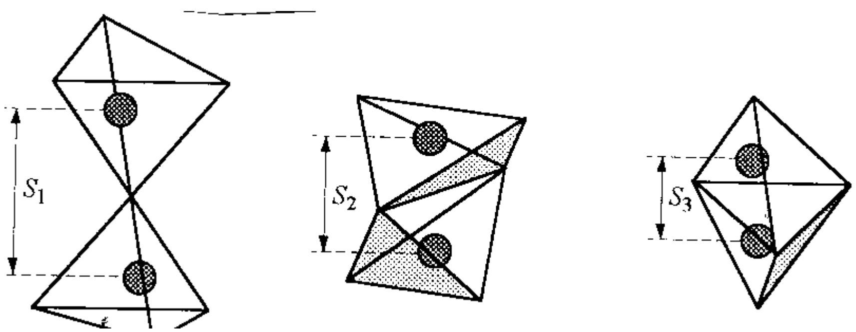
Lecture 2

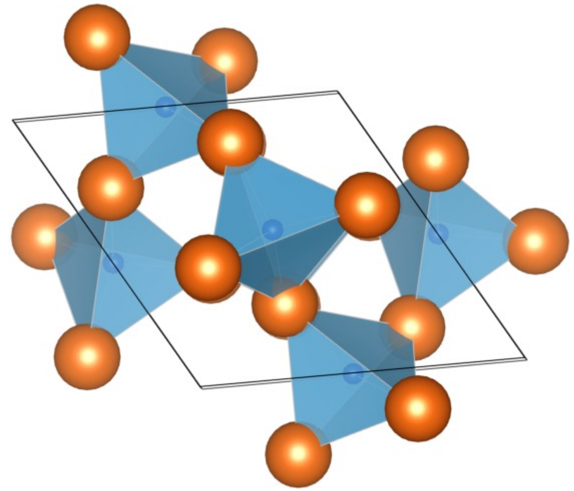
- Pauling rules, bonding and structures - continuation
- Simple crystalline structures – important examples
- Crystalline symmetry
- Macroscopic crystalline symmetry & point groups
- Point groups and real structures

Pauling rules -3, 4, 5

- **Rule 3:** The bond is strongest when coordination polyhedra share corners, less stable when they share edges, and least stable when they share faces.

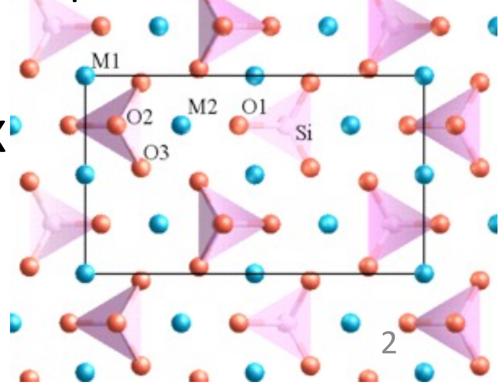


Why?



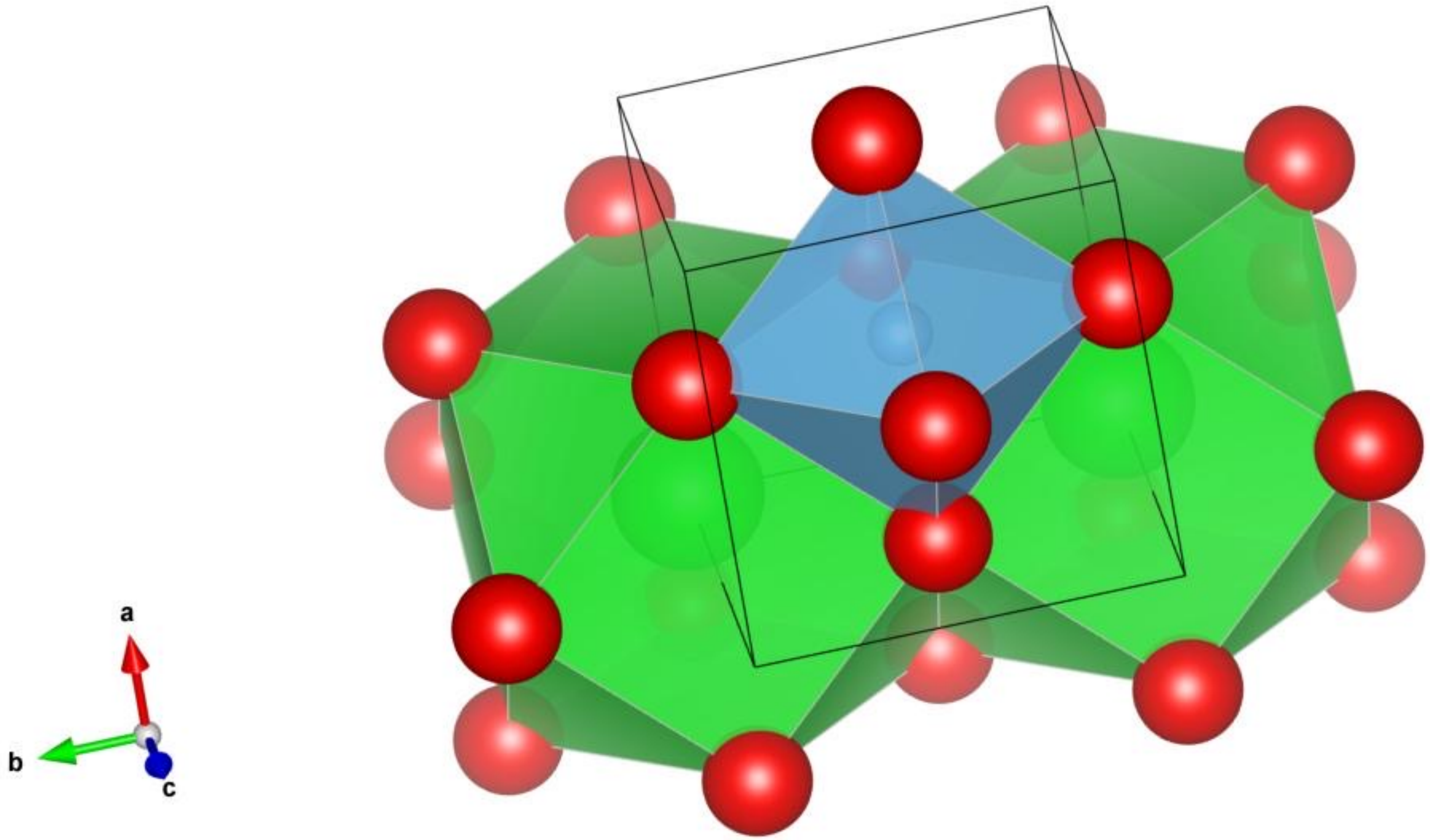
- **Rule 4:** Coordination polyhedra of small cations with large charge tend to share corners (or not share any elements: olivine $(Mg,Fe)_2SiO_4$)

- **Rule 5:** Simpler structures are more likely than complex (the rule of parsimony)



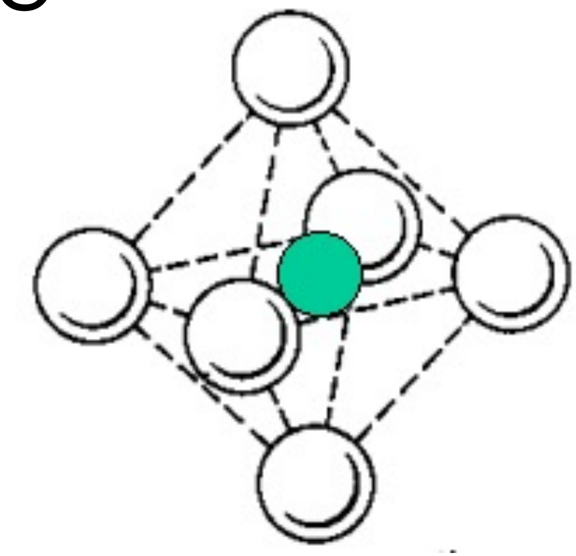
Polyhedra sharing – Rules 3 and 4

$BaTiO_3$, perovskite structure



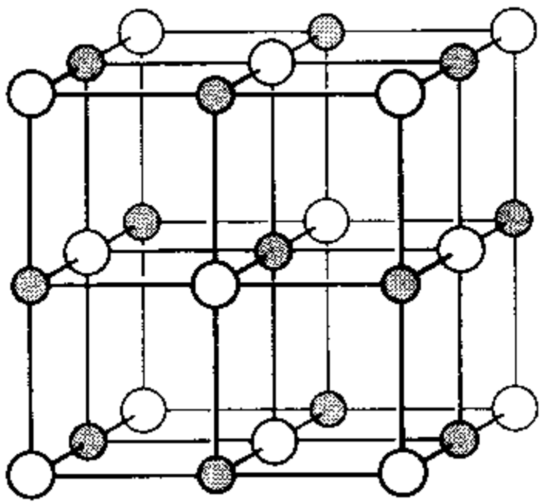
Ti^{+4} is small, heavily charges, and corresponding polyhedra share corners
- Compare this to Ba^{+2}

Pauling rules - MgO



For MgO:
rMg+2 = 0.86Å, rO = 1.26Å
rMg+2/rO = 0.86/1.26 = 0.68 --> CN(Mg)= 6 for Mg2+
Bonding force around Mg+ 2: +2 / 6=1/3
Oxygen CN: CN(O) x 1/3 + (-2) = 0 --> CN(O) = 6

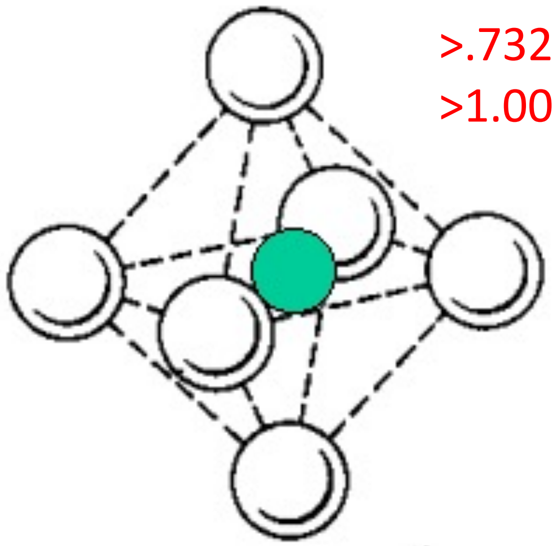
Are other Pauling rules obeyed?



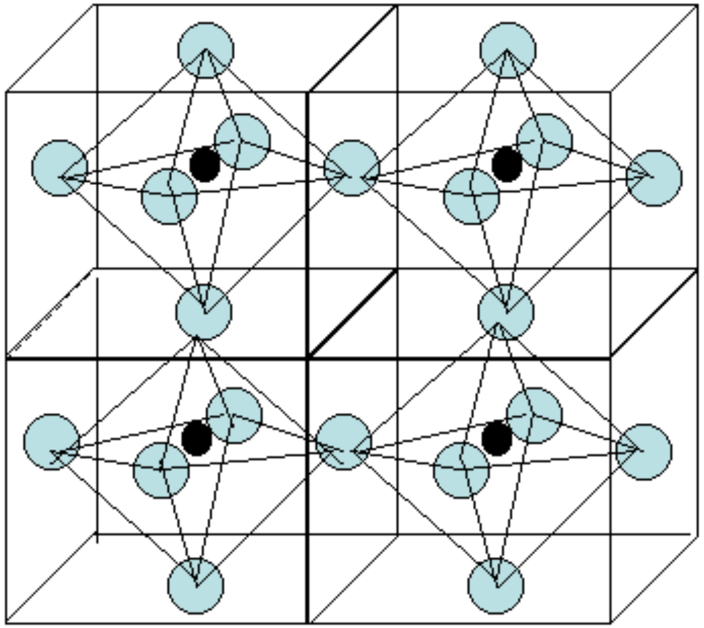
- What is the structure based on rules 1 and 2?

