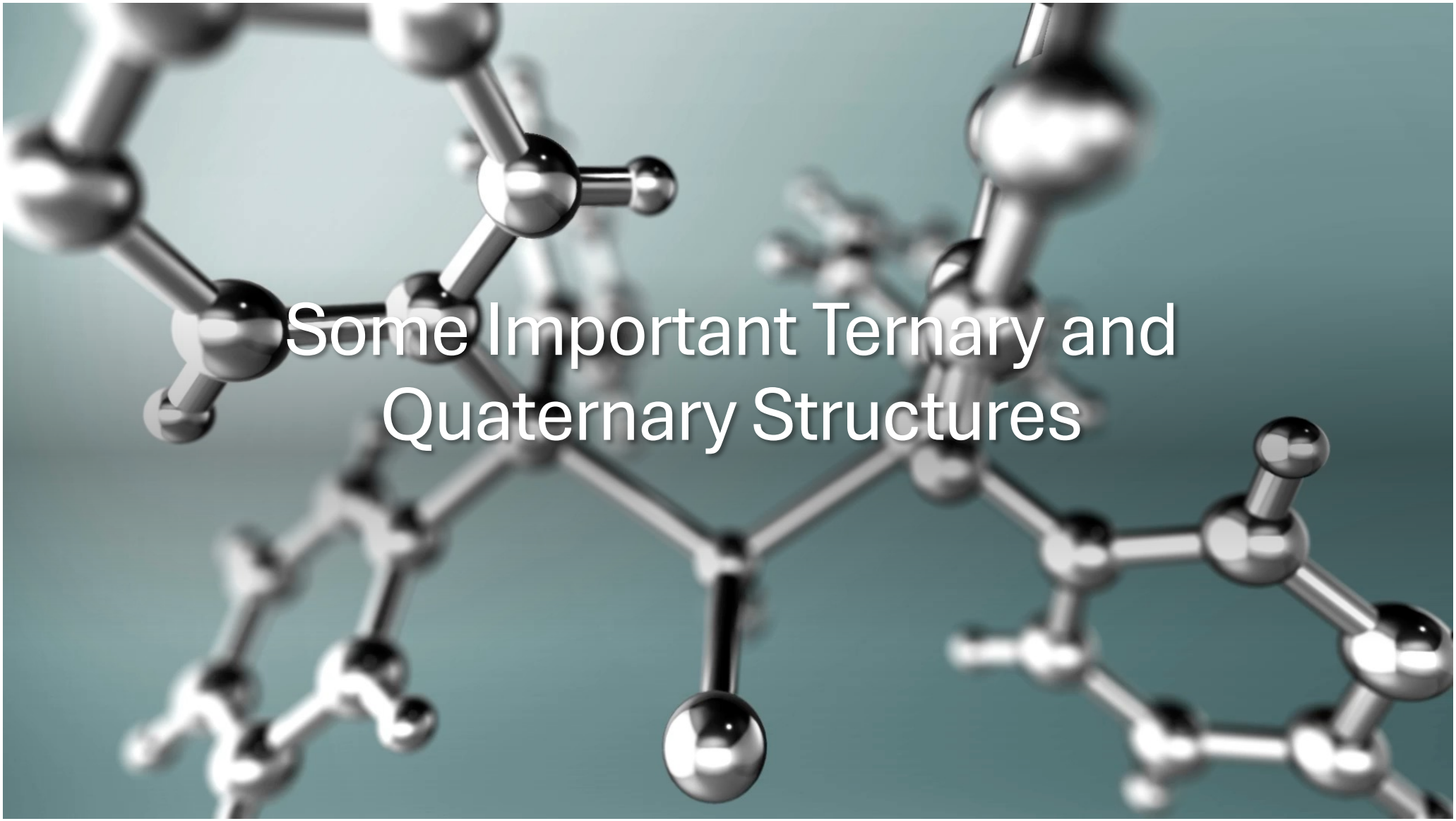
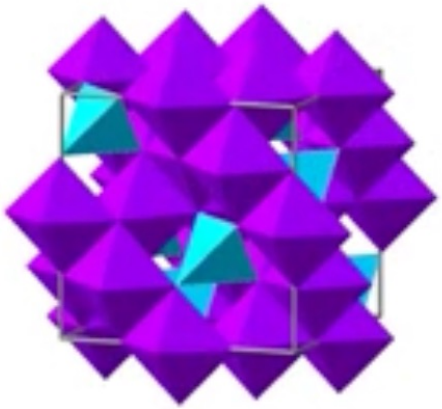

Some Important Ternary and
Quaternary Structures

Learning Objectives

- Recognize the structural features of **Spinel, Garnet, and Perovskite** lattices.
- Understand how **cation site preferences** (tetrahedral vs. octahedral) shape these structures.
- Relate these structures to **functional properties** (magnetism, lasers, ferroelectricity, piezoelectricity).
- Apply **Pauling's rule of parsimony** and coordination number analysis to complex solids.
- Use the **tolerance factor** concept to predict perovskite stability and distortions.

Spinel ($MgAl_2O_4$)



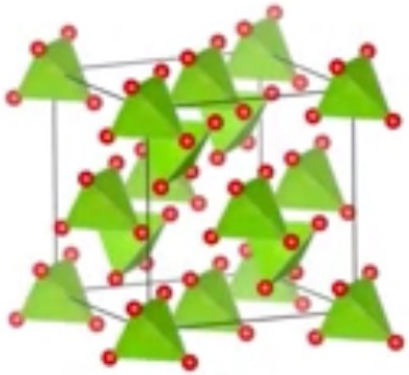
Compass (circa 4th Century BC)

Fe_3O_4 which has the spinel structure is the oldest technologically used magnetic material, used in compasses over 2000 years ago.

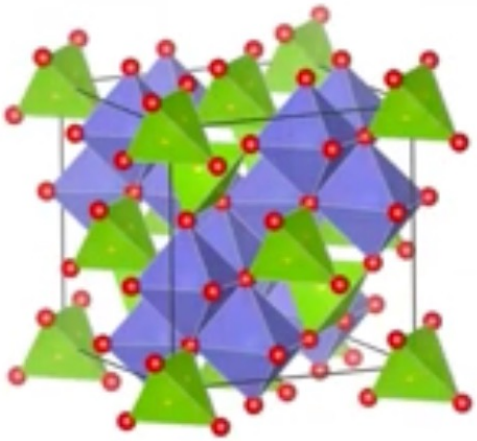
Table 1.7 Oxidation-state combinations for spinels.

