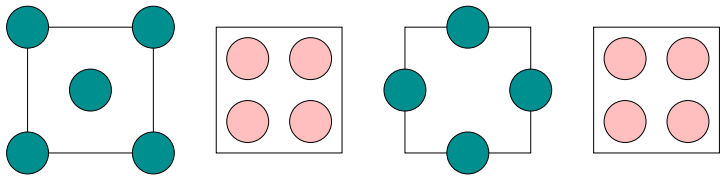
MATRL 218/CHEM 227: Class VII — Structures 3
More Structures

Ram Seshadri (seshadri@mrl.ucsb.edu)

AB_2 structures:

Fluorite CaF_2: SG = $Fm\bar{3}m$ (No. 225) a = 5.45 Å

Atom	x	y	z
Ca	0	0	0
F	1/4	1/4	1/4

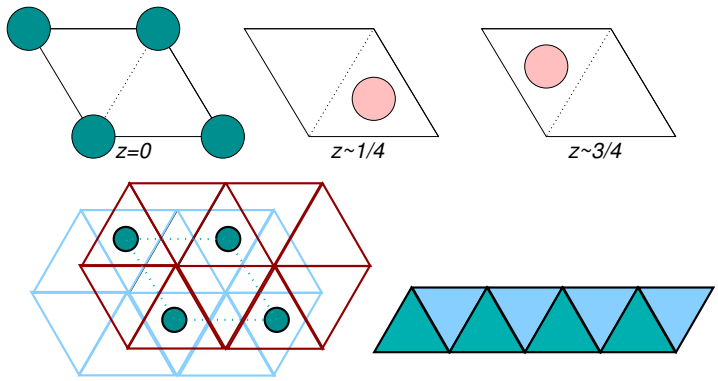


This structure type is also adopted by SrF_2, BaF_2, UO_2, ThO_2, Na_2O (the anti-type), ZrO_2 at high temperatures ...

ZrO_2 can be stabilized in the fluorite structure through doping with Ca^{2+} or Y^{3+} – these are *stabilized* zirconias and have many structural and electrochemical applications.