R/ NC
>.225 4
>.414 6
>.732 8
>1.00 12

Pauling rules – ReO_3



For ReO3:
rRe+6 = 0.76Å, rO = 1.26Å
rRe+6/rO = 0.77/1.26 = 0.61 --> CN(Re)= 6 for Re+6 $Re^{VI}O^{II}3$
Bonding force around Re+6: +6 / 6=1
Oxygen CN(O): CN(O) x1 + (-2) = 0 --> CN(O) = 2
Which type of coordination for O?
Each O is connected to 2 Re i.e. each O is the bridge between two octahedra.



Are other Pauling rules satisfied?
- Corners of octahedra are shared

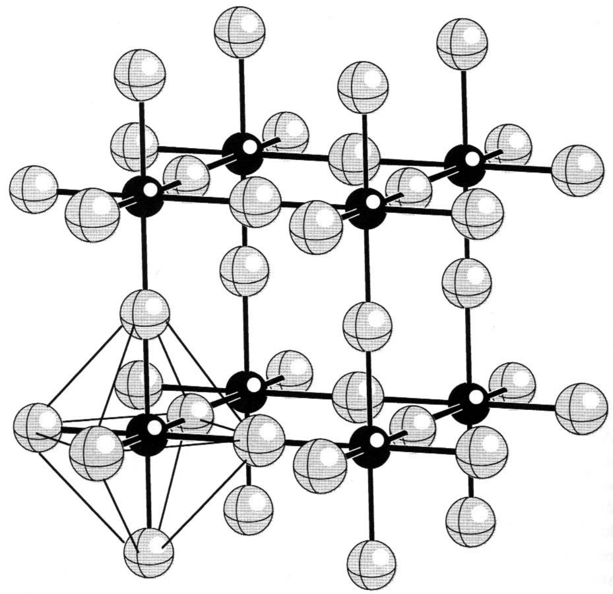


Figure 10.9. The structure of ReO_3. The Re are the smaller black spheres. The fact that Re is octahedrally coordinated and O is in two-fold coordination was deduced from Pauling's first two rules.

Pauling rules for structures with two cations -example of $BaTiO_3$

- Apply Pauling rules to determine coordination numbers (CN) for all ions in $BaTiO_3$. Specify coordination numbers of the anions to each cation.

- We start by finding radii of all ions.

Recommendation: use the table composed after Shannon and Prewitt from the previous lecture,

Pauling rules for structures with two cations
-example of BaTiO3-

We recall conditions for coordination of cation with respect to near-neighbor anions, which is given by:

r_{cation}/r_{anion}	CN(cation)
>.225	4
>.414	6
>.732	8
>1.00	12

CN(Ba)= 12

CN(Ti)= 6

Pauling rules for structures with two cations -example of $BaTiO_3$-

We now need to find coordination number of oxygen, CN(O).

For this we use Pauling second rule. <u>When there are two cations around oxygen, then the rule refers to both cations considered together:</u>

$CN(O)_{Ba}$*(Bond strength around Ba)+ $CN(O)_{Ti}$*(Bond strength around Ti) =absolute value of charge (valence) of oxygen.

We first find bond strengths for the cations:
For Ba: Bond strength around Ba=(valence of Ba)/CN(Ba)=2/12=1/6
For Ti: Bond strength around Ti=(valence of Ti)/CN(Ti)=4/6=2/3

Pauling rules for structures with two cations
-example of BaTiO3-

We get:

$CN(O)_{Ba}$ *(Bond strength around Ba)+ $CN(O)_{Ti}$*(Bond strength around Ti)= absolute value of charge of oxygen --->

$CN(O)_{Ba}$ *(1/6)+ $CN(O)_{Ti}$*(2/3)=2

This gives: $CN(O)_{Ba}$ =4, $CN(O)_{Ti}$=2

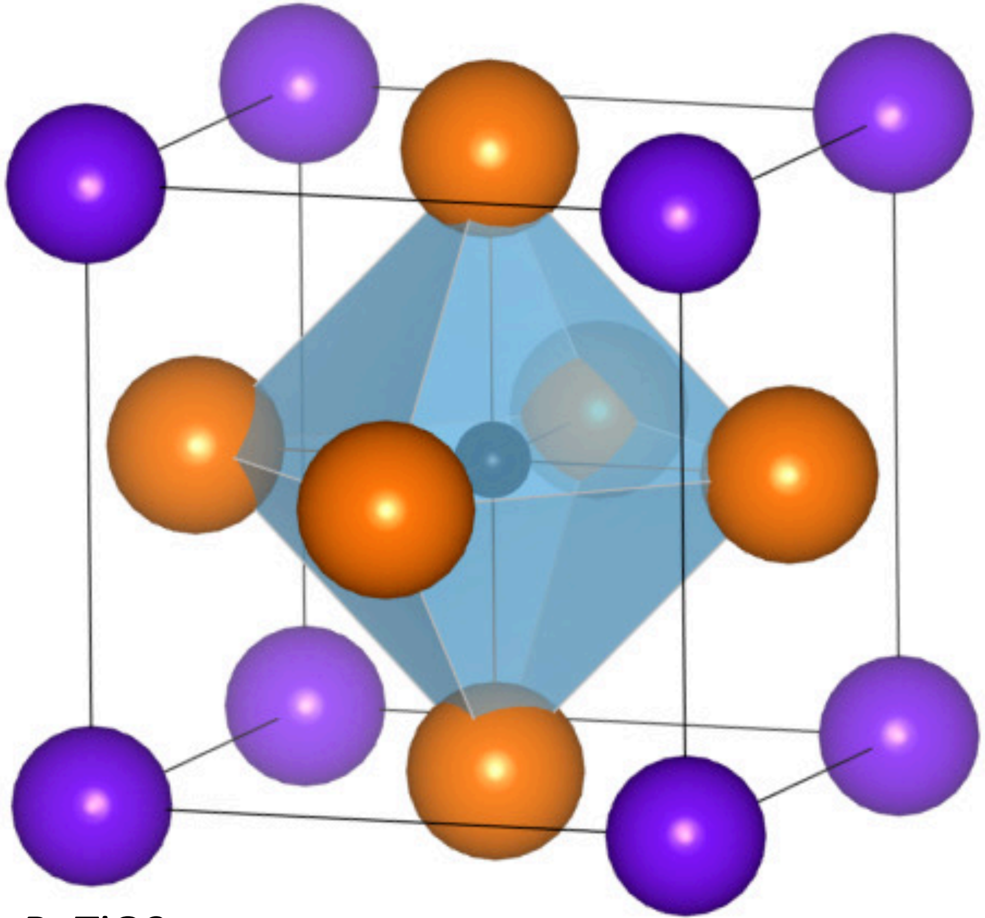
Therefore, each O anion is linked to 2 Ti ions, and 4 Ba ions. We write:

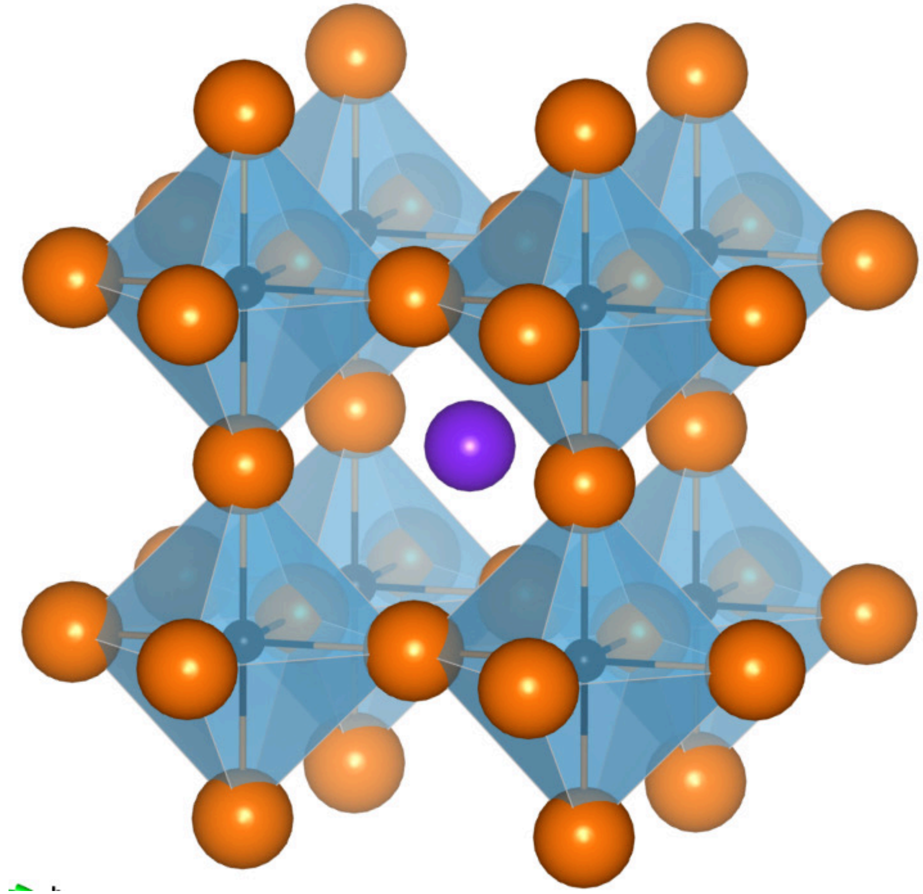
$$Ba^{XII}Ti^{VI}O_3^{II+IV} \rightarrow Ba^{XII}Ti^{VI}O_3^{VI}$$

$BaTiO_3$ perovskite structure

Check coordination numbers for oxygen:

$CN(O)_{Ba} = 4$, $CN(O)_{Ti} = 2$





BaTiO3
Black:Ti; orange: O; Purple: Ba

Pauling rules
-coordination number check-

- Taking $A_a^{CN(A)} B_b^{CN(B)} X_x^{CN(X)}$

where X is an anion, and A and B are cations, then:

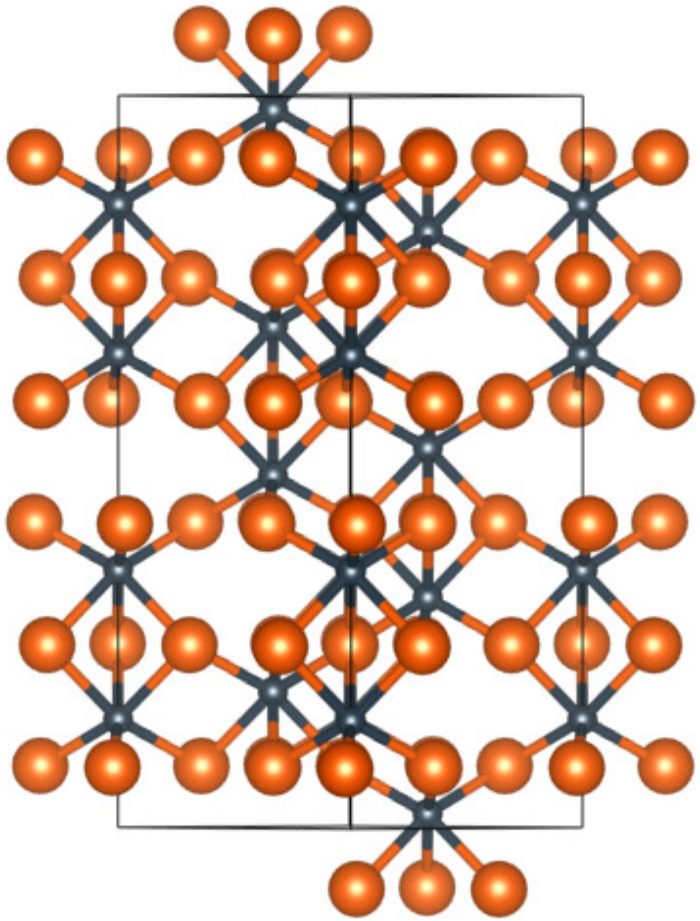
$$aCN(A) \quad + bCN(B) = xCN(X)$$

For BaTiO3:

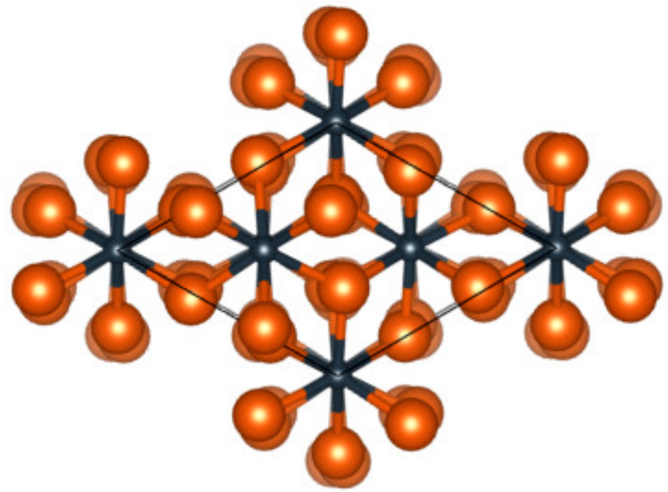
Check that the ratio between ions of different kinds is respected

$Ba^{XII} Ti^{VI} O_3^{VI}$ → 1*12+1*6=3*6

Pauling rules – limitations - comment on sharing of polyhedra example: Al_2O_3 (corundum, alumina)

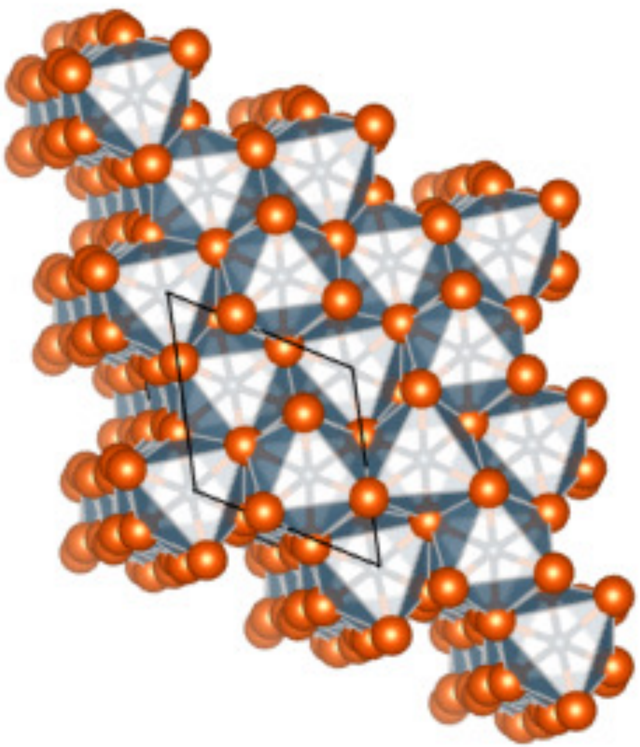


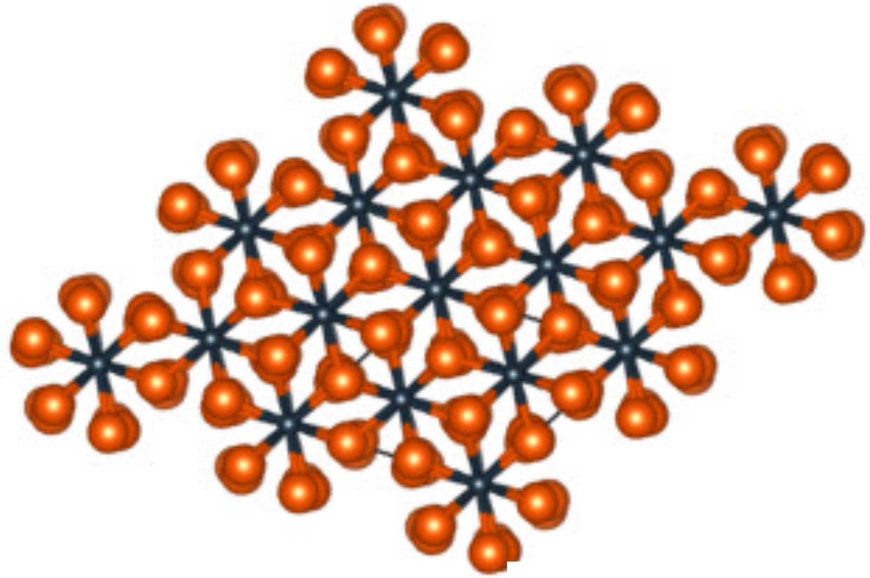
Unit cell view
Orange: O; Black: Al
Edge-shared octahedra
(we expect is shares corners rather than edges)



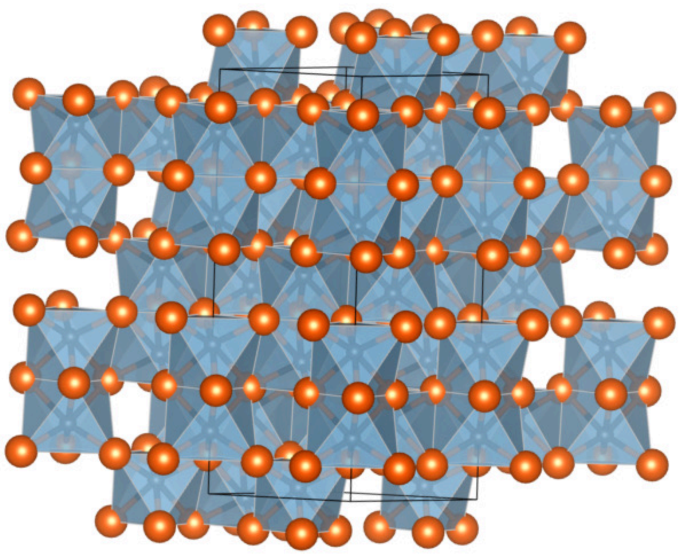
HCP, 2/3 of octahedral sites are filled, primitive trigonal, distorted tetrahedron

Pauling rules – comment on sharing of polyhedra example: Al_2O_3 (corundum, alumina)