Tetrahedron	Octahedron		Chemical formula of an example
1	3	4	$LiMn_2O_4$ (a = 8.245 Å)
2	3	3	$ZnFe_2O_4$ (a = 8.442 Å)
2	4	2	Fe_2TiO_4 (a = 8.521 Å)
3	2	3	Fe_3O_4 (a = 8.394 Å)
4	2	2	Ni_2SiO_4 (a = 8.045 Å)
5	1	2	$LiZnNbO_4$ (a = 6.082, c = 8.403 Å)
6	1	1	Na_2WO_4 (a = 9.108 Å)

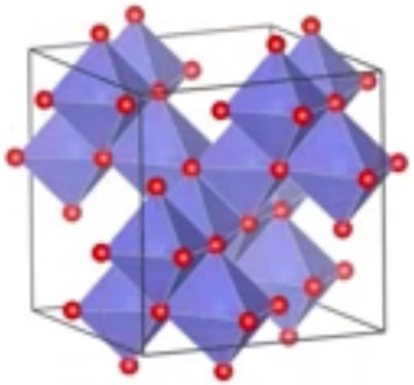
Spinel Structure



MgO_4 tetrahedra
not connected



ccp array of O
Al in 1/2 octahedral holes
Mg in 1/8 tetrahedral holes

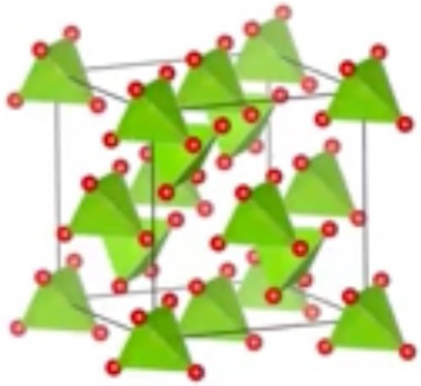


AlO_6 octahedra
share edges

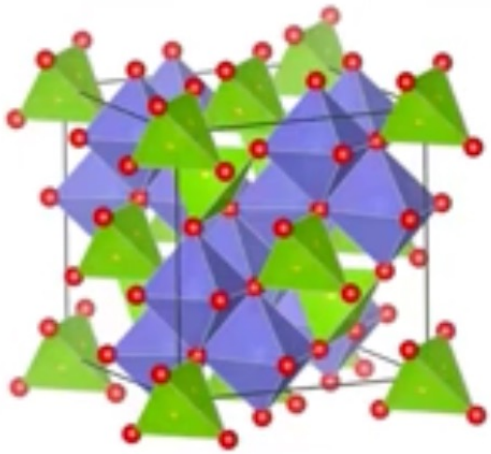
Space Group = $Fd\bar{3}m$
a = 8.086 Å

Atom	Site	Symmetry	x	y	Z
Mg	8a	$\bar{4}3m$	0	0	0
Al	16d	$m\bar{3}$	5/8	5/8	5/8
O	32e	m	0.384	0.384	0.384

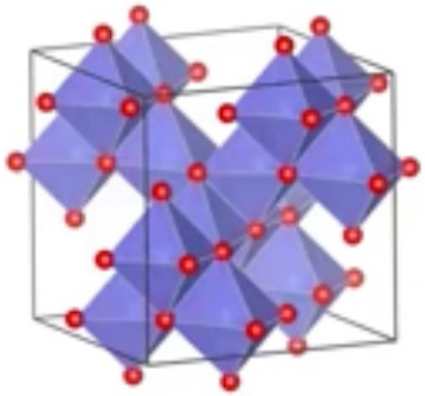
Spinel Structure



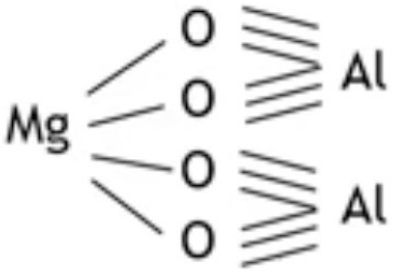
MgO_4 tetrahedra
not connected



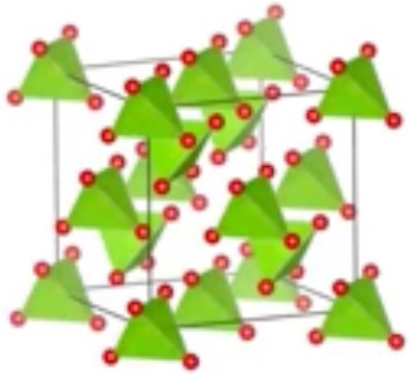
ccp array of O
Al in 1/2 octahedral holes
Mg in 1/8 tetrahedral holes