CdI_2: SG = $P\bar{3}m1$ (No. 164) a = 4.24 Å c = 6.84 Å

Atom	x	y	z
Cd	0	0	0
I	2/3	1/3	~ 0.25

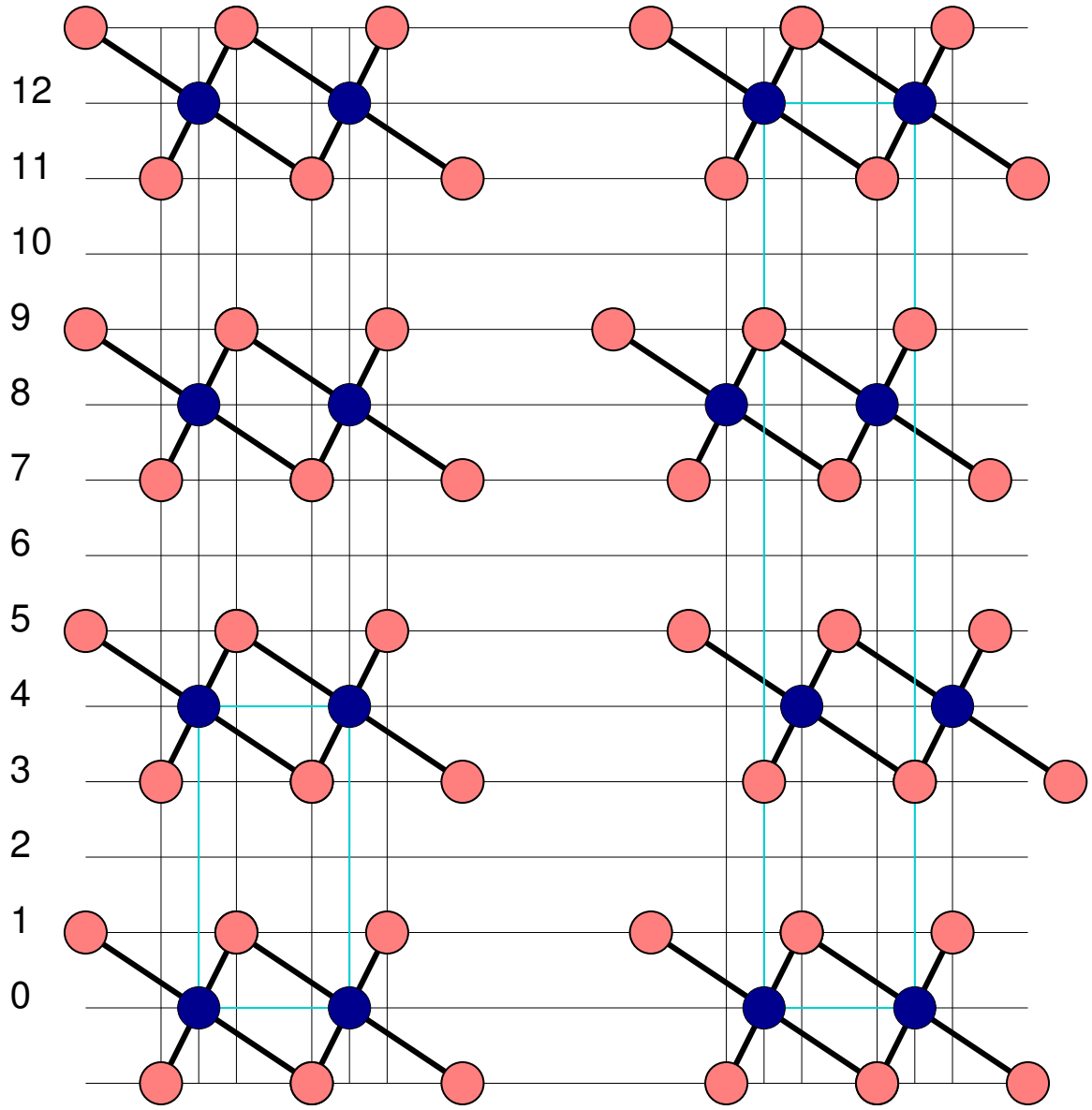


This structure type is also adopted by PbI_2, $MgCl_2$, $FeCl_2$, ZnI_2, $Cd(OH)_2$, $Mg(OH)_2$, TaS_2, NbS_2 ...

$CdCl_2$: SG = $R\bar{3}m$ (No. 166) a = 3.85 Å c = 17.46 Å

Atom	x	y	z
Cd	0	0	0
Cl	2/3	1/3	$\sim 1/12$

The $CdCl_2$ structure is to the CdI_2 structure what ABCABC stacking is to ABAB stacking:

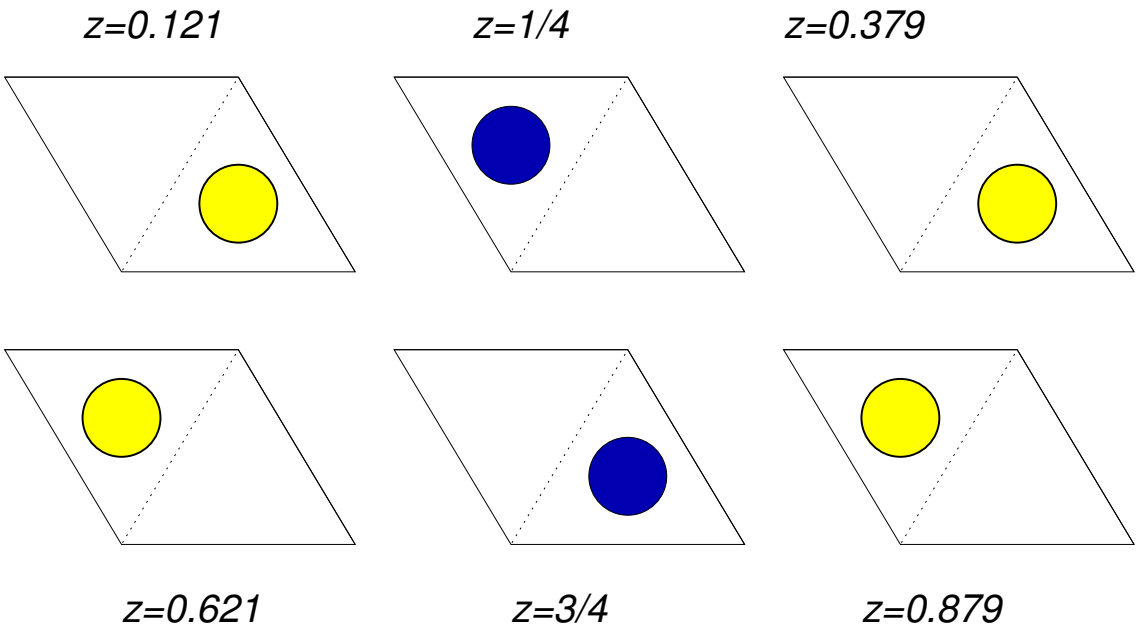


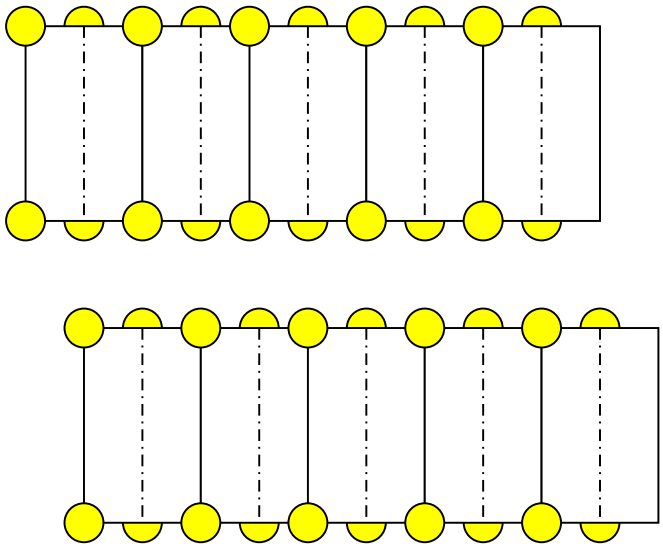
On the left is the structure of CdI_2 projected down the b axis and on the right is the structure of $CdCl_2$. The cyan-colored box marks the unit cell.

MoS_2: SG = $P6_3/mmc$ (No. 194) a = 3.160 Å c = 12.294 Å

Atom	x	y	z
Mo	1/3	2/3	1/4
S	1/3	2/3	0.621

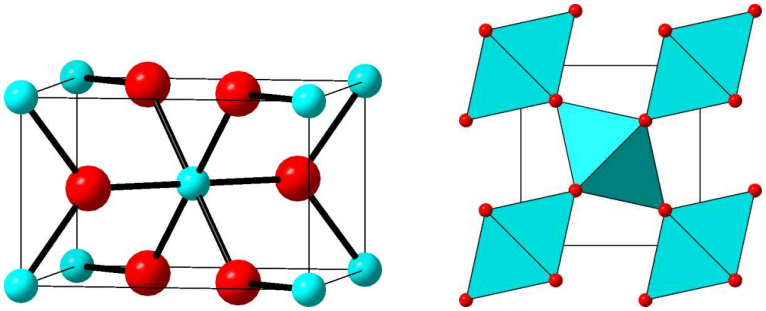
Unlike the CdI_2 structrure where the cations are octahedral, in MoS_2, the cations are in the centers of trigonal prisms formed by the S.





