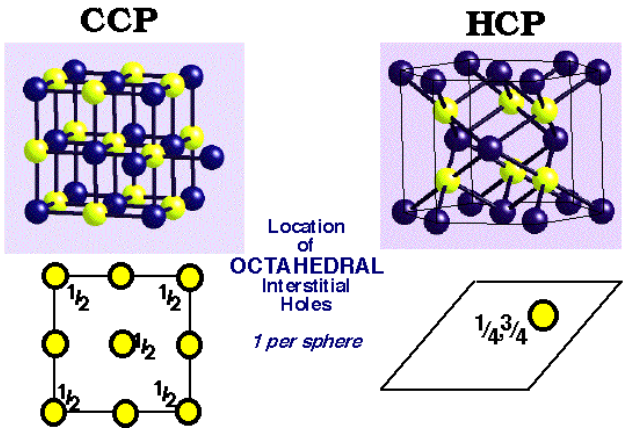
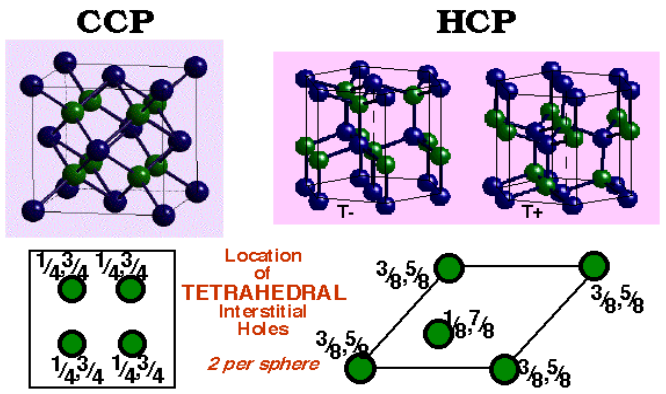


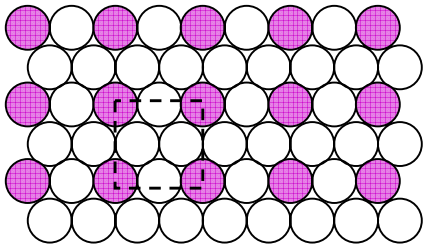


Structure (types) derived from dense closepacking of spheres

Principe:

- **A** Closepacked layers of different types of spheres
- **B** Filling of holes with smaller spheres (octahedra-, tetrahedra-, trig. bipyramidal.- holes)
- **C** Combinations of **A** and **B**

A



$TiAl_3$

$WAl_5 = WAl_3 + Al_2$

B Filling of holes (interstitial possitions)

AB_n M_mX
X = Packing sphere

Filling degree	AB_n	M_mX	Spherepacking ccp		hcp
All octaederholes		AB	MX	NaCl	NiAs
All tetraederholes		AB_2	M_2X	CaF_2	
½ teraederholes	AB	MX	ZnS(bl.)		ZnS(wu.)
½ octaederholes	AB_2	$M_{1/2}X$	$CdCl_2$		$CdI_2[Cd(OH)_2]$
$^1/_3$ octaeerholes	AB_3	$M_{1/3}X$	$CrCl_3$		BiI_3, β-$ZrCl_3$

C Mixed spheres in dense packed layers + filling of interstitial holes

A, B cations
X anion

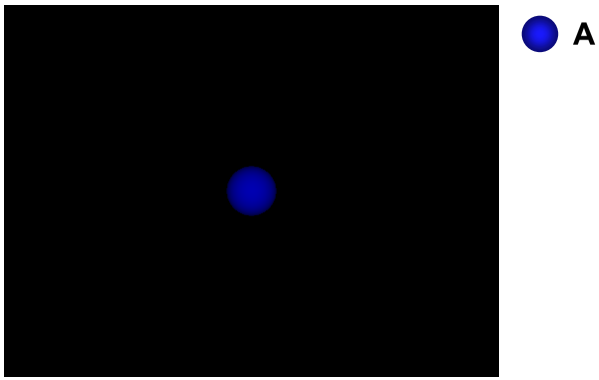
A and X of similar size
B is so small that it fits into octaeder holes

AX_3 densepacked layers

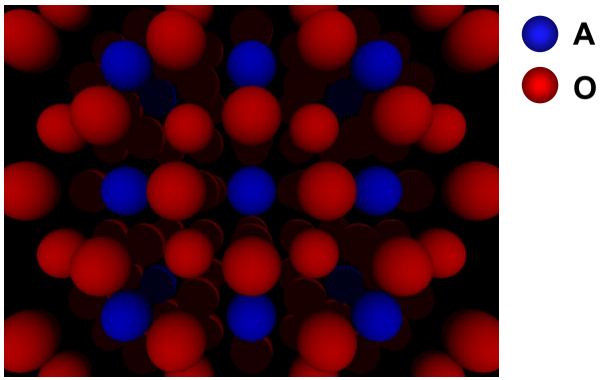
Those octahedra holes with 6 neighbours of X type is filled with B