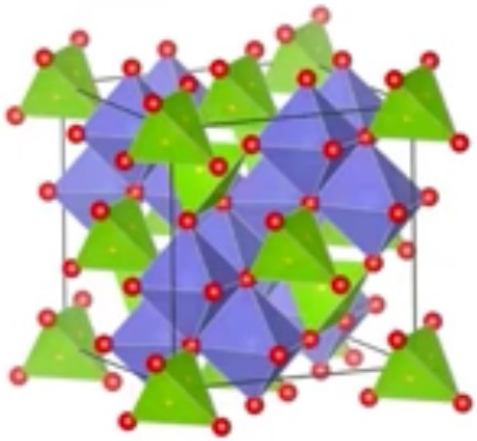
AlO_6 octahedra
share edges



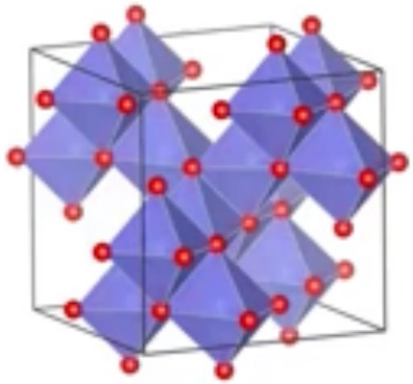
Spinel Structure



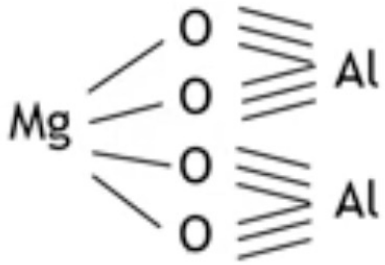
MgO_4 tetrahedra
not connected



ccp array of O
Al in 1/2 octahedral holes
Mg in 1/8 tetrahedral holes

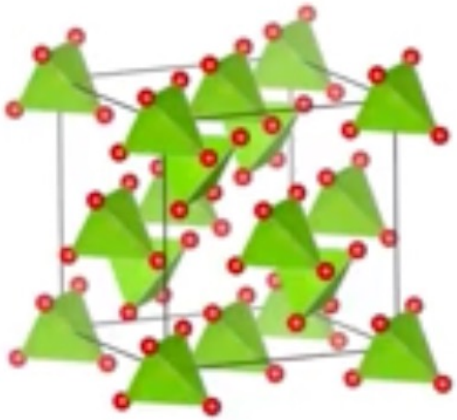


AlO_6 octahedra
share edges

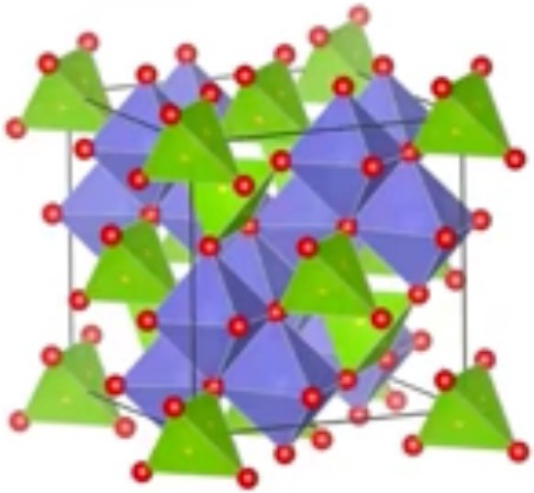


$$Mg^{[4]}Al_2^{[6]}O_4^{[1,3]}$$

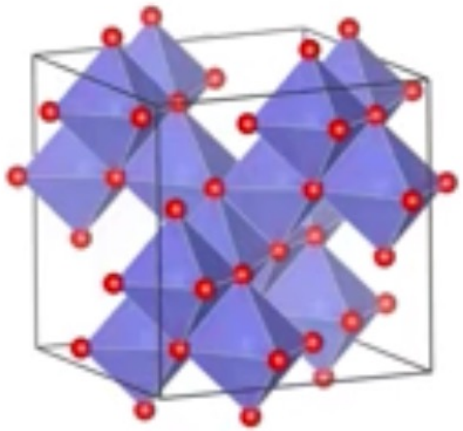
Spinel Structure



MgO_4 tetrahedra
not connected



ccp array of O
Al in 1/2 octahedral holes
Mg in 1/8 tetrahedral holes

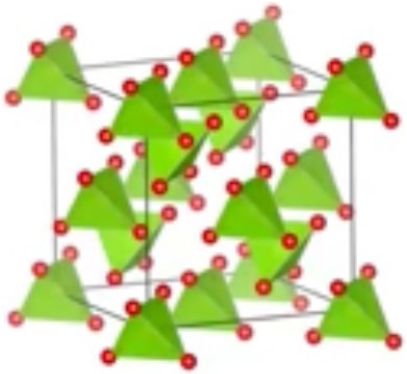


AlO_6 octahedra
share edges

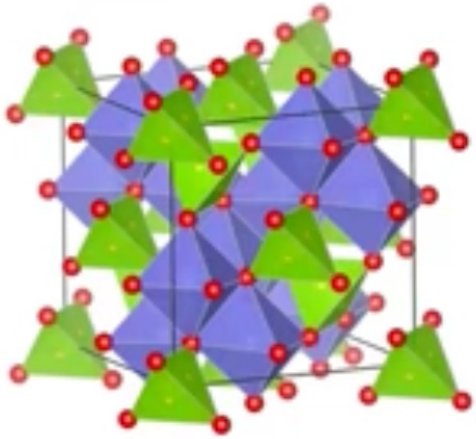
$$A^{[4]}B_2^{[6]}O_4^{[1,3]}$$

Normal spinel (e.g. $MgAl_2O_4$)
A tetrahedral (Mg), B octahedral (Al)

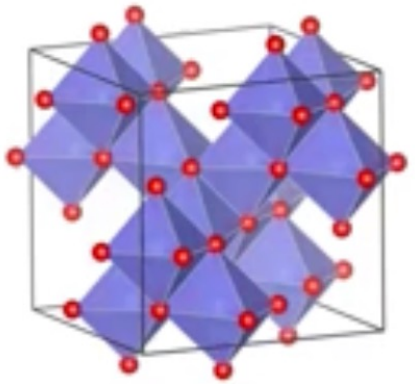
Spinel Structure



MgO_4 tetrahedra
not connected



ccp array of O
Al in 1/2 octahedral holes
Mg in 1/8 tetrahedral holes



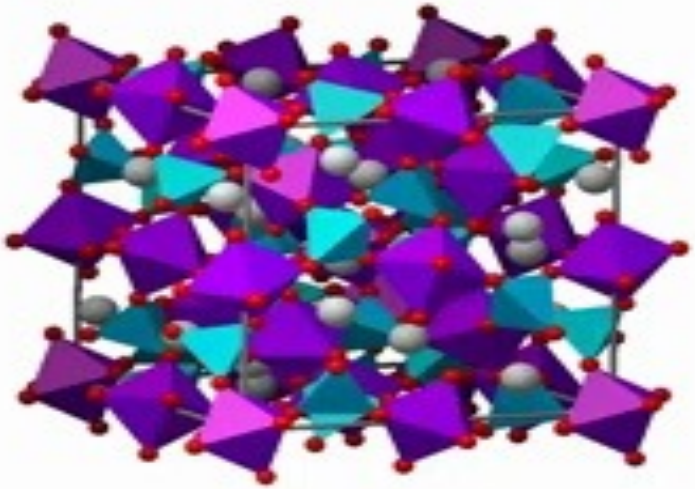
AlO_6 octahedra
share edges

$$A^{[4]}B_2^{[6]}O_4^{[1,3]}$$

Normal spinel (e.g. $MgAl_2O_4$)
A tetrahedral (Mg), B octahedral (Al)

Inverse spinel (e.g. $TiFe_2O_4$)
B tetrahedral (Fe)
B & A randomly octahedral (Fe,Ti)

Garnet (e.g. $Mg_3Al_2Si_3O_{12}$)



Nd^{3+} doped $Y_3Al_5O_{12}$ (YAG) is a popular laser crystal, that emits 1064 nm light.

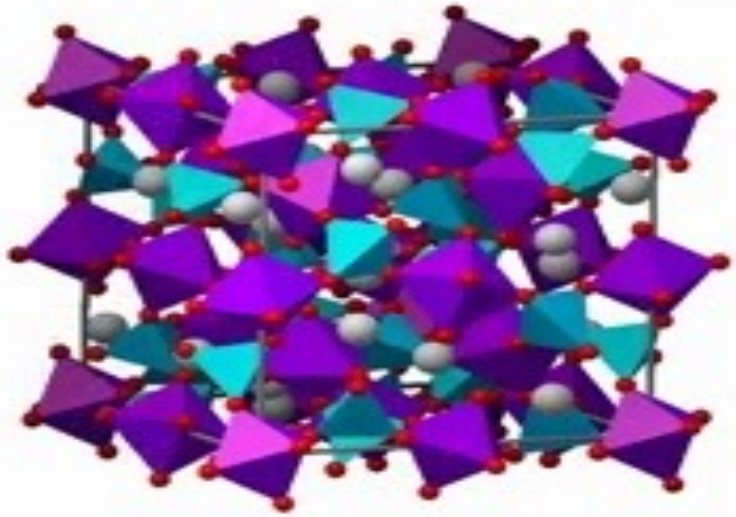
$Y_3Fe_5O_{12}$ (YIG) is an important magnetic material

Garnets where some Cr^{3+} replaces Al^{3+} are precious gemstones similar to ruby.

Table 1.8 Oxidation states in garnets [cube]$_3$[octahedron]$_2$[tetrahedron]$_3$O$_{12}$.