Rutile TiO_2: SG = $P4_2/mnm$ (No. 136) a = 4.592 Å c = 2.959 Å

Atom	x	y	z
Ti	0	0	0
O	0.3051	0.3051	0

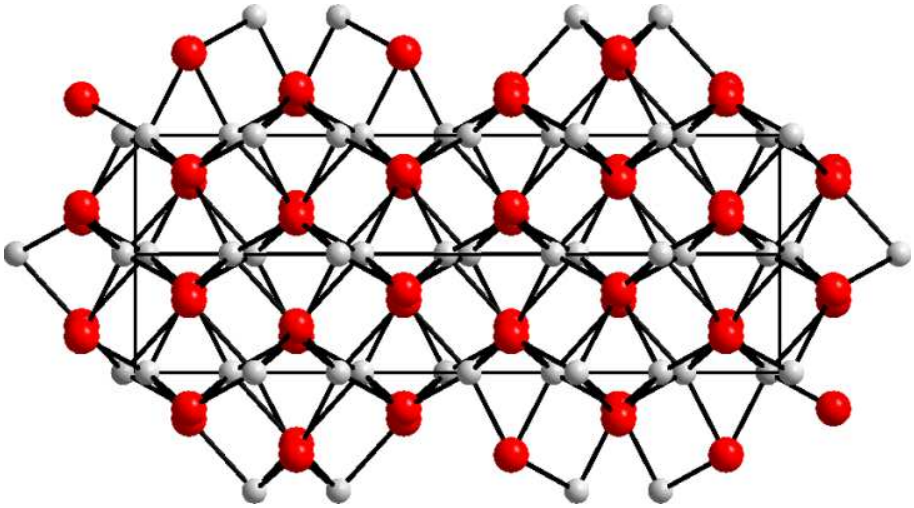


Left: The rutile structure showing the TiO_6 octahedron within a single unit cell.

Right: The rutile structure showing many TiO_6 octahedra sharing corners. The view is down the c axis. This is also the structure of CrO_2, MoO_2, RuO_2 ...

Al_2O_3: SG = $R\bar{3}c$ (No. 167) a = 4.759 Å c = 12.992 Å

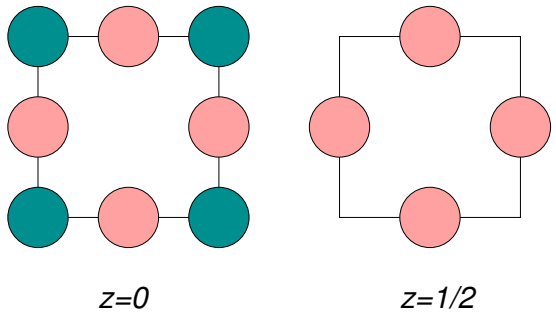
Atom	x	y	z
Al	0	0	0.35217
O	0.30168	0	1/4



The corundum structure with the c axis going from left to right. Red spheres are O and grey are Al.

ReO_3: SG = $Pm\bar{3}m$ (No. 221) a = 3.754 Å

Atom	x	y	z
Re	0	0	0
O	1/2	0	0

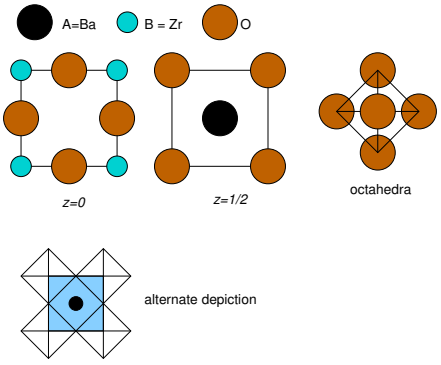


ABO_3 perovskite:

$BaZrO_3$ (A = Ba, B = Zr): SG = $Pm\bar{3}m$ (No. 221) a = 4.194 Å

Atom	Wyckoff	x	y	z
Ba	1b	1/2	1/2	1/2
Zr	1a	0	0	0
O	3d*	1/2	0	0

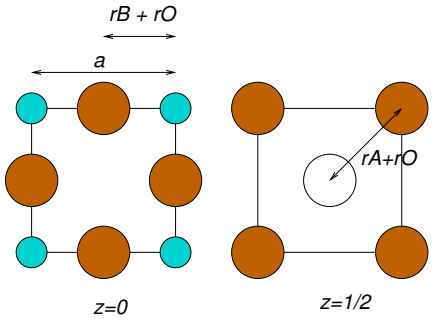
* 3d is ($\frac{1}{2}$,0,0), (0,$\frac{1}{2}$,0), (0,0,$\frac{1}{2}$)



Most perovskite structures are not cubic. $BaZrO_3$, $BaSnO_3$, $BaHfO_3$ are a few examples of the cubic ones.

In the cubic perovskite, we have:

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



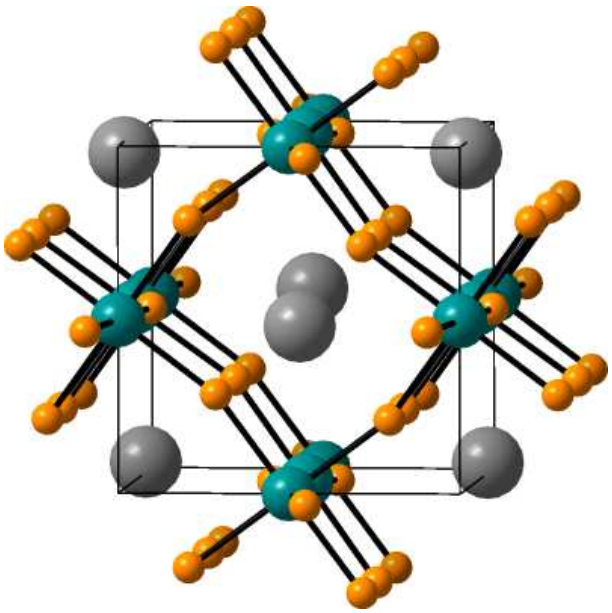
The *tolerance factor* of an ABO_3 perovskite is defined as:

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

For an ideal (cubic) perovskite, $t = 1$. Most perovskites have $t < 1$, and the structures are distorted. An example is the orthorhombic $CaZrO_3$, whose structure is given below:

$CaTiO_3$: SG = *Pbnm* (No. 62) a = 5.380 Å b = 5.440 Å c = 7.639 Å

Atom	Wyckoff	x	y	z
Ca	4*c*	0.0065	0.0356	1/4
Ti	4*b*	0	1/2	0
O1	4*b*	0.5711	-0.0161	1/4
O2	8*d*	0.2897	0.2888	0.0373



Here is the structure looking down the long c axis. The connectivity of the perovskite structure, namely the corner-shared octahedra are clearly seen. The large grey atoms are Ca.

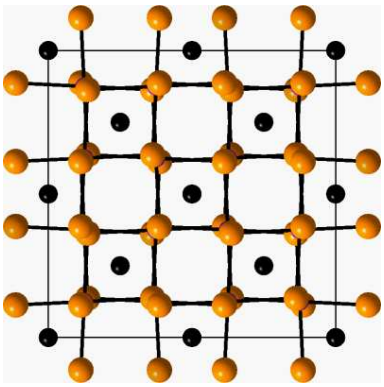
This structure is seen for $LnMO_3$ where Ln is a rare-earth (La, Pr, Nd ...) and M is Fe, Al, Sc, Cr, Ga, Co, V, Rh .... The structure is also observed in compounds such as $UCrS_3$, $NaMgF_3$, $CsCaH_3$ .... $MgSiO_3$ adopts the perovskite structure at high pressures and this is believed to be important for understanding the earth's mantle.

AB_2O_4 spinel:

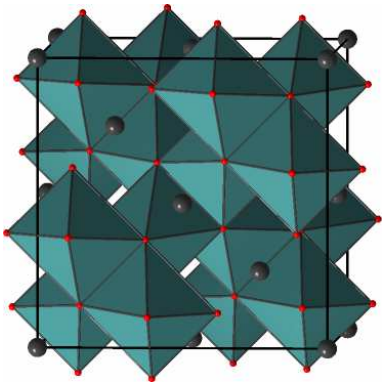
This structure has a cubic close packing (fcc) arrangement of oxide ions, with cations places in some of the interstitial tetrahedral and octahedral voids.

$MgAl_2O_4$: SG = $Fd\bar{3}m$ (No. 227) a = 8.09 Å
Structure described with center at $(\frac{1}{8},\frac{1}{8},\frac{1}{8})$

Atom	x	y	z
Mg	$\frac{5}{8}$	$\frac{5}{8}$	$\frac{5}{8}$
Al	0	0	0
O	0.390	0.390	0.390



The spinel, $MgAl_2O_4$. The Al atoms (hidden) are octahedrally surrounded by O. Mg atoms sit in tetrahedral interstices formed by O. The view is down one of the cubic axes of the structure.



The structure can also be regarded as being formed by strips of edge-sharing octahedra that are laid down forming a trellis. Tetrahedral voinds in formed by these strips of octahedra are where the Mg sit.

In $MgAl_2O_4$, the divalent Mg are in the tetrahedral site, and trivalent Al are in the octahedral site. Such an arrangement corresponds to a normal spinel. In an inverse spinel, the tetrahedral site might have a trivalent ion. An example is $MgFe_2O_4$, where one Fe^{3+} is tetrahedral and the other is octahedral. The Mg^{2+} is octahedral.

Spinels are formed by a number of transition elements, and by Mg_2TiO_4, Na_2MoO_4, Li_2NiF_4, $CuTi_2S_4$, Fe_3O_4 ....