ABX_3 perovskite type structure

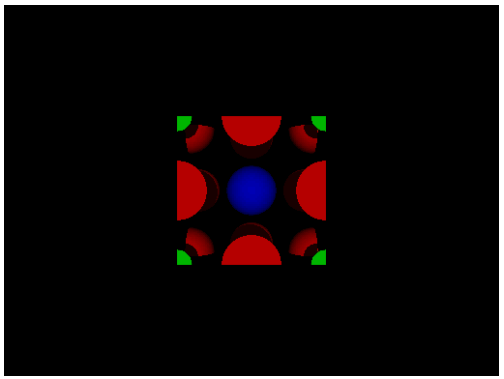
Perovskite



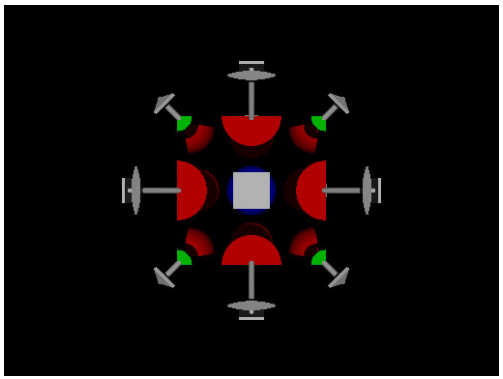
Perovskite



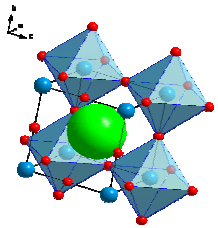
Perovskite



Perovskite



Perovskite



Property	Compound examples
Insulator	$LaGaO_3$, $LaAlO_3$, $LaCrO_3$, $LaFeO_3$
High-K dielectric	$BaTiO_3$, $Ba_2EuZrO_{5.5}$, $CaCu_3Ti_4O_{12}$
Semiconductivity	$LaMnO_3$, $PbCrO_3$, $RTiO_3$ (R = La...Tm)
Half metallicity	$LaBaMn_2O_{5.5}$, $YBaMn_2O_{5.5}$ Sr_2FeMoO_6, Ba_2FeMoO_6, Ca_2FeMoO_6, Ca_2FeReO_6
Metallic conductivity	$LaNiO_3$
Superconductivity	$YBa_2Cu_3O_7$, $HgBa_2CuO_4$, $La_{1.5}Nd_{0.5}CaBa_2Cu_5O_z$, $Bi_2Sr_2Ca_2Cu_3O_{10-d}$, $HgBa_2Ca_2Cu_3O_{8+d}$
Colossal magnetoresistance	$A_{0.3}La_{0.7}MnO_3$ (A = Ca, Sr, Pr, Pb)
Multi ferroics	$BiMnO_3$, $BiFeO_3$,
Ferroelacticity	$LaCoO_3$
Ferromagnetic	$SrRuO_3$, $LaMnO_{3.15}$, $La_{1-x}Ca_xMnO_3$, $Sr_{1-x}LaMnO_3$
Anti ferro	$BiMnO_3$, $LaFeO_3$, $LaMnO_3$
Piezoelectricity	$PbZr_{0.47}Ti_{0.53}O_3$
Spin glass	$CaRuO_3$
Multi valence materials	$Ca_3Co_2O_6$, $Sr_4Fe_4O_{11}$, $YBaMn_2O_{5.5}$

Space filling of polyhedra

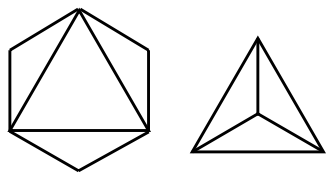
Structures can be described as connections of polyhedra that share:

- **Corners**
- **Edges**
- **Faces**

The polyhedra are simplified for visual clarity.

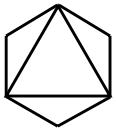
Type of polyhedra:

- **Tetrahedra**
- **Octahedra**
- **Trigonal prismatic**
- **…**



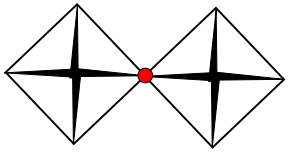
Basically the same types of polyhedra as mention for sphere packing

Limited units, Octahedra



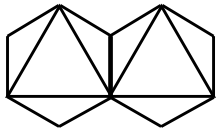
Isolated octahedra

MX_6



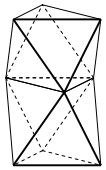
Dimer

M_2X_{11}
$(Nb_2F_{11}^-)$



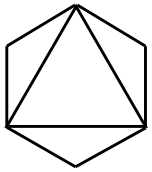
Dimer

M_2X_{10}
(Nb_2Cl_{10})
(U_2Cl_{10})



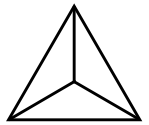
Dimer

M_2X_9
$(Fe_2(CO)_9)$
$(I_2O_9^{4-})$



Octahedra

Connected by:
Corners
Edges
(Faces)

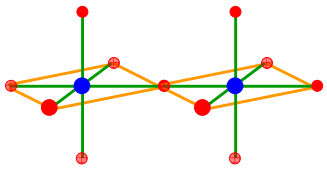


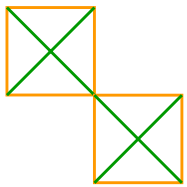
Tetrahedra

Connected by:
Corners
(Edges)

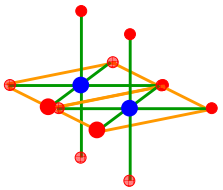
How these units connect will affect the chemical composition, and vice versa.

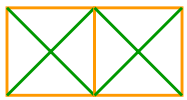
Polymerization of MX_6 octahedra



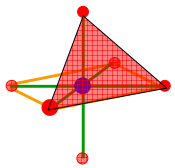


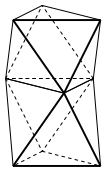
Corner sharing:
d(M-M) = 2*d(M-X)





Edge sharing:
d(M-M) = √2*d(M-X)





Face sharing:
d(M-M) = 1.16*d(M-X)