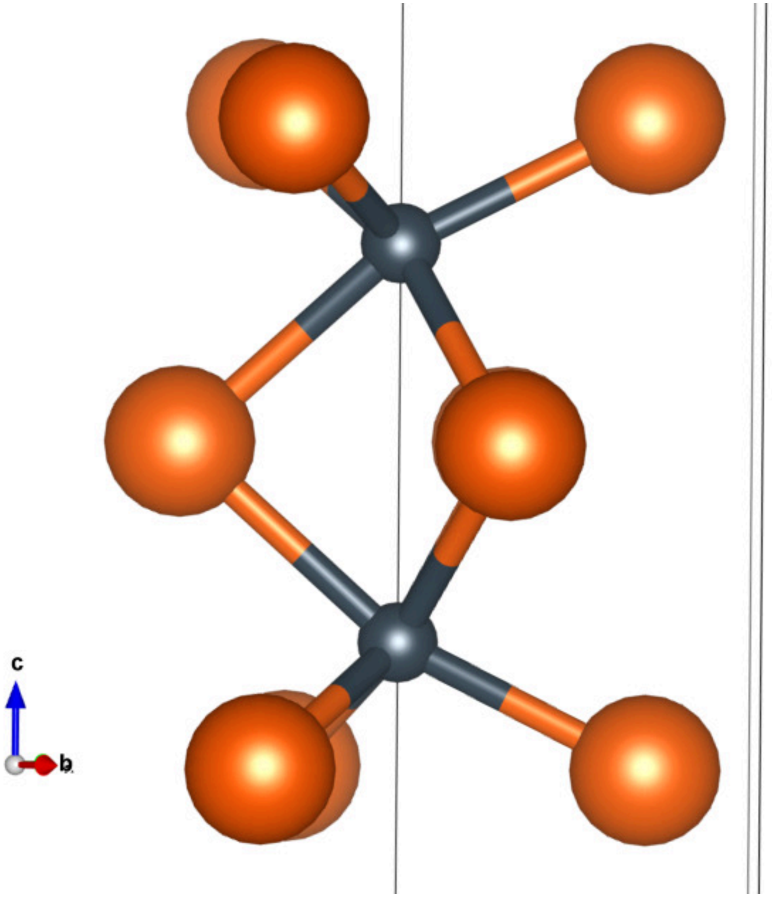


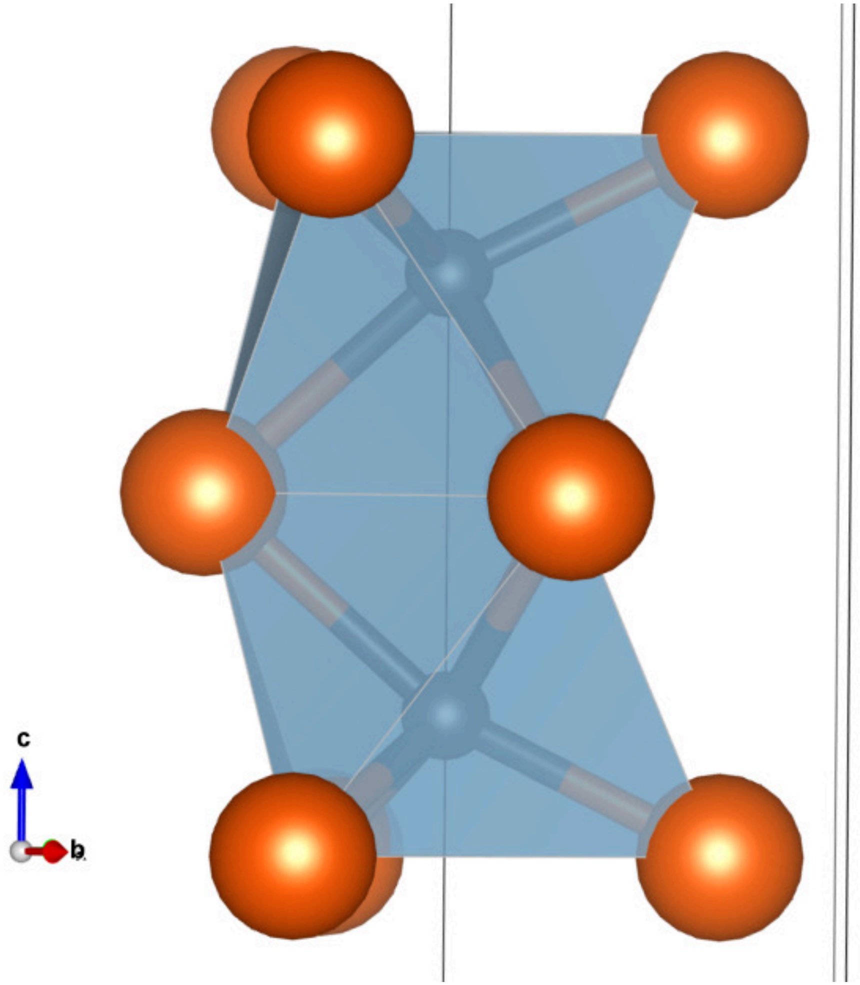


Side-sharing octahedra



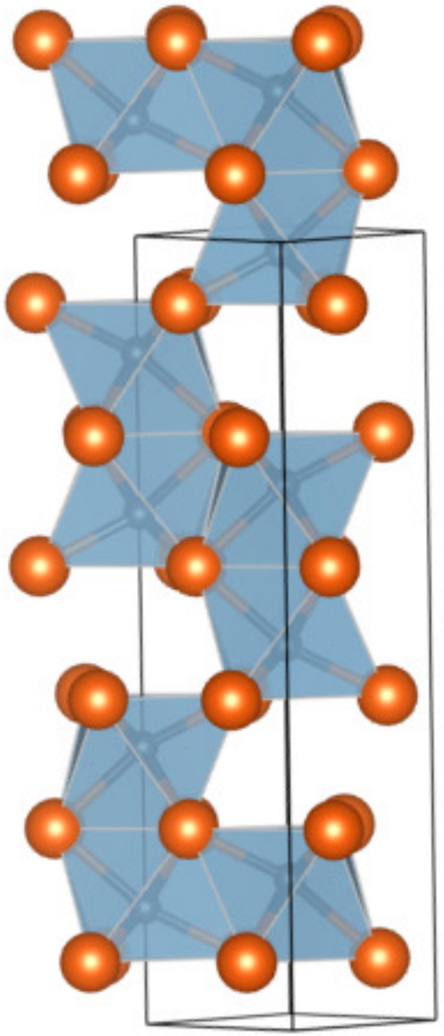
Pauling rules – comment on sharing of polyhedra example: Al_2O_3 (corundum, alumina)

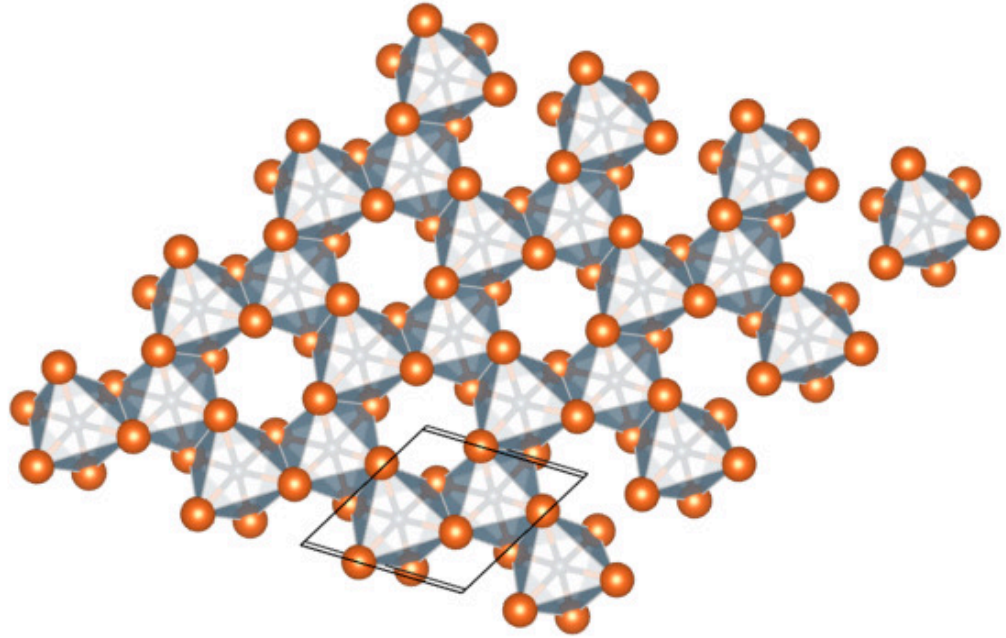




Octahedra are deformed to make distance between cations larger

Pauling rules – comment on sharing of polyhedra example: Al_2O_3 (corundum, alumina)





there are empty spaces in the structure, which allow for the distortion of tetrahedra

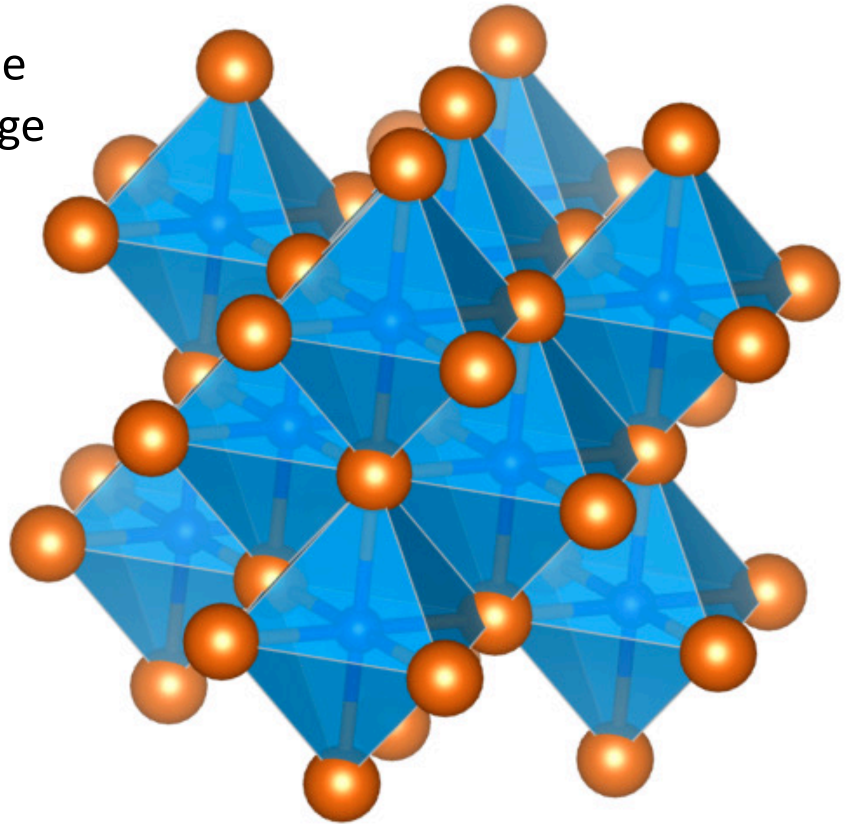
Important simple structures

- AX: MgO (rock-salt), CsCl (cesium cloride), ZnO (wurtzite), SiC (zinc blend) and its polymorphs
- AX2: SiO_2 (quartz), ZrO_2 (fluorite), TiO_2 (rutile)…
- A2X3: Al_2O_3 (corundum)…
- ABX3: $BaTiO_3$ (perovskite)…
- …

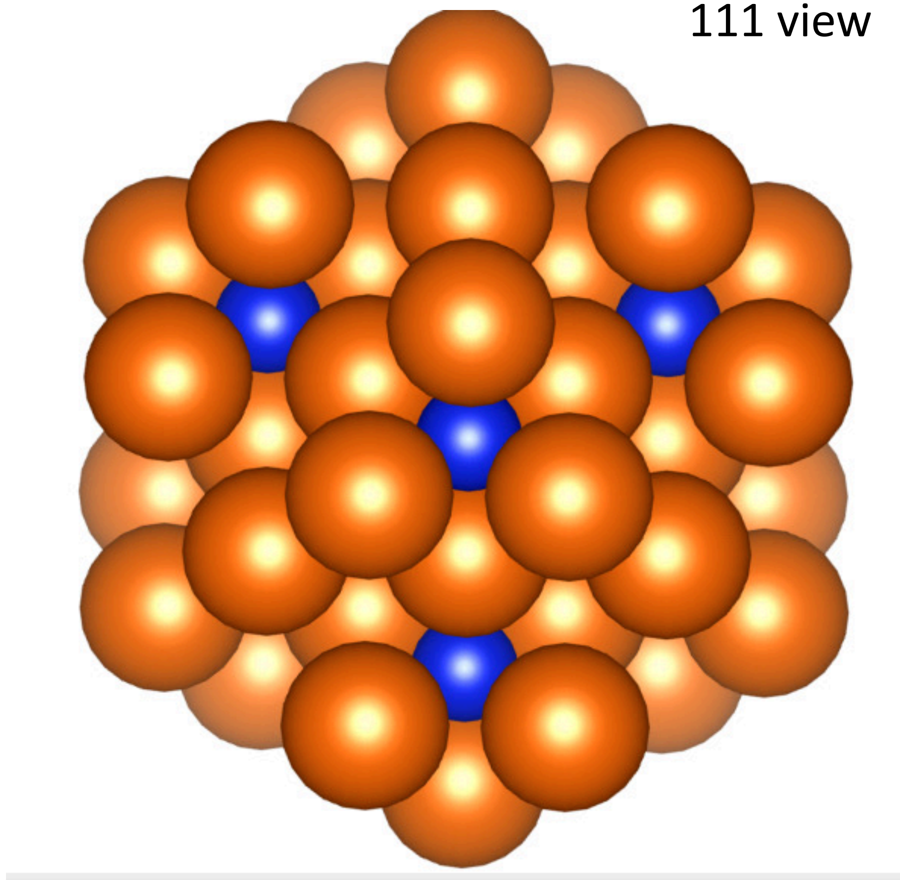
AX structures

Rock salt: LiF, KCl, MgO, NiO, CaO, TiC,… close cubic (FCC) packing- all octahedral sites are filled, tetrahedral sites empty;
Cubic structure Fm-3m

