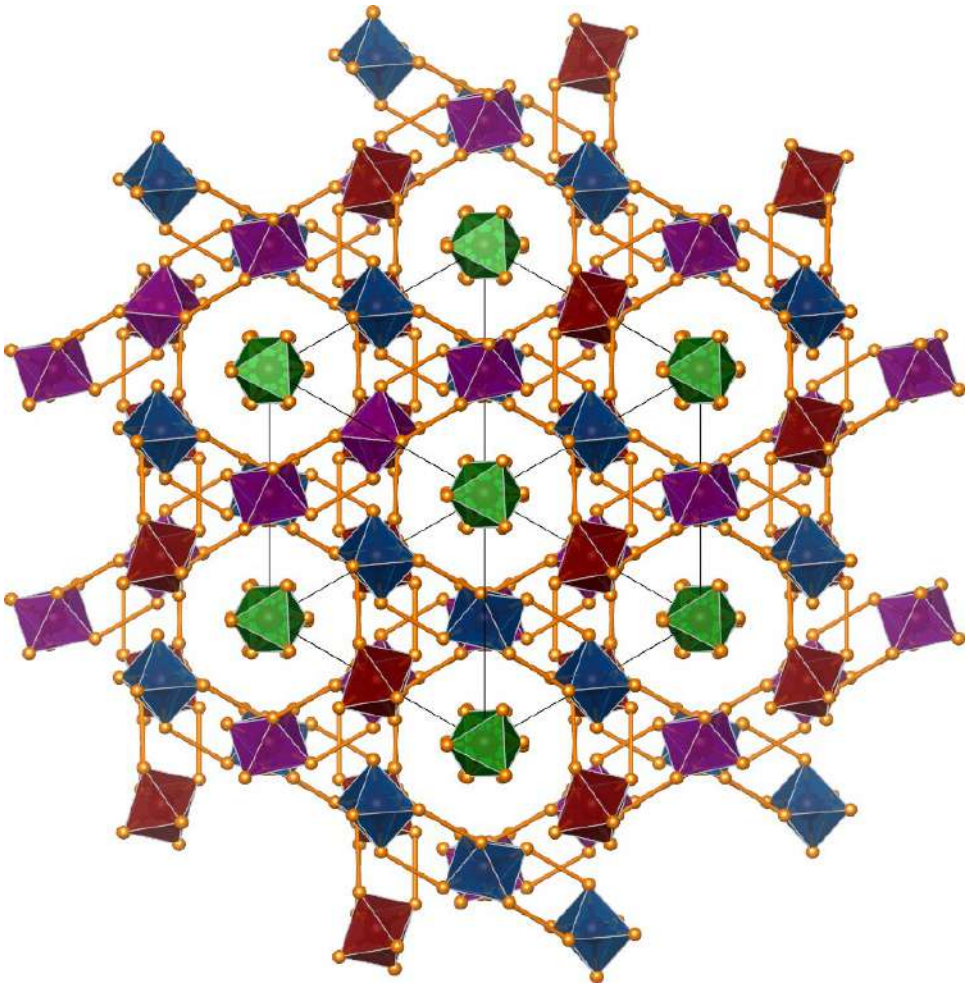


Most commonly studied for the triangular lattice on *R* site

$Gd_3Ga_2(GaO_4)_3$ is an archetype for magnetic frustration

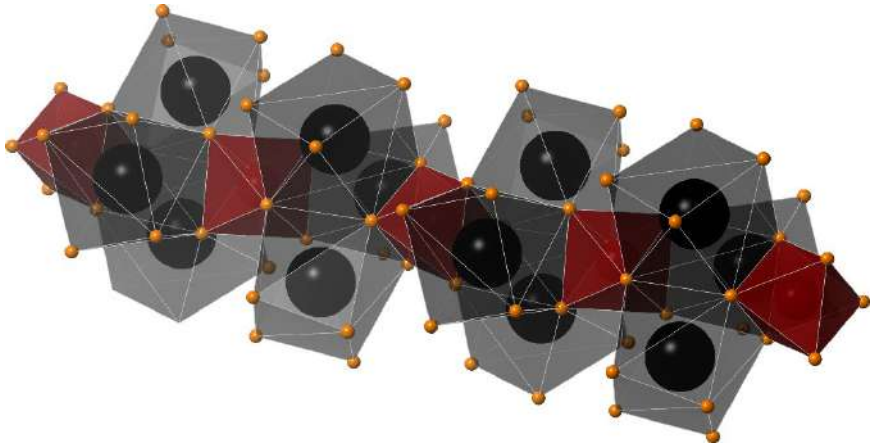


Garnets are not close-packed in the traditional sense



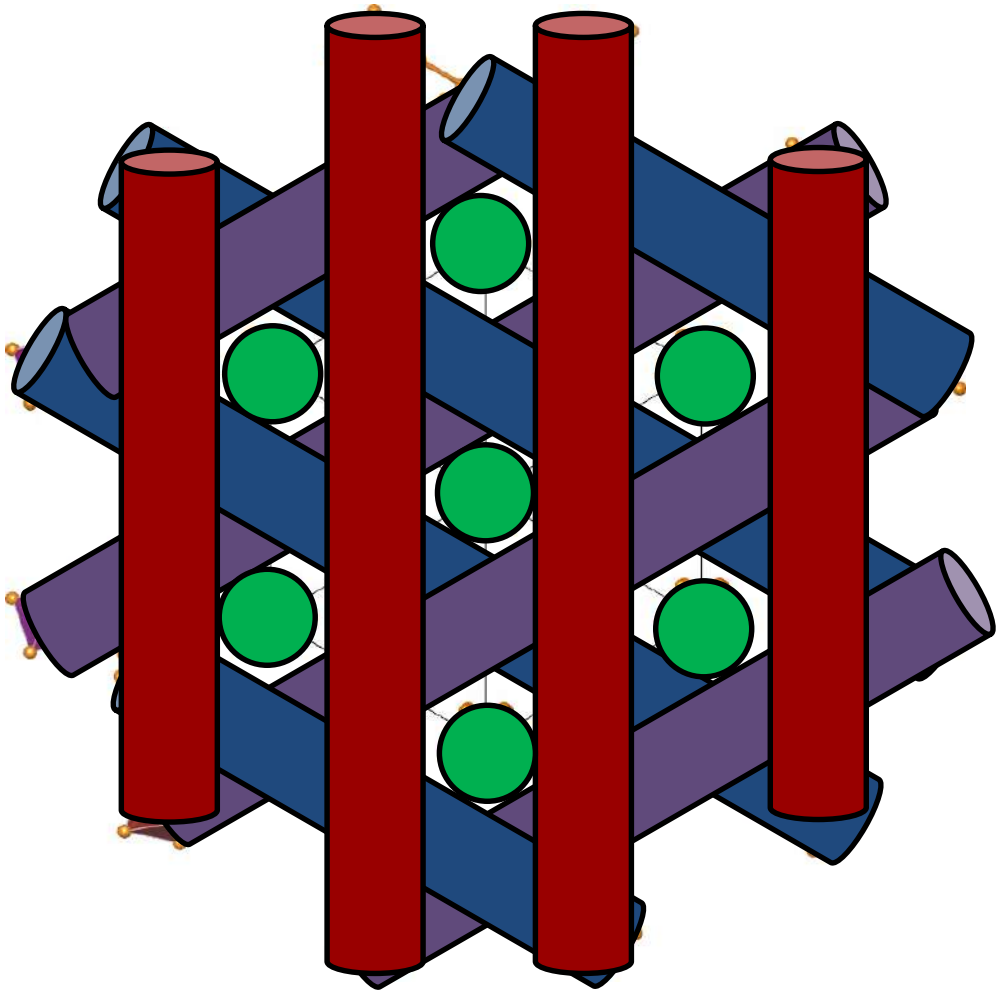
When viewed down the (111) axis, four symmetry-related rods consisting of alternating octahedral and trigonal prismatic sites (face of the rare-earth polyhedra) can be seen.