Calculation of interatomic distances in some simple structures

Structure type	Distance	Number of such distances	Magnitude of separation in terms of unit cell dimensions
Rock salt (cubic)	Na–Cl	6	$a/2 = 0.5a$
	Cl–Cl	12	$a/\sqrt{2} = 0.707a$
	Na–Na	12	$a/\sqrt{2} = 0.707a$
Zinc blende (cubic)	Zn–S	4	$a\frac{\sqrt{3}}{4} = 0.433a$
	Zn–Zn	12	$a/\sqrt{2} = 0.707a$
	S–S	12	$a/\sqrt{2} = 0.707a$
Fluorite (cubic)	Ca–F	4 or 8	$a\frac{\sqrt{3}}{4} = 0.433a$
	Ca–Ca	12	$a/\sqrt{2} = 0.707a$
	F–F	6	$a/2 = 0.5a$
Wurtzite* (hexagonal)	Zn–S	4	$a\sqrt{\frac{3}{8}} = 0.612a = \frac{3c}{8} = 0.375c$
	Zn–Zn	12	$a = 0.612c$
	S–S	12	$a = 0.612c$
Nickel arsenide* (hexagonal)	Ni–As	6	$a/\sqrt{2} = 0.707a = 0.433c$
	As–As	12	$a = 0.612c$
	Ni–Ni	2	$c/2 = 0.5c = 0.816a$
	Ni–Ni	6	$a = 0.612c$
Cesium chloride (cubic)	Cs–Cl	8	$a\frac{\sqrt{3}}{2} = 0.866a$
	Cs–Cs	6	a
	Cl–Cl	6	a
Cadmium iodide (hexagonal)	Cd–I	6	$a/\sqrt{2} = 0.707a = 0.433c$
	I–I	12	$a = 0.612c$
	Cd–Cd	6	$a = 0.612c$

*These formulae do not necessarily apply when c/a is different from the ideal value of 1.633.

Infinite structures built from octahedral AX_6 groups

Vertices only shared — HJØRNER

2 AX_5 chains:
cis: VF_5, CrF_5
trans: BiF_5, $(CrF_5)^{2-}$, α-UF_5

4 AX_4 layers:
cis: $BaMnF_4$
trans: SnF_4, K_2NiF_4

6 AX_3 frameworks:
ReO_3, $Sc(OH)_3$,
FeF_3 etc.,
Perovskite,
W bronzes,
pyrochlore

Vertices and edges shared — H + K

AX_3, A_3X_8, A_2X_5 layers (V oxyhydroxides)
AX_2 frameworks
Rutile structure
α-AlO . OH
Eu_3O_4
$CaTi_2O_4$
α-MnO_2
BeY_2O_4
(Table 5.5)
AX_3 layer: MoO_3
AX_3 framework: $CaTa_2O_6$

Edges only shared — KANTER

2 AX_4 chains: $TeCl_4$, NbI_4
3 AX_3 layer: YCl_3, BiI_3
4 AX_3 double chain: NH_4CdCl_3
AX_3 layer: NH_4HgCl_3
A_3X_8 layer: Nb_3Cl_8
6 AX_2 layer: CdI_2, $CdCl_2$
AX_2 double layer: MOCl, γ-MO . OH
AX_2 framework: $Cu_2(OH)_3Cl$

Vertices, edges, and faces shared

α-Al_2O_3 (corundum)
γ-$Cd(OH)_2$

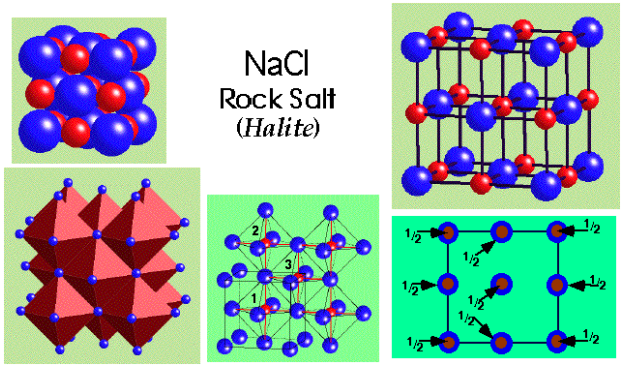
Vertices and faces shared

ABO_3 structures: hexagonal $BaTiO_3$; high-$BaMnO_3$, $BaRuO_3$ (Table 5.6)

Faces and edges shared
Nb_3S_4

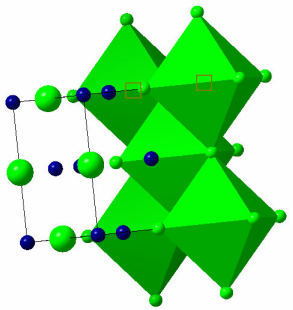
Faces only shared — FLATER

2 AX_3 chain: ZrI_3, Ba NiO_3, Cs $NiCl_3$

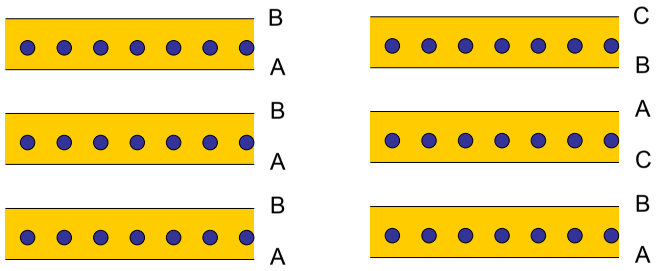


CCP Cl- with Na+ in all Octahedral holes
Lattice: fcc
Motif: Cl at (0,0,0); Na at (1/2,0,0)
4NaCl in unit cell
Coordination: 6:6 (octahedral)
Cation and anion sites are topologically identical

NaCl
$NaCl_6$, $ClNa_6$



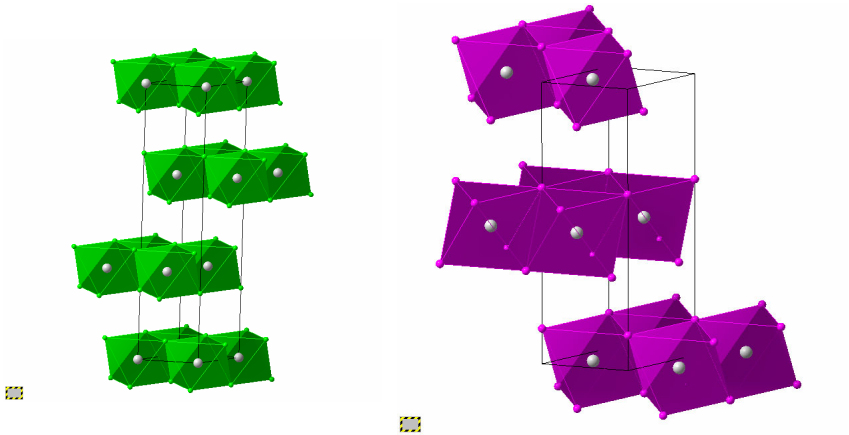
$CdCl_2$ / CdI_2 type structures



Within the layers: CdX_6-octahedra
Between the layers: only van der Waals interactions