Cube	Octahedron	Tetrahedron	Examples
2	6	2	$Ca_3Te_2Zn_3O_{12}$ a = 10.930 Å
3	3	3	$Y_3Fe_2Fe_3O_{12}$ a = 12.376 Å
2	3	4	$Mg_3Al_2Si_3O_{12}$ a = 11.459 Å
1	3	5	$Na_3Sc_2V_3O_{12}$ a = 10.913 Å

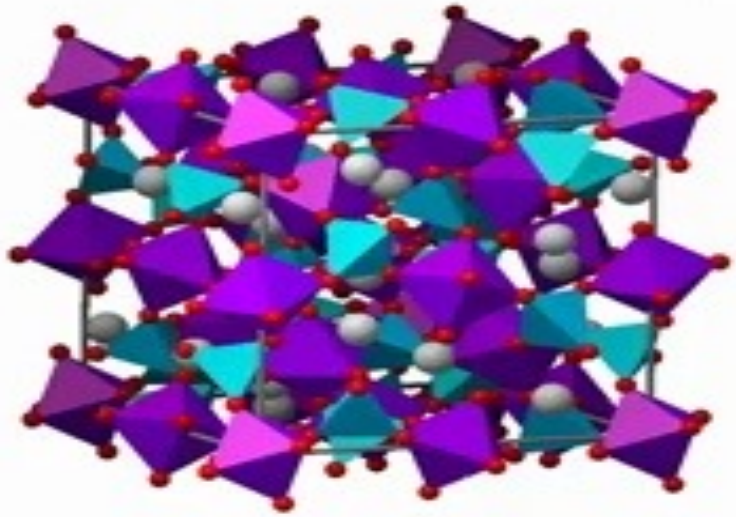
Garnet (e.g. $Mg_3Al_2Si_3O_{12}$)



Space Group = $Ia\bar{3}d$
a = 11.459 Å

Atom	Site	Symmetry	x	y	Z
Al	16a	$\bar{3}$	0	0	0
Mg	24c	222	1/8	0	1/4
Si	24d	$\bar{4}$	3/8	0	1/4
O	96h	1	0.034	0.050	0.654

Garnet (e.g. $Mg_3Al_2Si_3O_{12}$)



$$Mg_3^{[8]}Al_2^{[6]}Si_3^{[4]}O_{12}^{[2,1,1]}$$

Space Group = $Ia\bar{3}d$
a = 11.459 Å

Atom	Site	Symmetry	x	y	Z
Al	16a	$\bar{3}$	0	0	0
Mg	24c	222	1/8	0	1/4
Si	24d	$\bar{4}$	3/8	0	1/4
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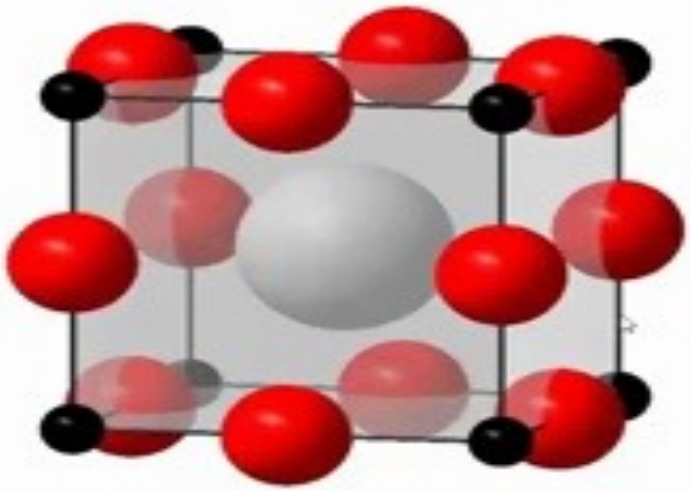
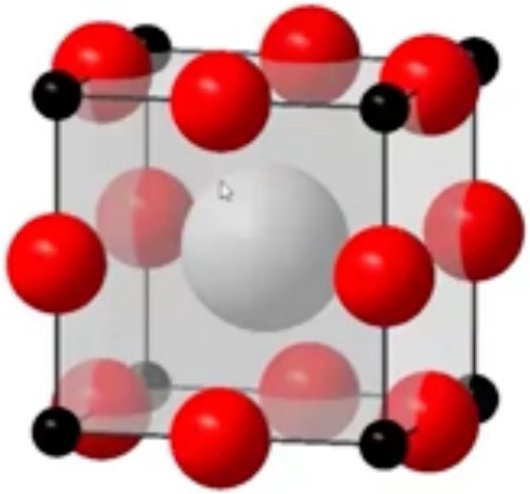
Perovskites



Space Group = $Pm\bar{3}m$
a = 4.0 Å

Atom	Site	Symmetry	x	y	z
Sr	1b	$m\bar{3}m$	1/2	1/2	1/2
Ti	1a	$m\bar{3}m$	0	0	0
O	3d	$4/mmm$	1/2	0	0

Perovskites

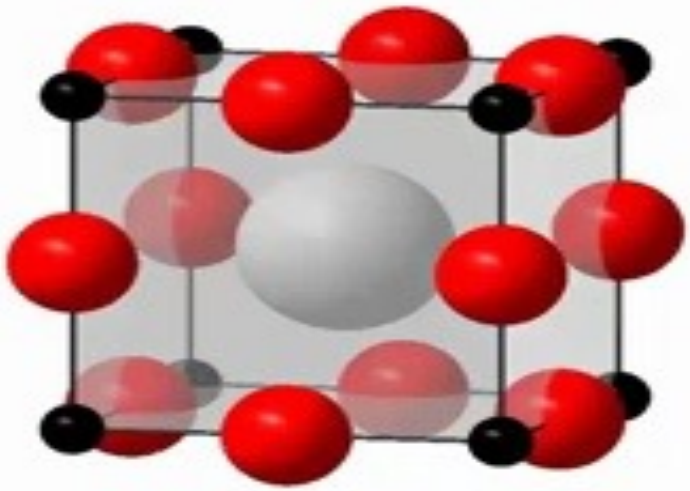


Space Group = $Pm\bar{3}m$
a = 4.0 Å

Atom	Site	Symmetry	x	y	z
Sr	1b	$m\bar{3}m$	1/2	1/2	1/2
Ti	1a	$m\bar{3}m$	0	0	0
O	3d	$4/mmm$	1/2	0	0

$$Sr^{[12]}Ti^{[6]}O_3^{[4,2]}$$

Perovskites



Space Group = $Pm\bar{3}m$
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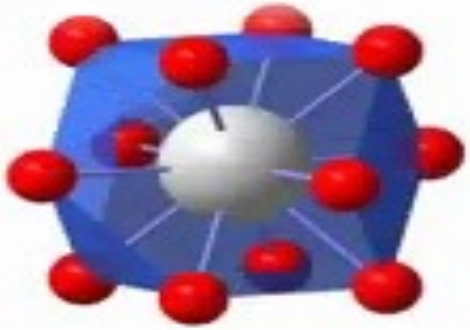
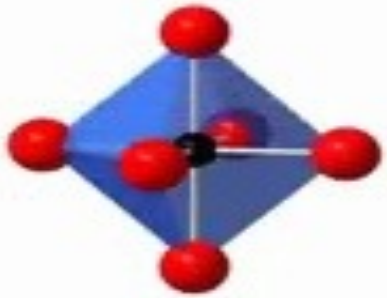
Atom	Site	Symmetry	x	y	z
Sr	1b	$m\bar{3}m$	1/2	1/2	1/2
Ti	1a	$m\bar{3}m$	0	0	0
O	3d	$4/mmm$	1/2	0	0