These rods, bound together by the tetrahedral site, form a network of close-packed rods as described by O'Keefe and Andersson



O'Keefe and Andersson *Acta Cryst A* 33 *914* (1977)

Garnet lattice composed of a network of close-packed rods



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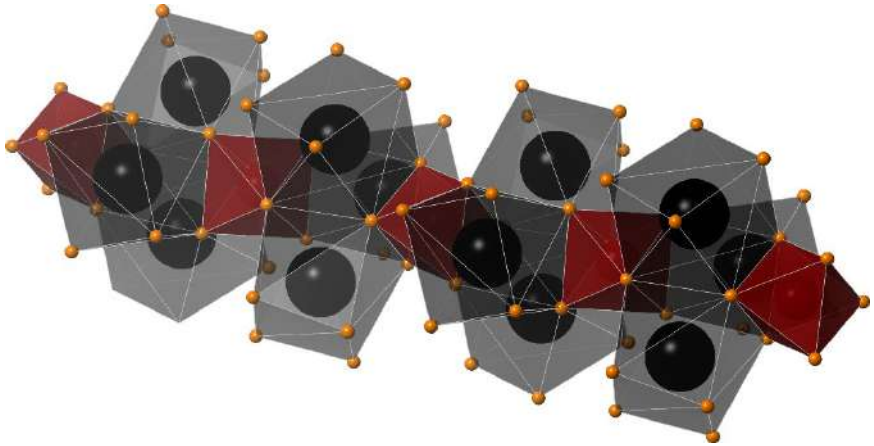

Zeier, Melot *et al. ACS Appl. Mater. Interfaces* 6, 10900–10907, (2014)