Polytypes:
in 2-dimensions -> same structure with strong bonds
different repetition in the 3rd direction, can have week bonds

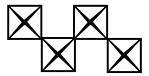
$CdCl_2$ CdI_2



Infinite systems; octahedra by cornersharing

Number of corners shared in a given octahedra:
2, (3), 4, (5), 6

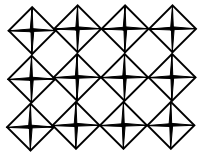
AX_5 chains: (cis-, trans-)



cis- VF_5

trans- BiF_5

AX_4 layers:



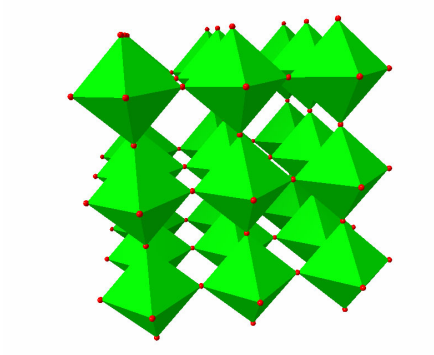
SnF_4
K_2NiF_4

AX_3 3D network:

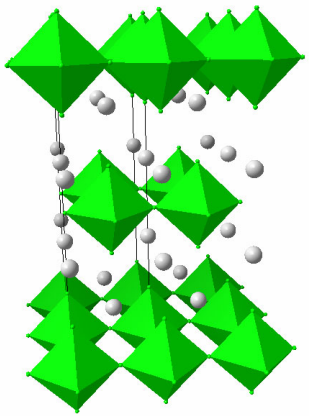
ReO_3
FeF_3

ABX_3 perovskite

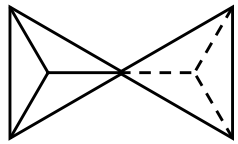
ReO_3



K_2NiF_4

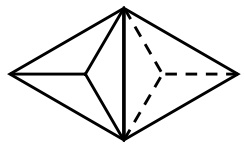


Polymerization of MX_4 tetrahedra

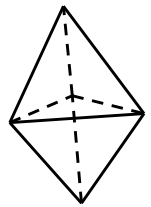


Corner sharing:
d(M-M) = 2*d(M-X)

2.0 only observed for SiO_4
Si^{4+} - Si^{4+} repulsions



Edge sharing:
d(M-M) = 1.16*d(M-X)



Face sharing:
d(M-M) = **0.67***d(M-X)

Structures based on tetrahedas

Vertices only shared, Vertices common to two tetrahedra

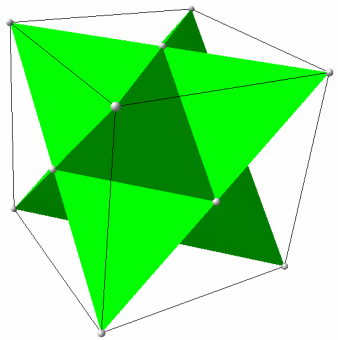
No. shared vertices	Formula	Type of complex	Examples
1	A_2X_7	Finite molecule or pyro ion	Cl_2O_7, $S_2O_7^{2-}$, etc.
2	$(AX_3)_n$	Cyclic molecule, or meta-ion infinite chain	S_3O_9, Se_4O_{12}, $(PNCl_2)_n$ $(P_4O_{12})^{4-}$, $(Si_3O_9)^{6-}$, $(SO_3)_n$, $(PO_3)_n^{n-}$
3	$(A_2X_5)_n$	Finite polyhedral, double chain, layer or 3D structure	P_4O_{10} $Al[AlSiO_5]$ P_2O_5, $Li_2Si_2O_5$ P_2O_5, $La_2[Be_2O_5]$
4	$(AX_2)_n$	Layer, double layer, or 3D structure	HgI_2 (red) $CaSi_2Al_2O_8$ (hexag.) SiO_2 structures, GeS_2
		Vertices common to three tetrahedra	
3	$(AX_2)_n$	Infinite layer	AlOCl, GaOCl

Structures based on tetrahedas

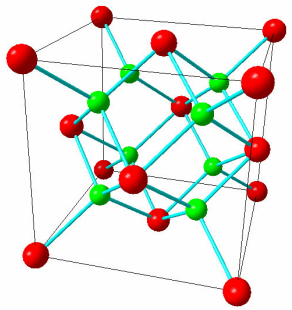
Edges only shared, Edges common to two tetrahedra

No. shared edges	Formula	Type of complex	Examples
1	A_2X_6	Finite dimer	Al_2Cl_6, Fe_2Cl_6
2	$(AX_2)_n$	Infinite chain	$BeCl_2$, SiS_2, $Be(CH_3)_2$
3	$(A_2X_3)_n$	Infinite double chain	$Cs(Cu_2Cl_3)$
4	$(AX)_n$	Infinite layer	LiOH, PbO
6	$(A_2X)_n$	3D structures	Li_2O, F_2Ca
		Vertices and edges shared	
	$(AX)_n$	Double layer	La_2O_3, Ce_2O_2S, U_2N_2Sb
	$(AX)_n$	3D structure	β-BeO