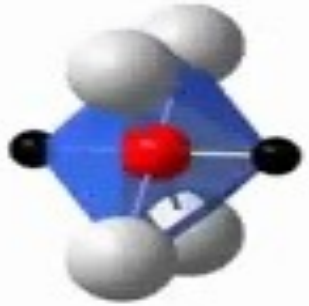
$$Sr^{[12]}Ti^{[6]}O_3^{[4,2]}$$



A-site
Cubo-octahedron



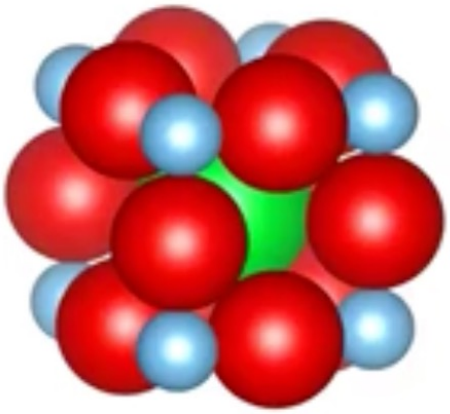
B-site
Octahedron



Anion

Tolerance Factor

Goldshmidt developed a simple yet accurate geometric description of the perovskite structure, which allows us to predict the likelihood of an octahedral tilting distortion. He referred to this parameter as the tolerance factor, t:



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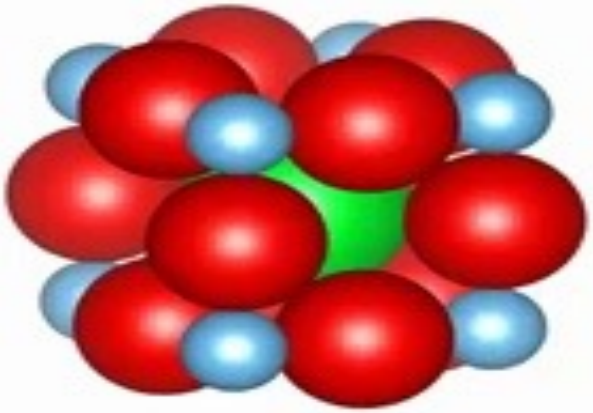

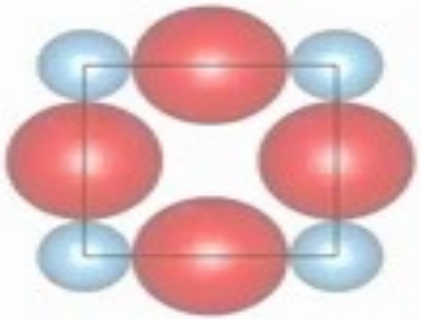

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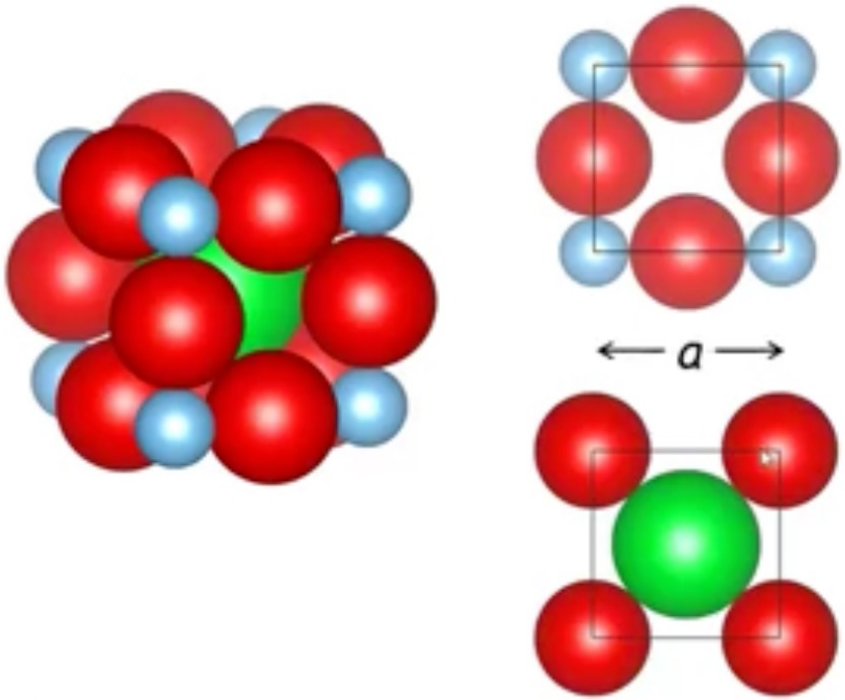

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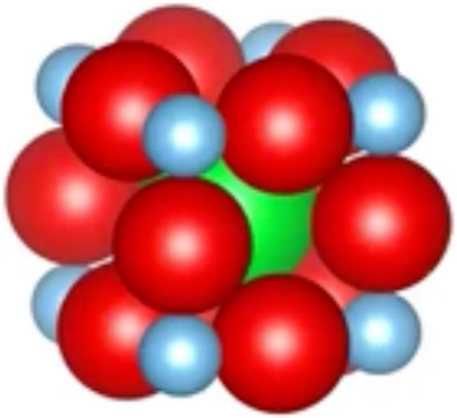
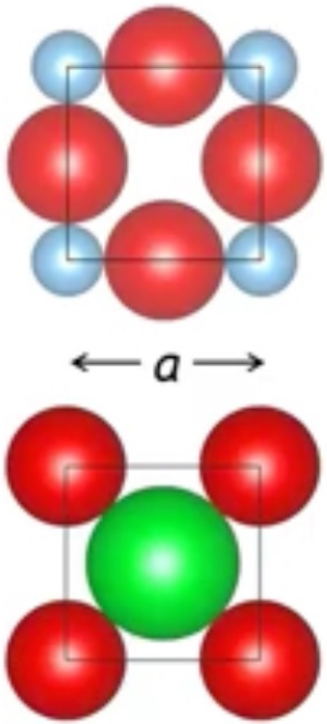