Mg: blue
O: orange



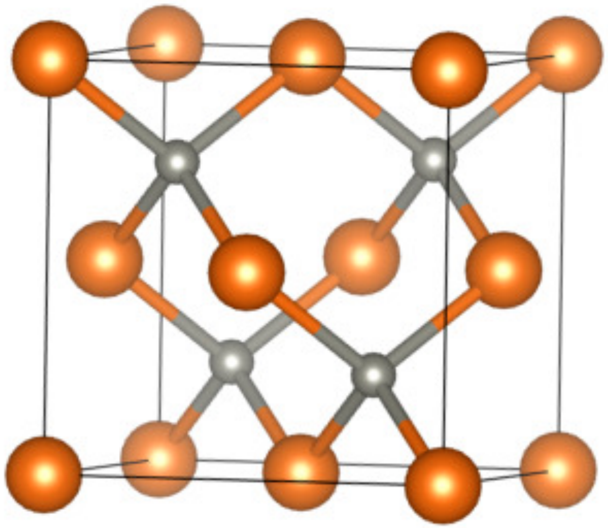
111 view

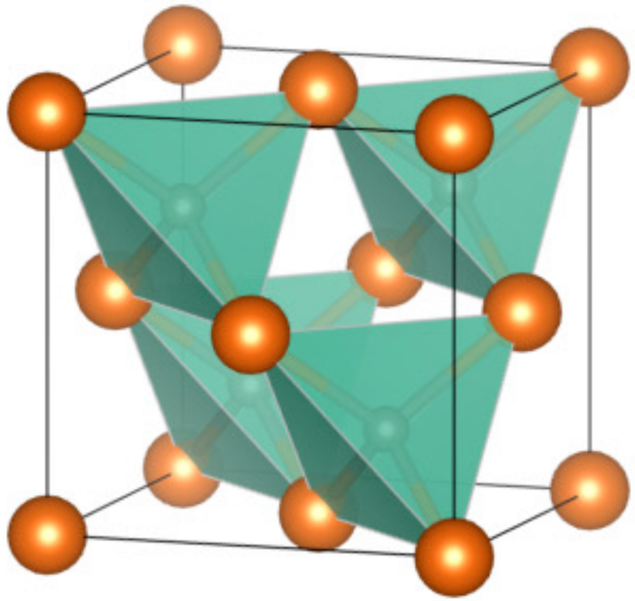


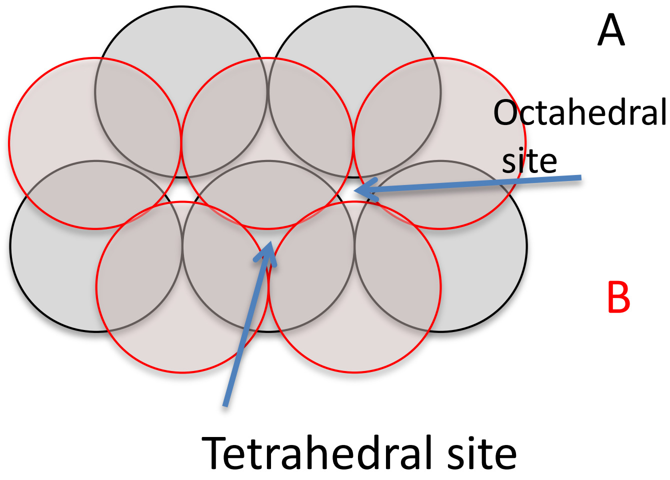
AX structures

Zincblende: ZnO, ZnS, BeO, SiC, BN, GaAs,… close cubic packing (FCC)-
Small cations in tetrahedral sites. Half of tetrahedral sites filled.
Cubic structure F-43m – it is different from the example on the previous slide

Orange: O
Gray: Zn





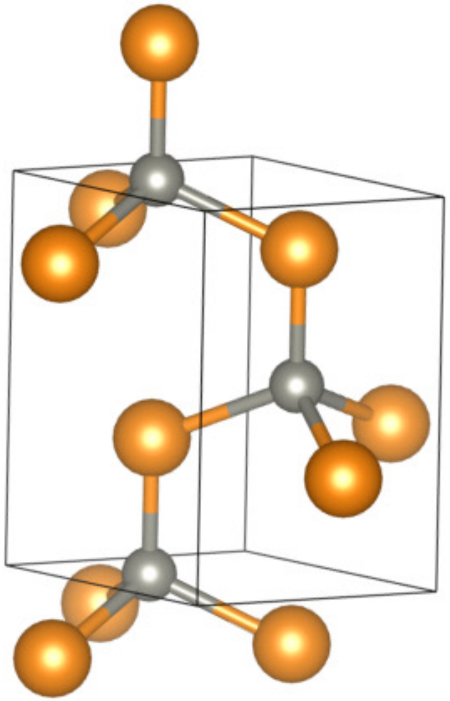


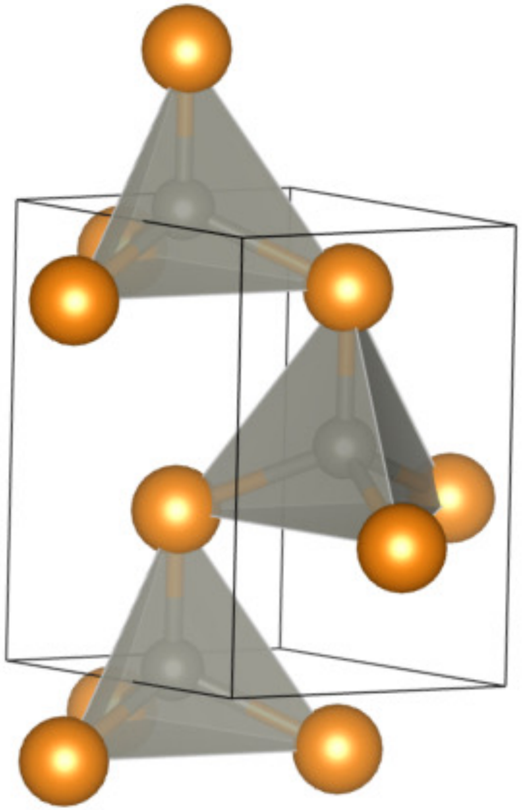
Cubic but not centrosymmetric! - Zincblend is piezoelectric: to be discussed later

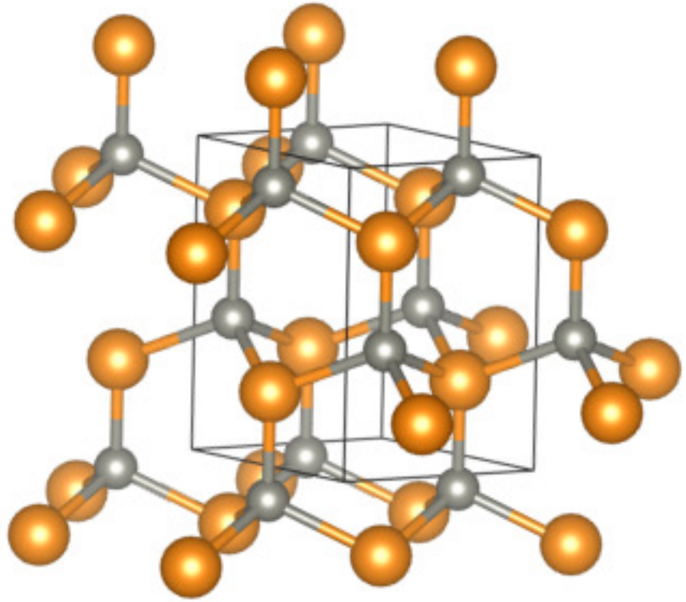
AX structures

Wurtzite: ZnO, AlN, SiC,,… hexagonal close packing (HCP)-
Small cations filling tetrahedral sites. Half of tetrahedral sites filled.

Hexagonal structure







Orange: O
Gray: Zn

This structure is polar: to be discussed later

Polytypes and polymorphs

- Zincblend and wurtzite are polytypes:
  - FCC or hexagonal, half of tetrahedral sites filled

the same atoms arranged in a different packing

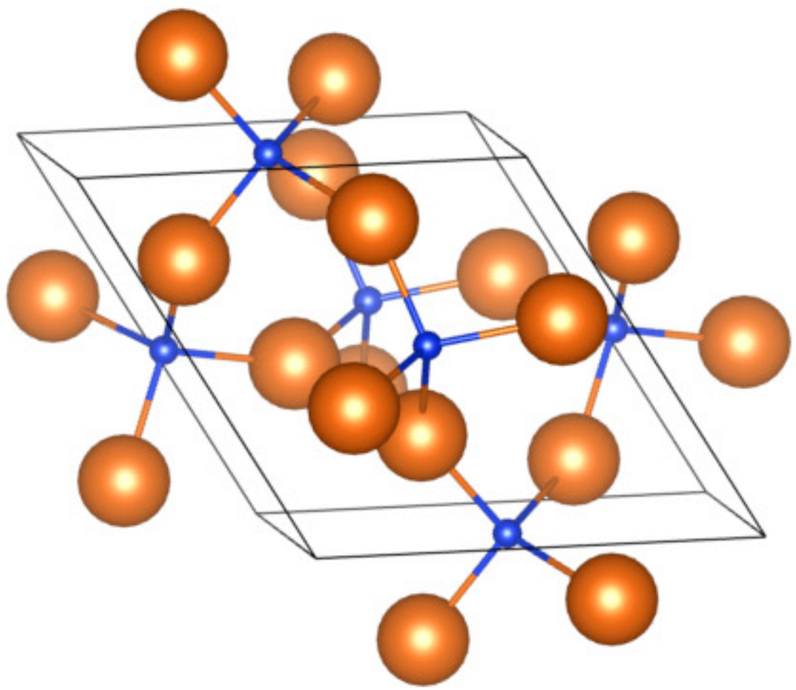
SiC: a large number of polytypes (dozens)

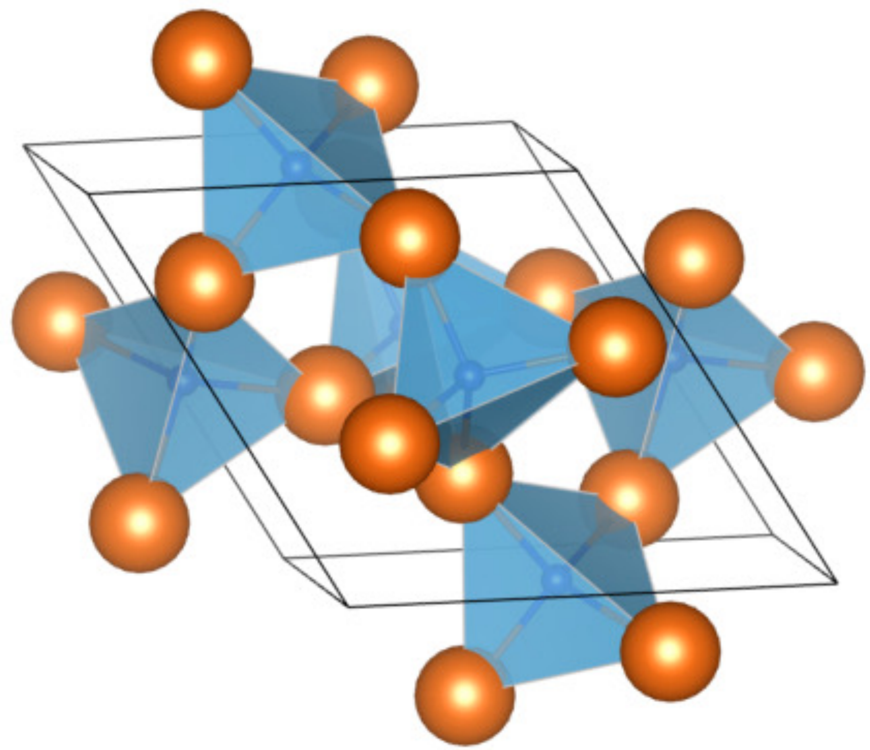
Polymorphs: compound appears in different crystalline forms.