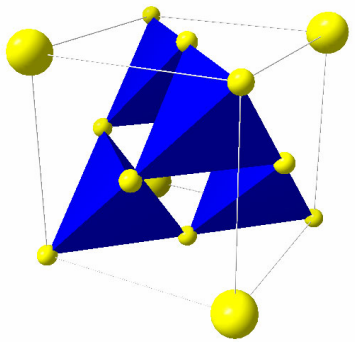
CaF_2
FCa_4 - tetraheda



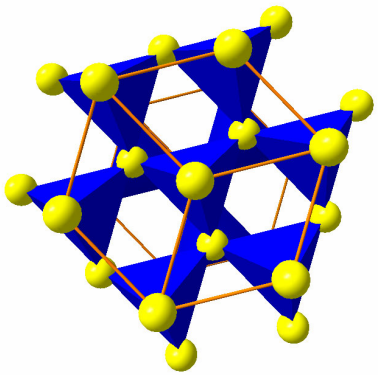
Na_2O
NaO_4 - tetraheda

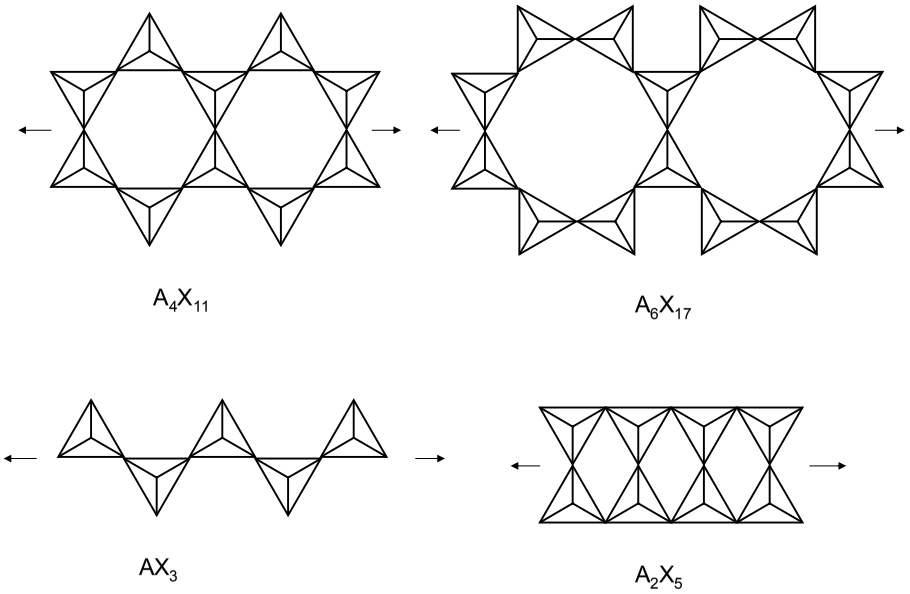


Sink blende
ZnS_4, SZn_4



Wurtsitt
ZnS_4, SZn_4





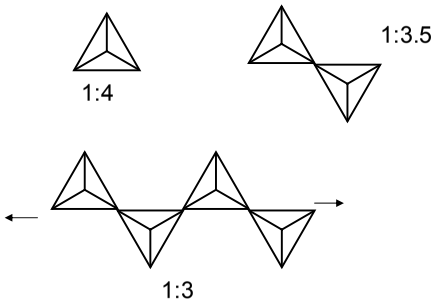
Silicates:

SiO_4 tetrahedas

Corner (vertice) sharing, never edge or face (too strong Si^{4+}-Si^{4+} repulsions)

Only two SiO4 tetrahedra share a common corner

Bridging oxygens count ½
Non-bridging count 1



Rings	1:3
Double rings	1:2.5
Layer	1:2.5
Double layer	…
3D	1:2

Relation between chemical formula and silicate anion structure.

Si:O ratio	Number of oxygens per Si: bridging	non-bridging	Type of silicate anion	Examples
1:4	0	4	isolated SiO_4^{4-}	Mg_2SiO_4 olivine, Li_4SiO_4
1:3.5	1	3	dimer $Si_2O_7^{6-}$	$Ca_3Si_2O_7$ rankinite, $Sc_2Si_2O_7$ thortveite
1:3	2	2	chains $(SiO_3)_n^{2n-}$	Na_2SiO_3, $MgSiO_3$ pyroxene
			rings, eg $Si_3O_9^{6-}$	$CaSiO_3$*, $BaTiSi_3O_9$ benitoite
			$Si_6O_{18}^{12-}$	$Be_3Al_2Si_6O_{18}$ beryl
1:2.5	3	1	infinite sheets $(Si_2O_5)_n^{2n-}$	$Na_2Si_2O_5$
1:2	4	0	3D framework	SiO_2†

* $CaSiO_3$ is dimorphic. One polymorph has $Si_3O_9^{6-}$ rings. The other polymorph has infinite $(SiO_3)_n^{2n-}$ chains.
† The three main polymorphs of silica, quartz, tridymite and cristobalite each have a different kind of 3D framework structure.