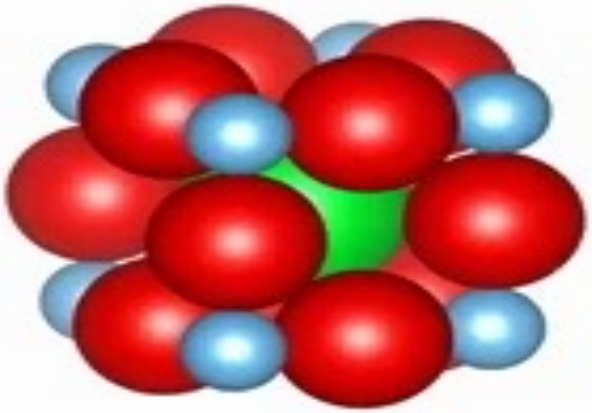
$$a = 2(r_B + r_X)$$

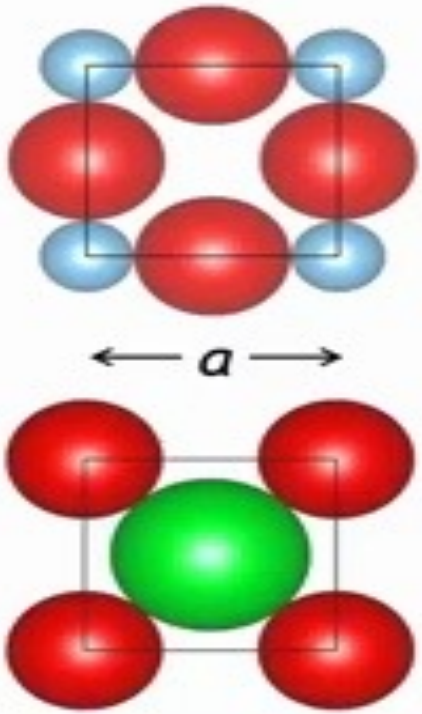
$$a = \frac{2(r_A + r_X)}{\sqrt{2}}$$

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

Tolerance Factor

Goldshmidt developed a simple yet accurate geometric description of the perovskite structure, which allows us to predict the likelihood of an octahedral tilting distortion. He referred to this parameter as the tolerance factor, t:





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

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

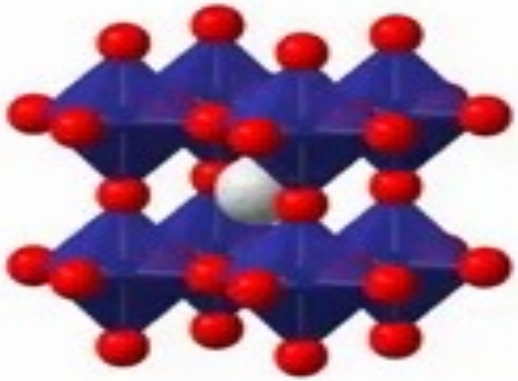
$t > 1$ A too big
$t = 1$ perfect fit
$t < 1$ A too small

Size Mismatch and ABO_3 Compounds

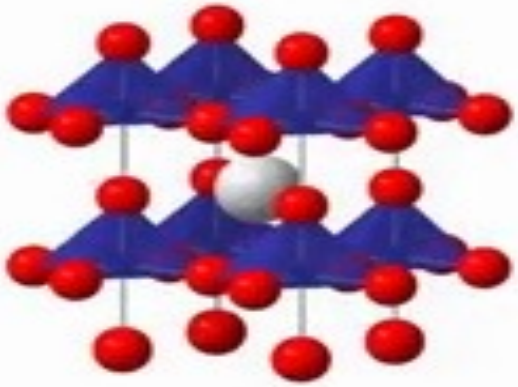
Compound	*a* (Å) A-cation	*a* (Å) B-cation	Tolerance Factor (t)
$BaMnO_3$	4.17	3.81	4.17/3.81 = 1.09
$BaTiO_3$	4.17	3.93	1.06
$SrTiO_3$	3.93	3.93	1.00
$CaMnO_3$	3.72	3.81	0.976
$CaTiO_3$	3.72	3.93	0.946
$MgTiO_3$	3.33	3.93	0.847

Not Perovskite Distorted Perovskite

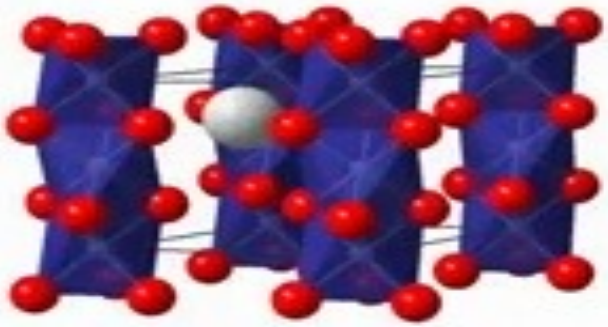
$ATiO_3$ Structures (t > 1)



$SrTiO_3$
Tolerance Fact. = 1.00
Cubic Perovskite



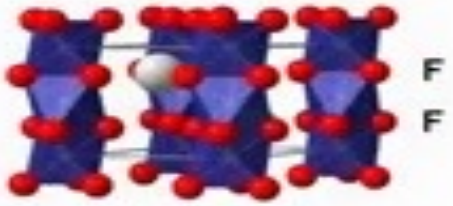
$BaTiO_3$
Tolerance Fact. = 1.06
Distorted Perovskite



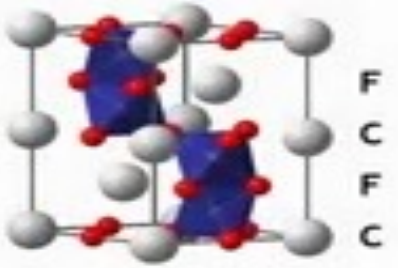
$BaMnO_3$
Tolerance Fact. = 1.09
2H "Hexagonal" Perovskite

As the tolerance factor rises above 1.00 the connectivity of the octahedral corner sharing network starts to break down, first subtly and then more dramatically.

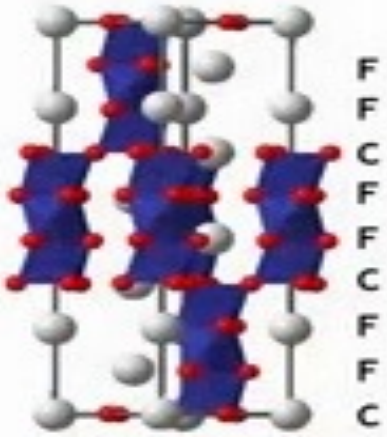
“Hexagonal/Rhombohedral Perovskites”



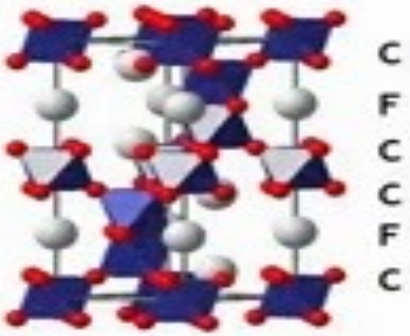
2H ($BaMnO_3$)



4H (HP-$BaRuO_3$)