If transformation from one phase to another can take place by small displacements of atoms the transformation is called ***displacive***. If transformation requires bond braking it is called ***reconstructive.***

AX_2 structures

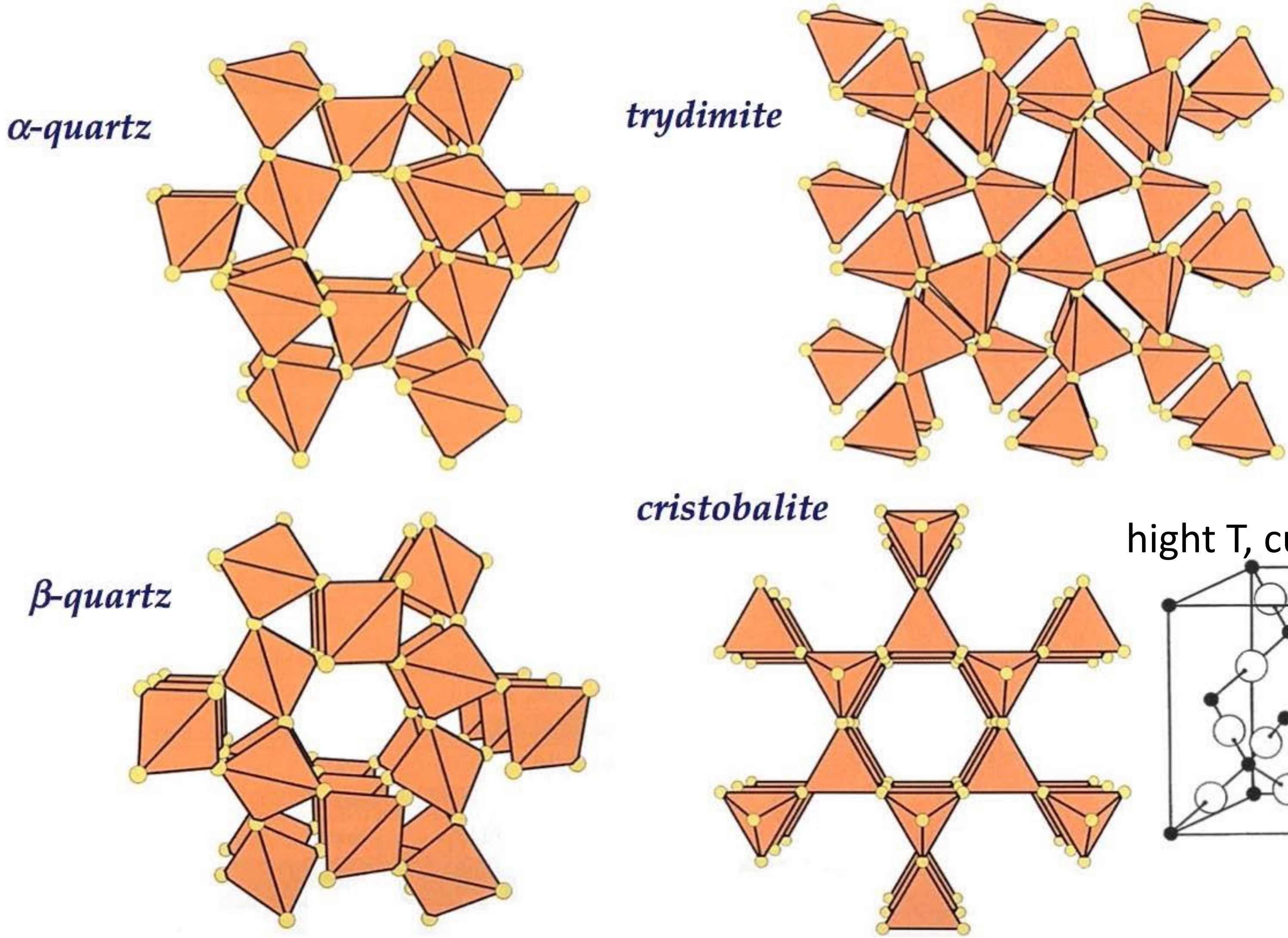
SiO2 (silica) - Si filling half of tetrahedral sites.
Trigonal structure



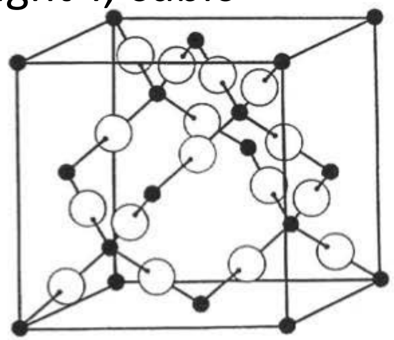


Alpha-quartz is noncentrosymmetric (piezoelectric)

Polymorphs of quartz



hight T, cubic



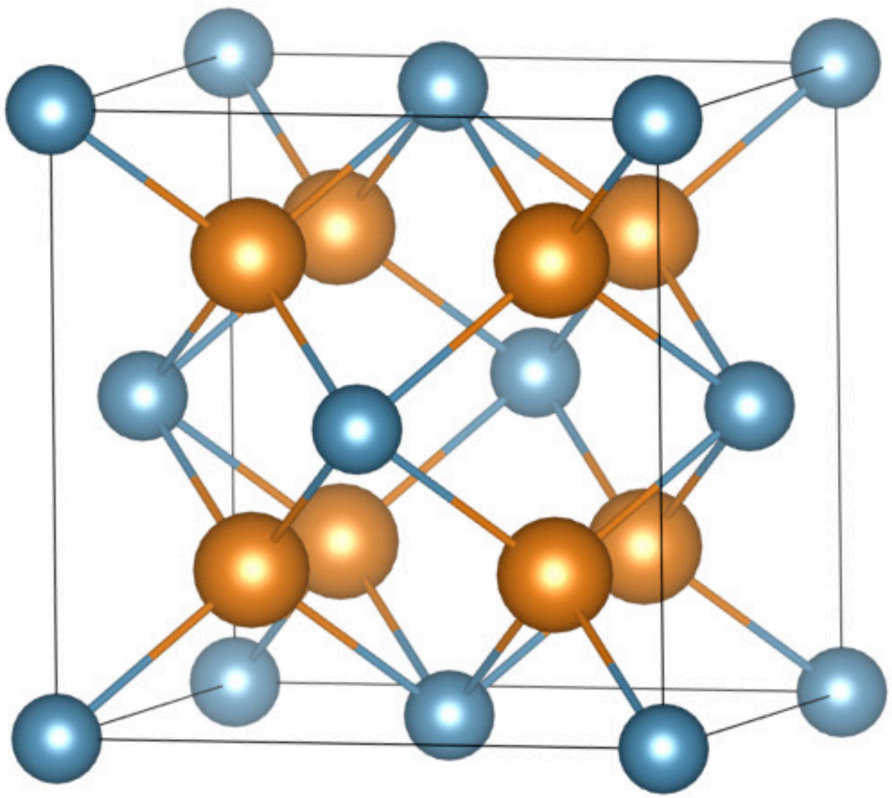
Glass-ceramic technology, W. Hoeland & G. Beall, The American Ceramic Society, 2002

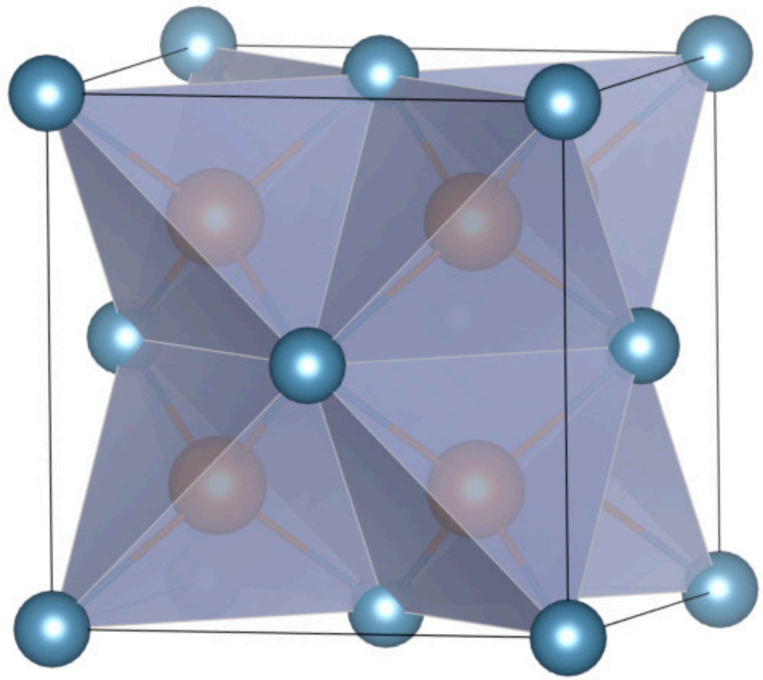
AX_2 structures

Fluorite: CaF_2, ZrO_2, CeO_2,…

8-fold coordination of cations. 4-fold coordination of anions

Cubic structure, some ditortions may result in materials with new properties (e.g. Ferroelectricity/antiferroelectricity)





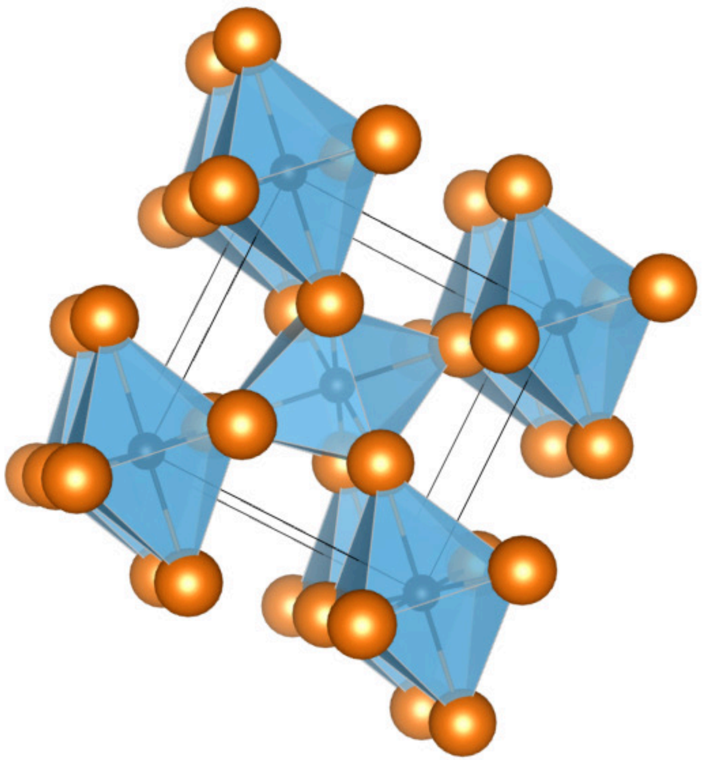
Orange: O,F Blue: Cation

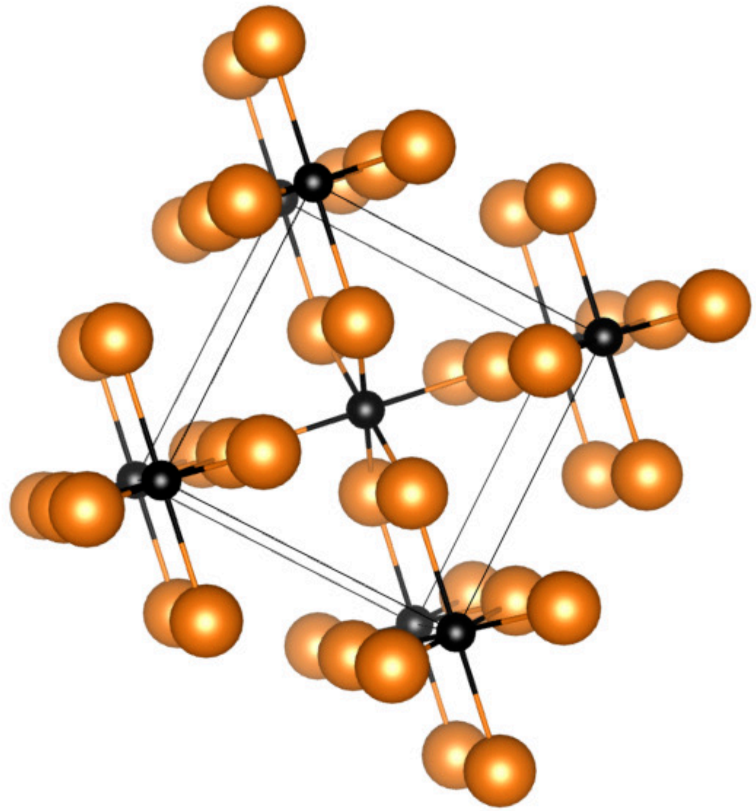
AX_2 structures

Rutile: TiO_2, SnO_2, PbO_2, VO_2, NbO_2, TeO_2, MoO_2, WO_2, MnO_2, RuO_2, OsO_2, IrO_2 , GeO_2

