Materials 218/UCSB: Class VIII:
More crystal structures: ABO_3 (perovskite), AB_2O_4 (spinel), A_2BO_4 (K_2NiF_4)

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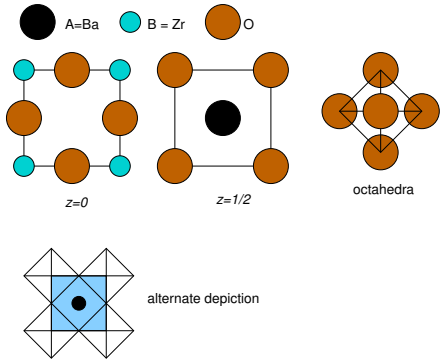
ABO_3 perovskite:

$BaZrO_3$ (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

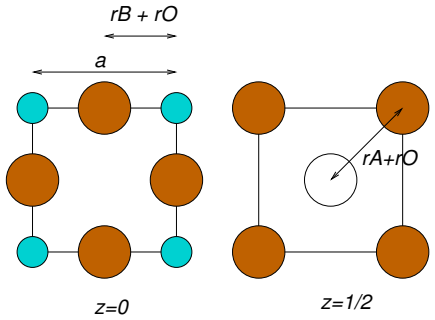
* $3d$ is ($\frac{1}{2}$,0,0), (0,$\frac{1}{2}$,0), (0,0,$\frac{1}{2}$)



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:

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



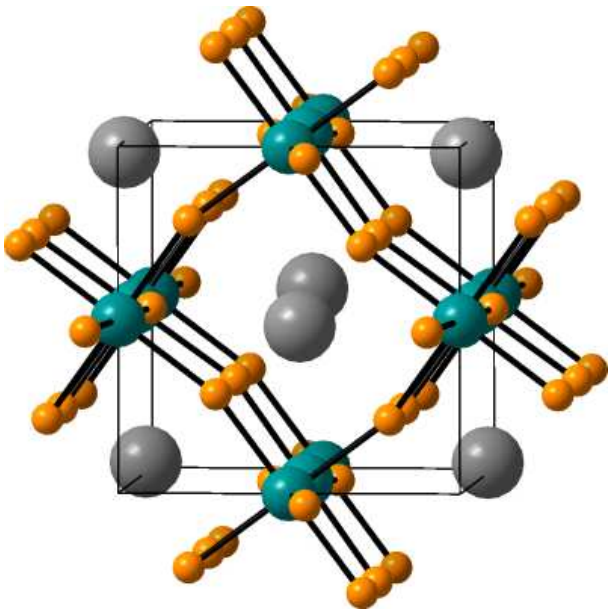
The *tolerance factor* of an ABO_3 perovskite is defined as:

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

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.

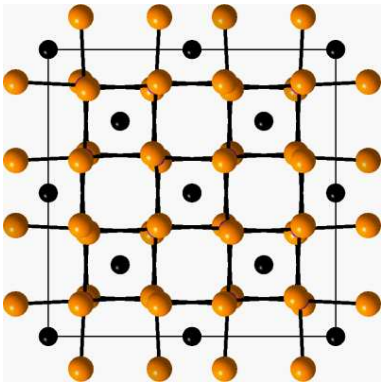
This structure is seen for $LnMO_3$ where Ln is a rare-earth (La, Pr, Nd ...) and M is Fe, Al, Sc, Cr, Ga, Co, V, Rh .... The structure is also observed in compounds such as $UCrS_3$, $NaMgF_3$, $CsCaH_3$ .... $MgSiO_3$ adopts the perovskite structure at high pressures and this is believed to be important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

AB_2O_4 spinel:

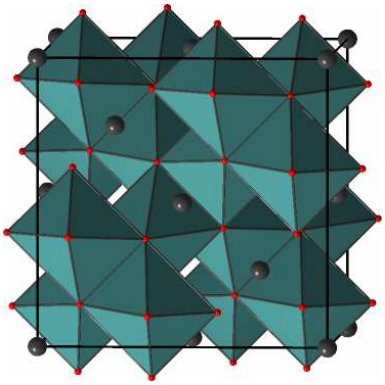
This structure has a cubic close packing (fcc) arrangement of oxide ions, with cations places in some of the interstitial tetrahedral and octahedral voids.

$MgAl_2O_4$: 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.

Also see the handout.

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 ....