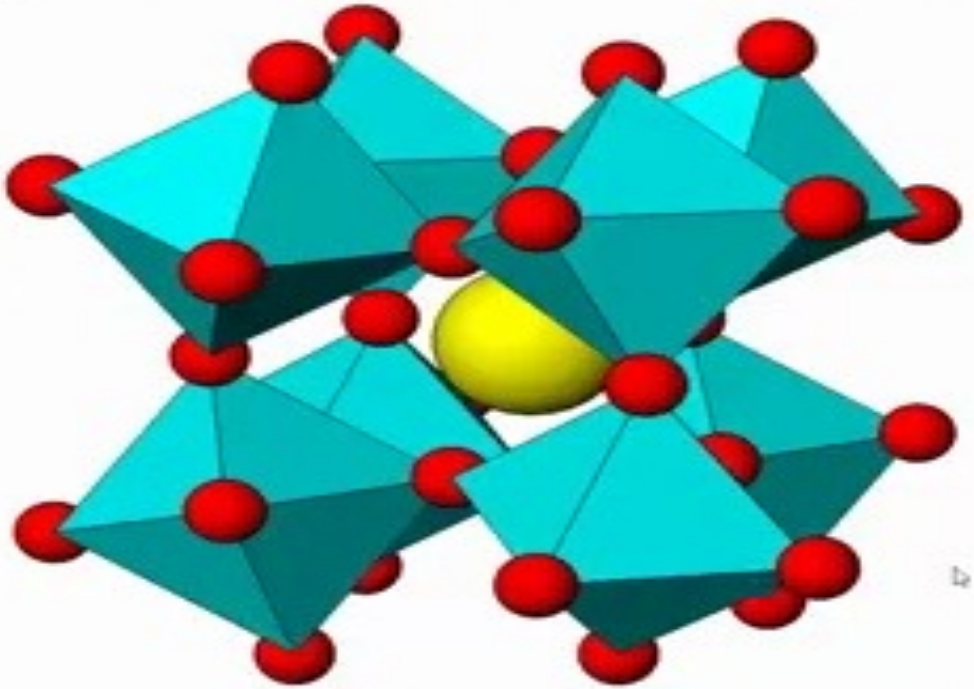


9R ($BaRuO_3$)



6H ($BaTiO_3$)

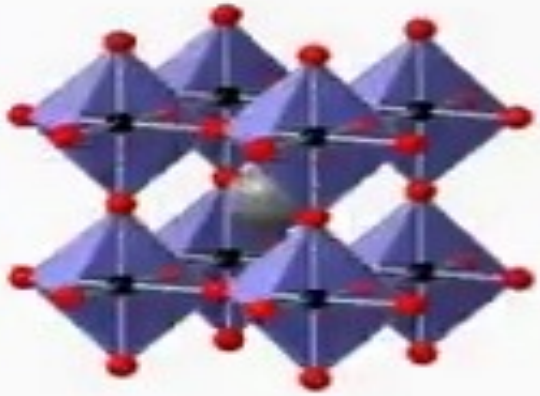
Crystal Structure - $CaTiO_3$



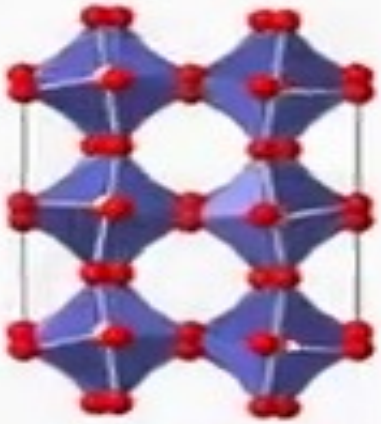
$1 > t > 0.9$

The undersized A-site cation causes a distortion commonly referred to as an octahedral tilting distortion. The Ti environment is still an octahedron, but the Ca coordination number is reduced to 8.

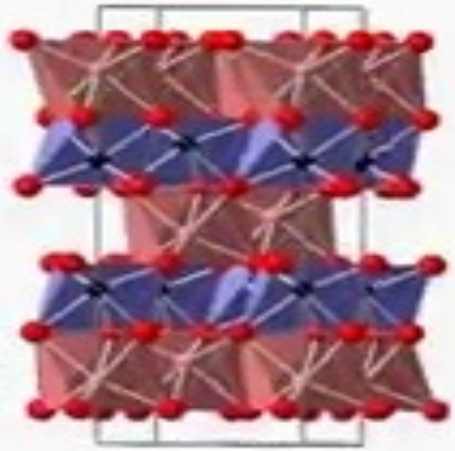
$ATiO_3$ Structures (t < 1)



$SrTiO_3$
Tolerance Fact. = 1.00
Cubic Perovskite
Sr Coord. # = 12



$CaTiO_3$
Tolerance Fact. = 0.95
Distorted Perovskite
Ca Coord. # = ~8



$MgTiO_3$
Tolerance Fact. = 0.85
Ilmenite
Mg Coord. # = 6

As the tolerance factor falls below 1.00 the octahedral begin to rotate so that some of the anions can maintain contact with the A-site cation. This is called an octahedral tilting distortion. The ilmenite structure emerges when the tolerance factor decreases beyond a certain point.

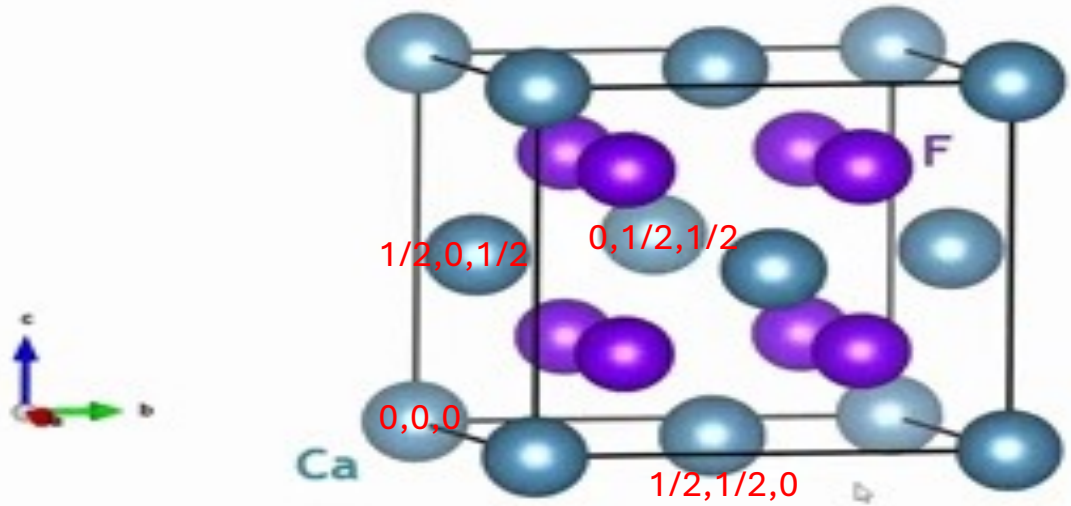
Summary

- **Spinel (AB_2O_4):**
  - Cubic close-packed O^{2-} lattice.
  - Normal vs. inverse site distributions.
  - Important for **magnetism** (e.g., Fe_3O_4).
- **Garnet ($X_3Y_2Si_3O_{12}$):**
  - Multiple cation sites: cubic (8), octahedral (6), tetrahedral (4).
  - Technological uses: **lasers (Nd:YAG), magnetic materials (YIG), gemstones**.
- **Perovskite (ABO_3):**
  - Corner-sharing octahedra with A in 12-coordination.
  - Stability governed by **Goldschmidt tolerance factor (t)**.
  - Distortions → ferroelectric ($BaTiO_3$), piezoelectric, or hexagonal variants.
  - Ubiquitous in **functional oxides** (superconductors, dielectrics, photovoltaics).