ZnS

Structural polymorphs:

Zink blende **Stable at normal P,T**
Wurstitt **Stable at T > 1020 °C at P = 1 atm**

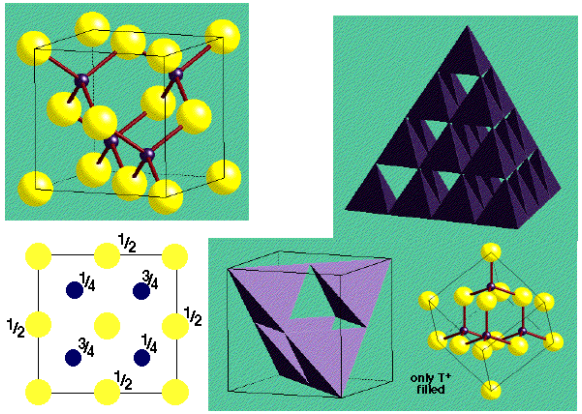
Metastable at RT, but transforms by crushing

Thermodinamics
Kinetics

Zink blende
ccp
½ tetraedra holes filled

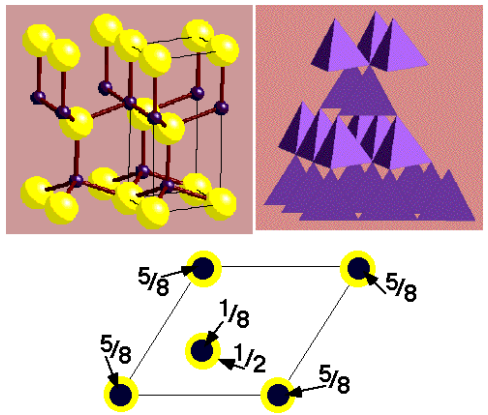
Wurstitt
hcp
½ tetraedra holes filled

ZnS *Zinc Blende* (*Sphalerite*)



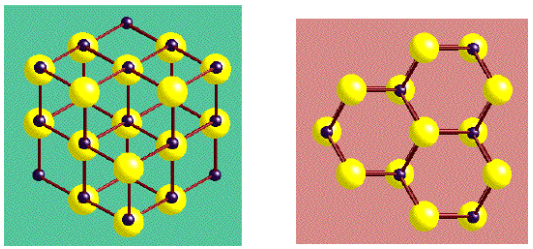
CCP S^{2-} with Zn^{2+} in half Tetrahedral holes (only T+ {or T-} filled)
Lattice: fcc
4ZnS in unit cell
Motif: S at (0,0,0); Zn at (1/4,1/4,1/4)
Coordination: 4:4 (tetrahedral)
Cation and anion sites are topologically identical

ZnS *Wurtzite*



HCP S2- with Zn2+ in half Tetrahedral holes (only T+ {or T-} filled)
Lattice: Hexagonal - P
a = *b*, *c* Å Ã(8/3)*a*
Motif: 2S at (0,0,0) & (2/3,1/3,1/2); 2Zn at (2/3,1/3,1/8) & (0,0,5/8)
2ZnS in unit cell
Coordination: 4:4 (tetrahedral)

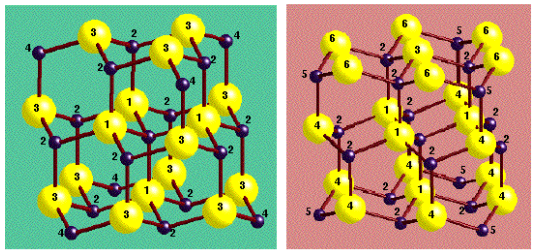
PLAN VIEWS



Zinc Blende **Wurtzite**

CCP ABC repeat *HCP AB repeat*

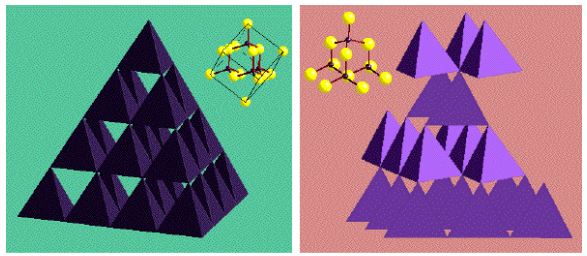
COORDINATION ENVIRONMENTS



Zinc Blende Wurtzite

4 Nearest Neighbours (***Tetrahedral***)
12 Next-Nearest Neighbours
Cuboctahedral ***Anti-Cuboctahedral***
Very different Next, Next-Nearest Neighbour Coordinations & beyond

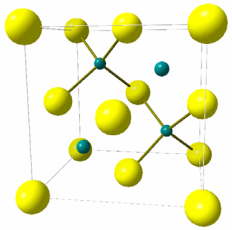
POLYHEDRAL REPRESENTATIONS



Zinc Blende Wurtzite

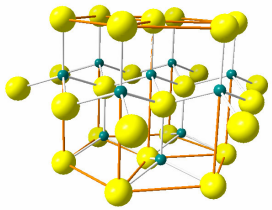
Vertex-linked tetrahedra only, but layers skewed in Wurtzite, & not in Blende

Zink-blende



ZnS_4 –tetrahedra
Diamond type structure if Zn = S
Non-centrosymmetric

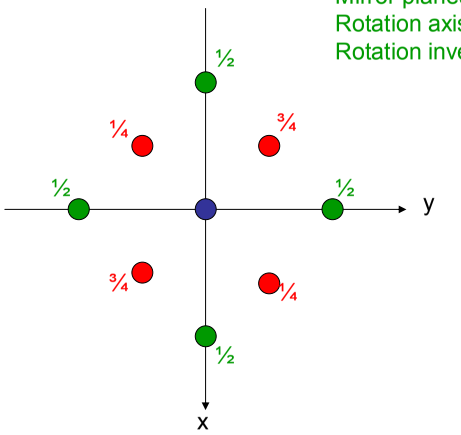
Wurtsitt



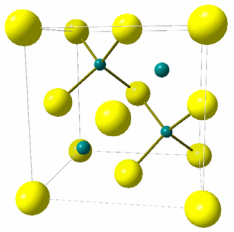
ZnS_4 –tetrahedra of + type

Point symmetry

S in (0,0,0)



Check for:
Inversion
Mirror planes
Rotation axis
Rotation inversion axis



Cubic crystal system: Xabc
a = along <100>
b = along <111>
c = along <110>

a) 2, -2, 4, -4 ?
b) 3, -3 ?
c) 2, -2 (=m) ?