HCP packing; One half of octahedral sites filled by cations;

Tetragonal structure



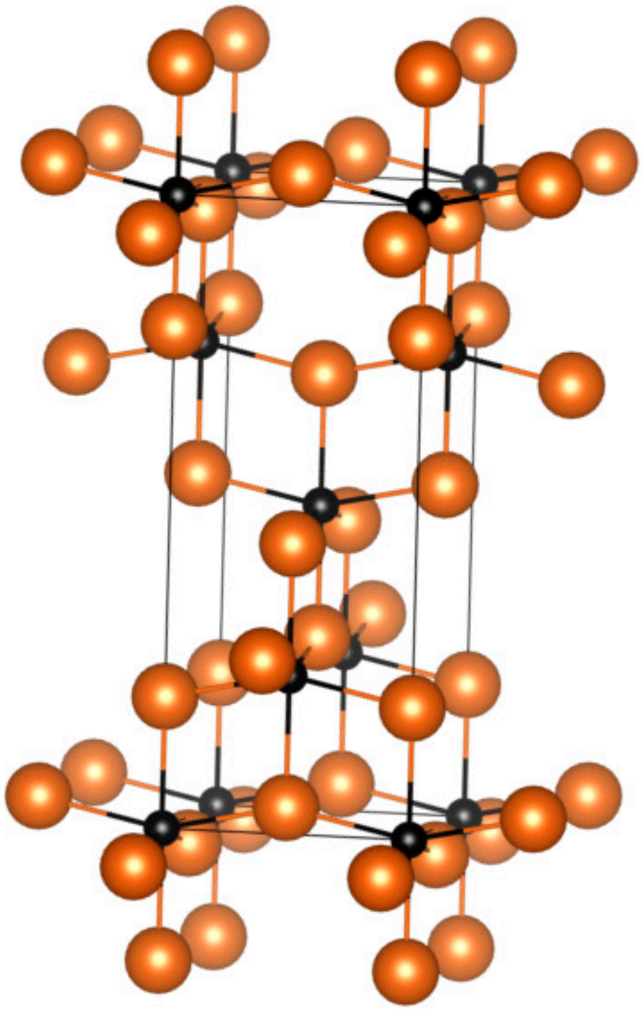


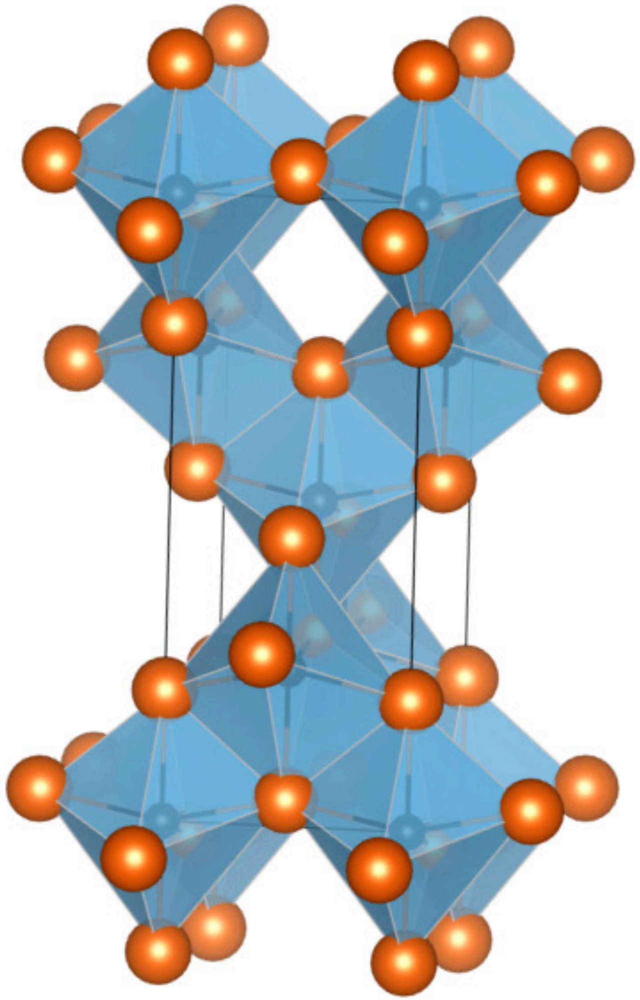
AX$_2$ structures

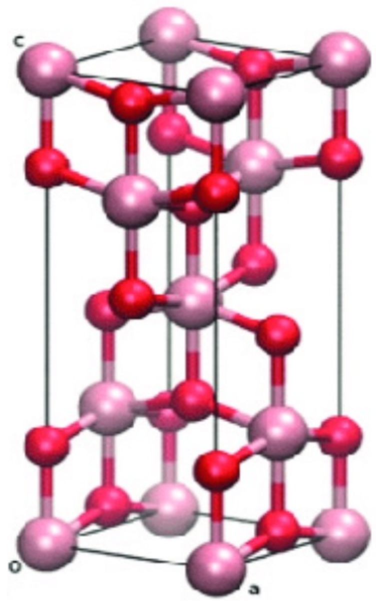
Anatase: TiO_2 polytype; A tetragonal structure;

CCP packing;

Here oxygen octahedra are sharing edges (Pauling rule is not respected – a metastable structure)



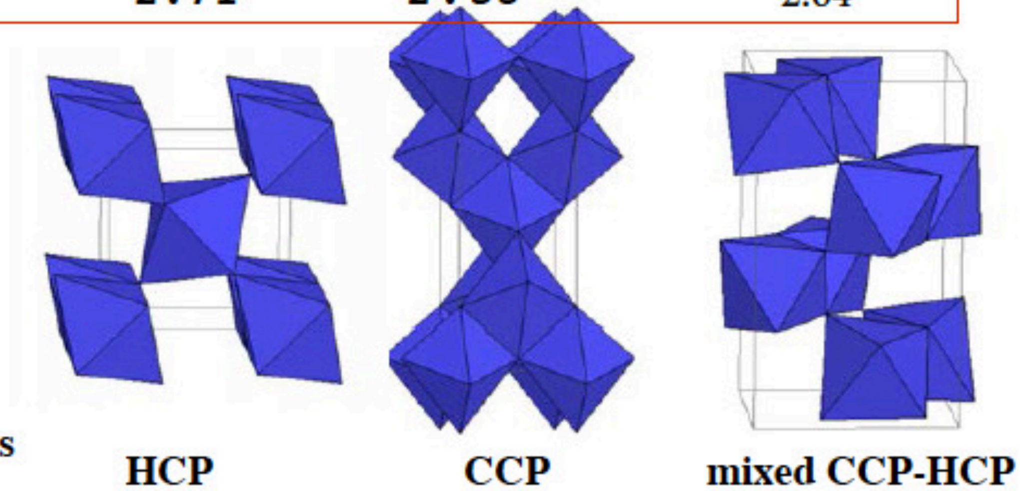




TiO2

	Rutile	Anatase	Brookite
	TiO_2	TiO_2	TiO_2
Form.Wt.	79.890	79.890	79.890
Z	2	4	8
CrystalSystem	Tet	Tet	Orth
PointGroup	4/mmm	4/mmm	mmm
SpaceGroup	$P4_2/mnm$	$I4_1/amd$	Pbca
UnitCell			
a(Å)	4.5845	3.7842	9.184
b(Å)			5.447
c(Å)	2.9533	9.5146	5.145
Vol	62.07	136.25	257.38
MolarVol	18.693	20.156	19.377
Density	4.2743	3.895	4.123
n	2.71	2.53	2.64