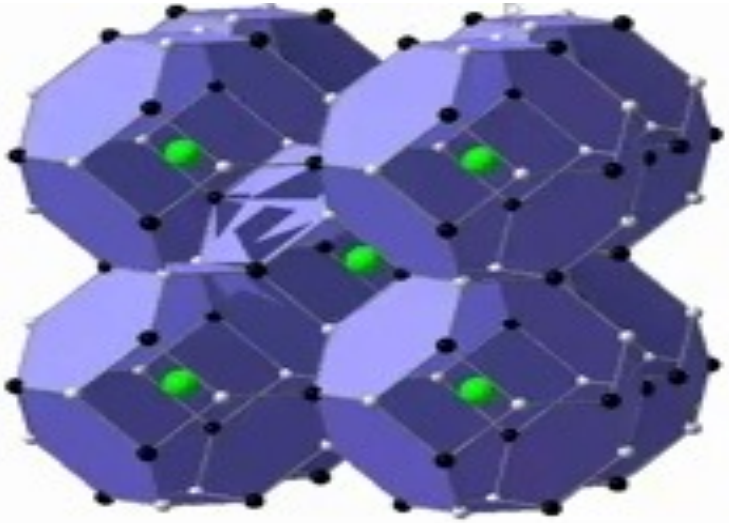
CaF_2 (fluorite)

Space Group		$Fm\bar{3}m$ (#225)		
Lattice parameters		$a = 5.46$ Å		
Atom	Wyckoff Site	x	y	z
Ca	4a	0	0	0
F	8c	1/4	1/4	1/4

Space Group	$Fm\bar{3}m$ (#225)			
Lattice parameters	$a = 5.46$ Å			
Atom	Wyckoff Site	x	y	z
Ca	4a	0	0	0
F	8c	1/4	1/4	1/4



Ca (4a)	0,0,0	½,½,0	½,0,½	0,½,½
F (8c)	¼,¼,¼	¾,¾,¼	¾,¼,¾	¼,¾,¾
	¼,¼,¾	¾,¾,¾	¾,¼,¼	¼,¾,¼

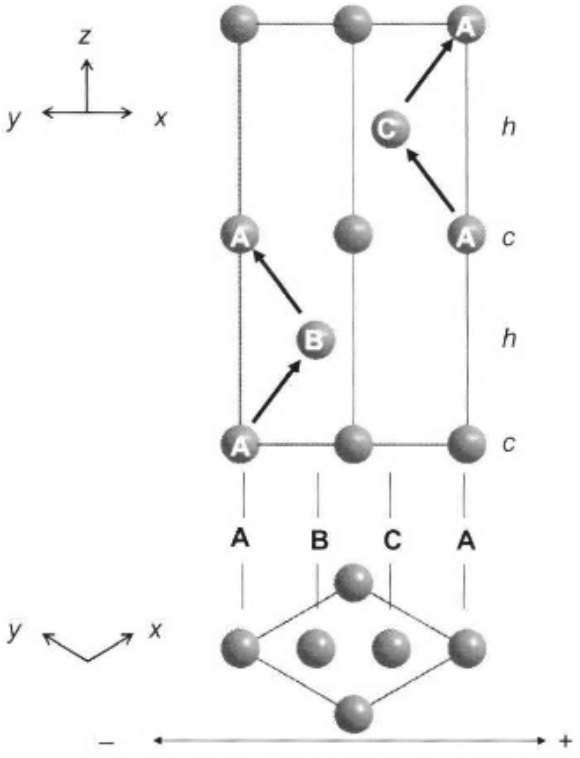


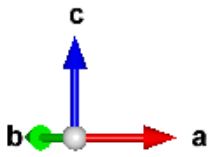
The sodalite cages share hexagonal faces (6-rings) to form a body centered cubic arrangement.

In sodalite the openings to the cages are sufficiently small (6 tetrahedra around the ring, openings of ~2.6 Å) that guest molecules cannot get in or out (not microporous).

Space group: $P\bar{4}3n$
a = 8.875 Å

Na1	8e	0.1777(2)	0.1777(2)	0.1777(2)
Al1	6d	1/4	0	1/2
Si1	6c	1/4	1/2	0
O1	24i	0.1387(3)	0.1484(3)	0.4375(2)
Cl1	2a	0	0	0



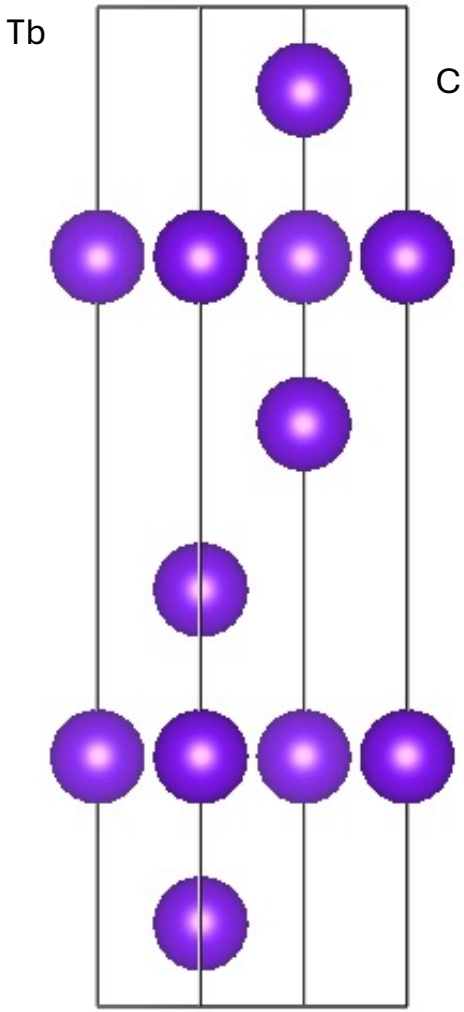


Ramsdell symbol: 4H
Jagodzinski–Wyckoff notation: $(hc)_2$

ICSD #102655
$P6_3/mmc$ (194) hexagonal
a = 3.770, c = 12.159 Å

Atom	Wyck.	x	y	z
La	2a	0	0	0
La	2c	⅓	⅔	¼

Figure 1.22 How to analyze sphere packing in hexagonal structures (α-La shown).



$(hcc)_2$

Generalized 8−N Rule

NaTl

$$VEC_A = \frac{e_C \cdot m + e_A \cdot n}{n}$$

$$VEC_A = \frac{1 \cdot 1 + 3 \cdot 1}{1} = 4$$

$$VEC_A = 8 + CC(^m/_n) - AA$$

$$4 = 8 + CC(^m/_n) - AA$$

$$AA = 4$$

NaTl