-43m

ZnS – würtsitt

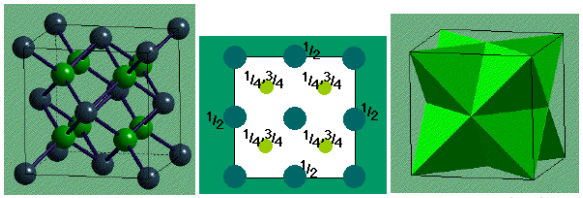
Z = 2 pr. hexagonal unit cell

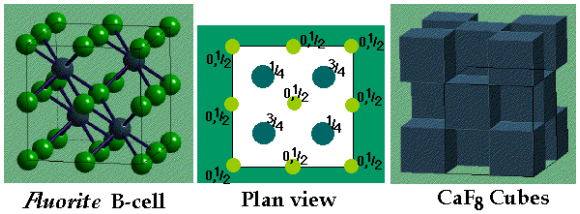
Other related structures:

MX	**ZnO**
$MM'X_2$	**$LiGaO_2$**
$M_2M'M''X_4$	**Li_2BeSiO_4**
	$LiPO_4$
	…

Polymorph		ZnS (blende), ZnS (wurtsitt)		
Allotrope modifications		Diamond, graphite, C_{60})		
Polytypes		$CdCl_2$, CdI_2		
…ABC…	vs.	…AB…		
…ABCA…	vs.	…ABAC…	vs.	…AVACB…

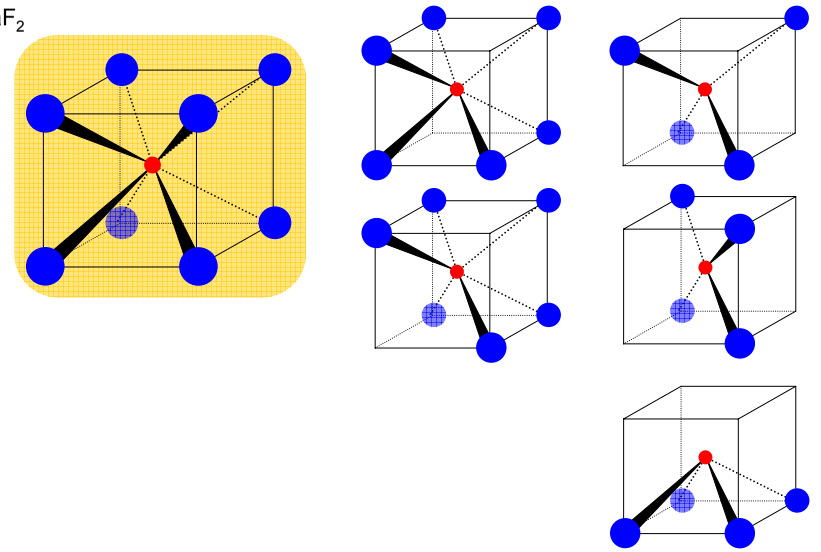
?

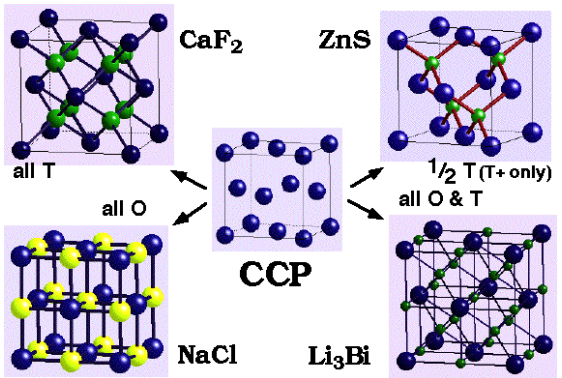




CCP Ca2+ with F- in all Tetrahedral holes
Lattice: fcc
Motif: Ca2+ at (0,0,0); 2F- at (1/4,1/4,1/4) & (3/4,3/4,3/4)
4CaF2 in unit cell
Coordination: Ca2+ 8 (cubic) : F- 4 (tetrahedral)
In the related Anti-Fluorite structure Cation and Anion positions are reversed

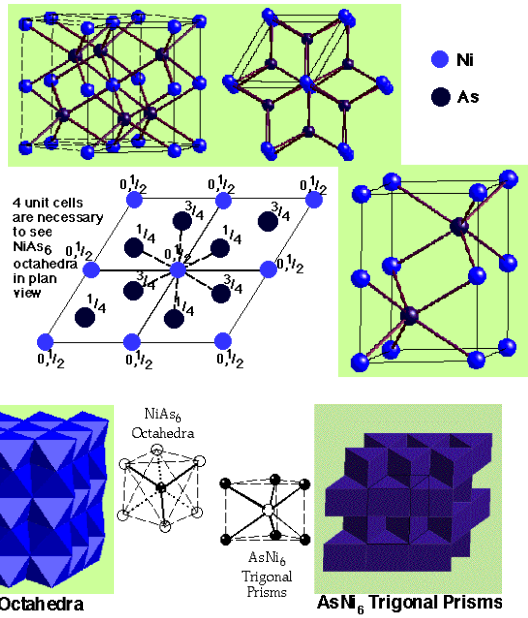
CaF_2



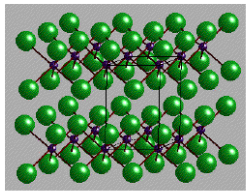


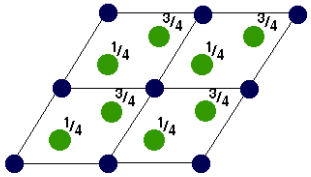
NiAs *Nickel Arsenide*

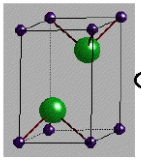
HCP As with Ni in all Octahedral holes
Lattice: Hexagonal - P
a = *b*, *c* Å Ã(8/3)*a*
Motif: 2Ni at (0,0,0) & (0,0,1/2)
2As at (2/3,1/3,1/4) &
(1/3,2/3,3/4)
2NiAs in unit cell
Coordination: Ni 6 (octahedral) :
As 6 (trigonal prismatic)



CdI2 *Cadmium Iodide*

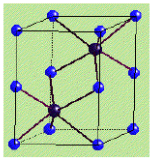


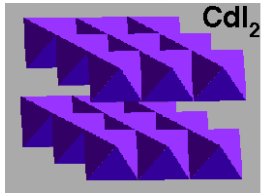


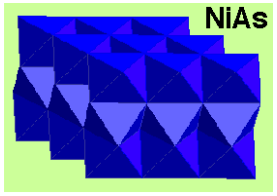


Comparison

CdI_2 *vs* NiAs

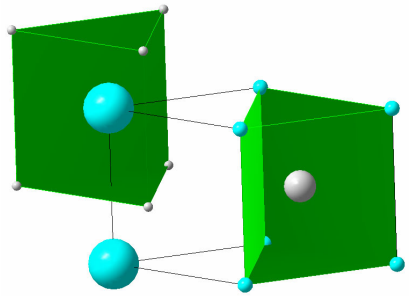




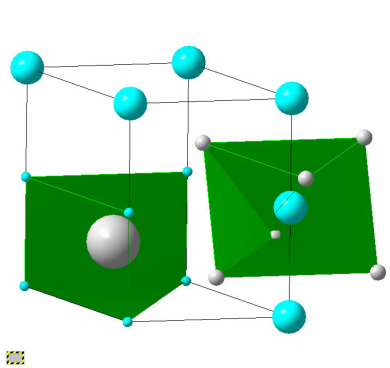


Lattice: Hexagonal - P
Motif: Cd at (0,0,0); 2I at (2/3,1/3,1/4) & (1/3,2/3,3/4)
1CdI2 in unit cell
Coordination: Cd - 6 (Octahedral) : I - 3 (base pyramid)

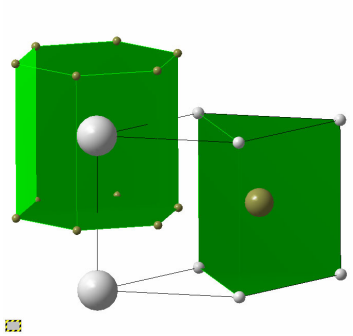
WC
WC_6, CW_6 trigonal prismatic



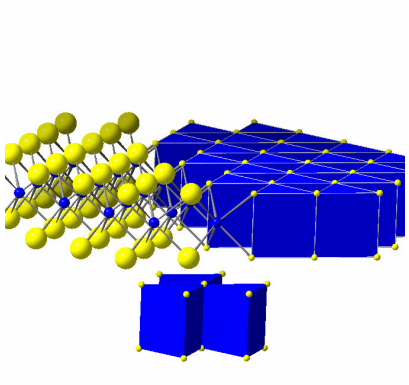
NiAs
$NiAs_6$ octahedra
$AsNi_6$ trigonal prismatic



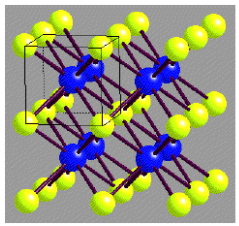
AlB_2
AlB_{12} hexagonal prismatic
BAl_6 trigonal prismatic

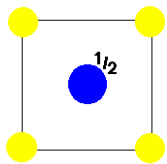


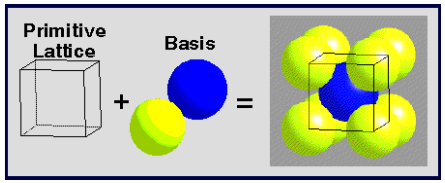
MoS_2
SMo_3 trigonal pyramid
MoS_6 trigonal prismatic



CsCl *Cesium Chloride*

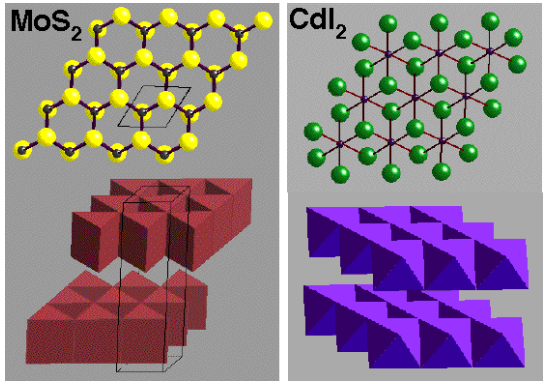






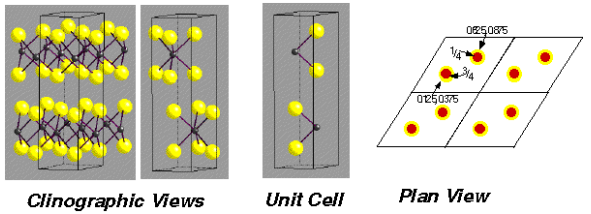
- *Lattice*: Cubic - P (N.B.**Primitive!**)
- *Motif*: Cl at (0,0,0); Cs at ($^1/_2$,$^1/_2$,$^1/_2$)
- **1**CsCl in unit cell
- *Coordination*: 8:8 (cubic)
- Adoption by chlorides, bromides and iodides of larger cations, *e.g.* Cs^+, Tl^+, NH_4^+

MoS2 *Molybdenite*



Note: Hexagonal layers of S atoms are **NOT** Close-packed in 3D
Lattice: Hexagonal - P
Motif: 2Mo at (2/3,1/3,3/4) & (1/3,2/3,1/4)
4I at (2/3,1/3,1/8), (2/3,1/3,3/8), (1/3,2/3,5/8) & (1/3,2/3,7/8)
2MoS2 in unit cell
Coordination: Mo 6 (**Trigonal Prismatic**) : S 3 (base pyramid)

MoS2 *Molybdenite*



Clinographic Views *Unit Cell* *Plan View*