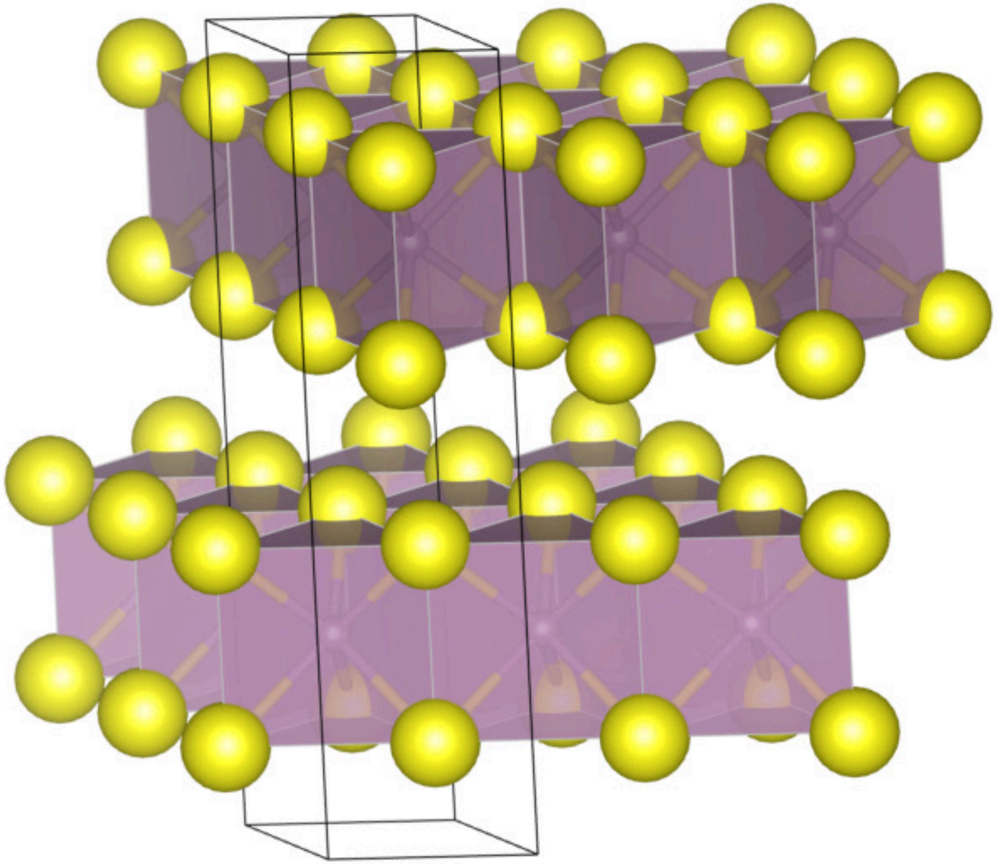
High density → high refractive index

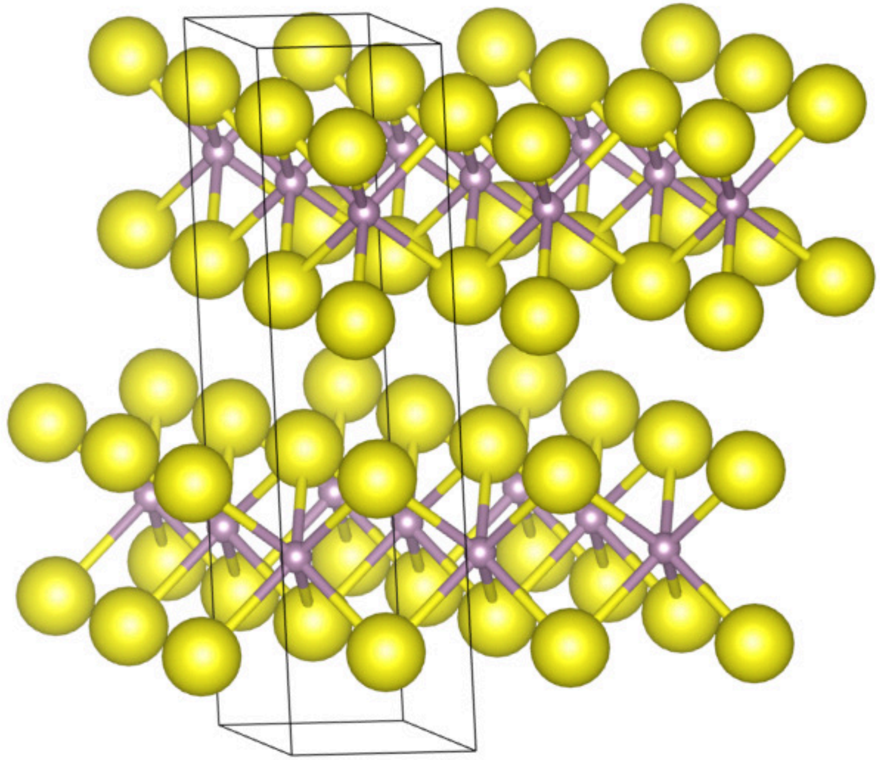


Natural polymorphs of totania

AX_2 structures

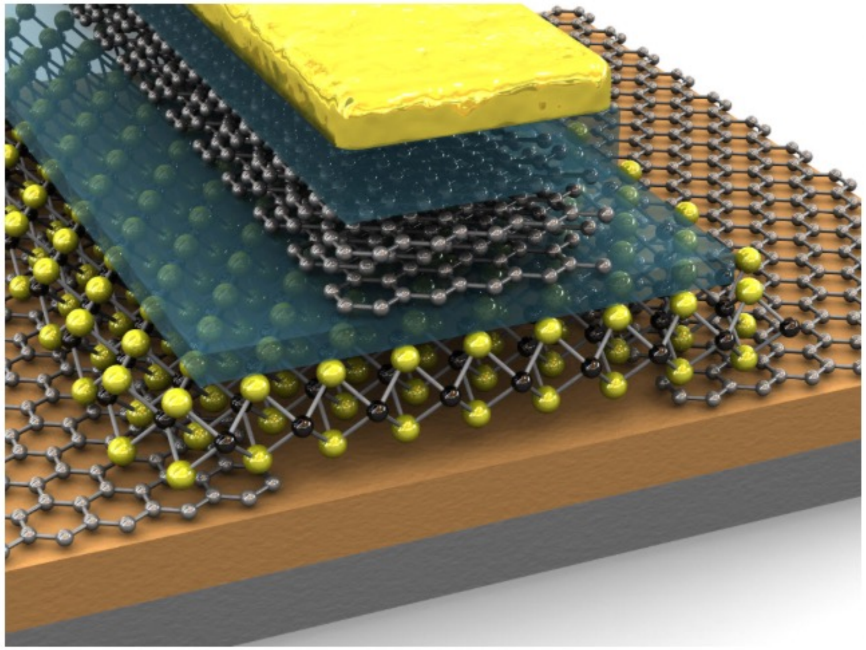
Layer structures: Molybdenum disulfide: MoS_2 polytype, WS_2, Van der Waals bonds between planes. Hexagonal structure



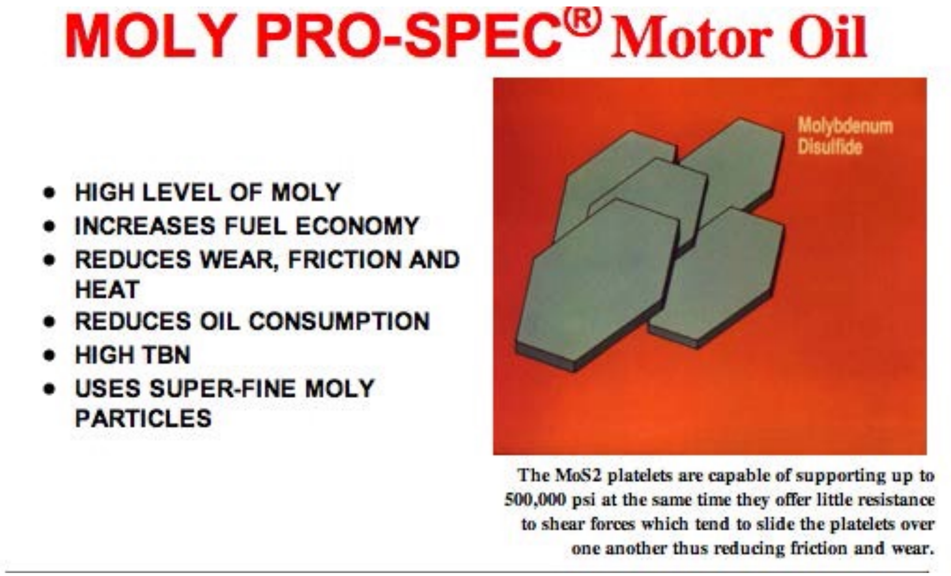


Trigonal prismatic coordination of S around Mo

MoS_2 applications



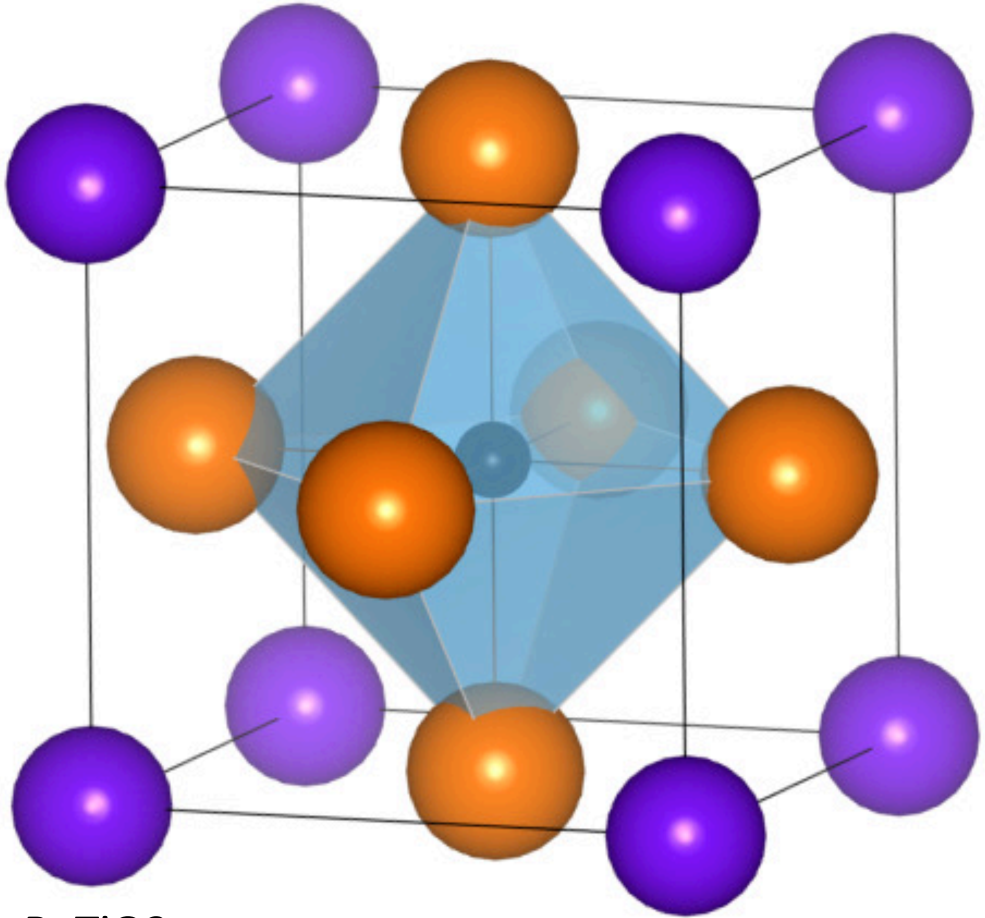
Graphene and molybdenite combine into a flash memory prototype. Yellow-black molecules: molybdenite; gray hexagons: graphite (credit: EPFL)



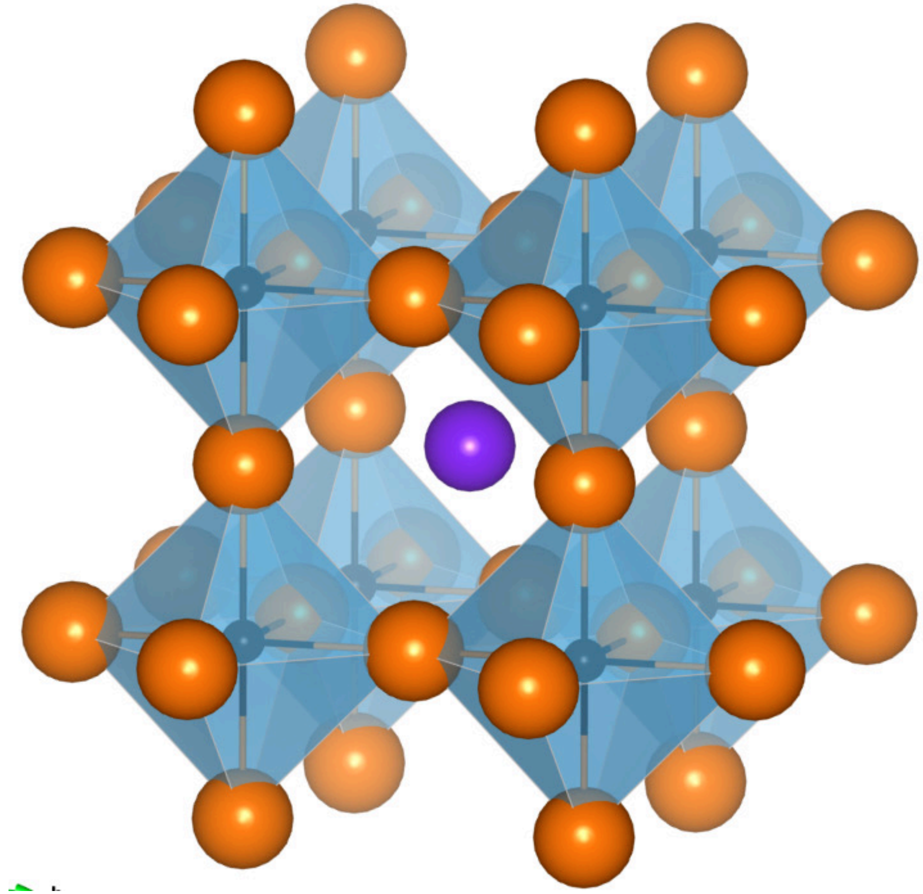
- MoS_2 is a transition metal dichalcogenide (TMD) with a layered structure similar to graphene.
- Unlike graphene (which is gapless), monolayer MoS_2 has a direct bandgap (~1.8 eV), making it highly suitable for transistors, photodetectors, and optoelectronic applications.

ABX_3 structures

ABX3: perovskites $BaTiO_3$, $Pb(Zr,Ti)O_3$, $CH_3NH_3PbI_3$
FCC derived structure; cubic parent structure, distortion in low-temperature phases (tetragonal, rhombohedral) – new properties



BaTiO3
Black:Ti; orange: O; Purple: Ba

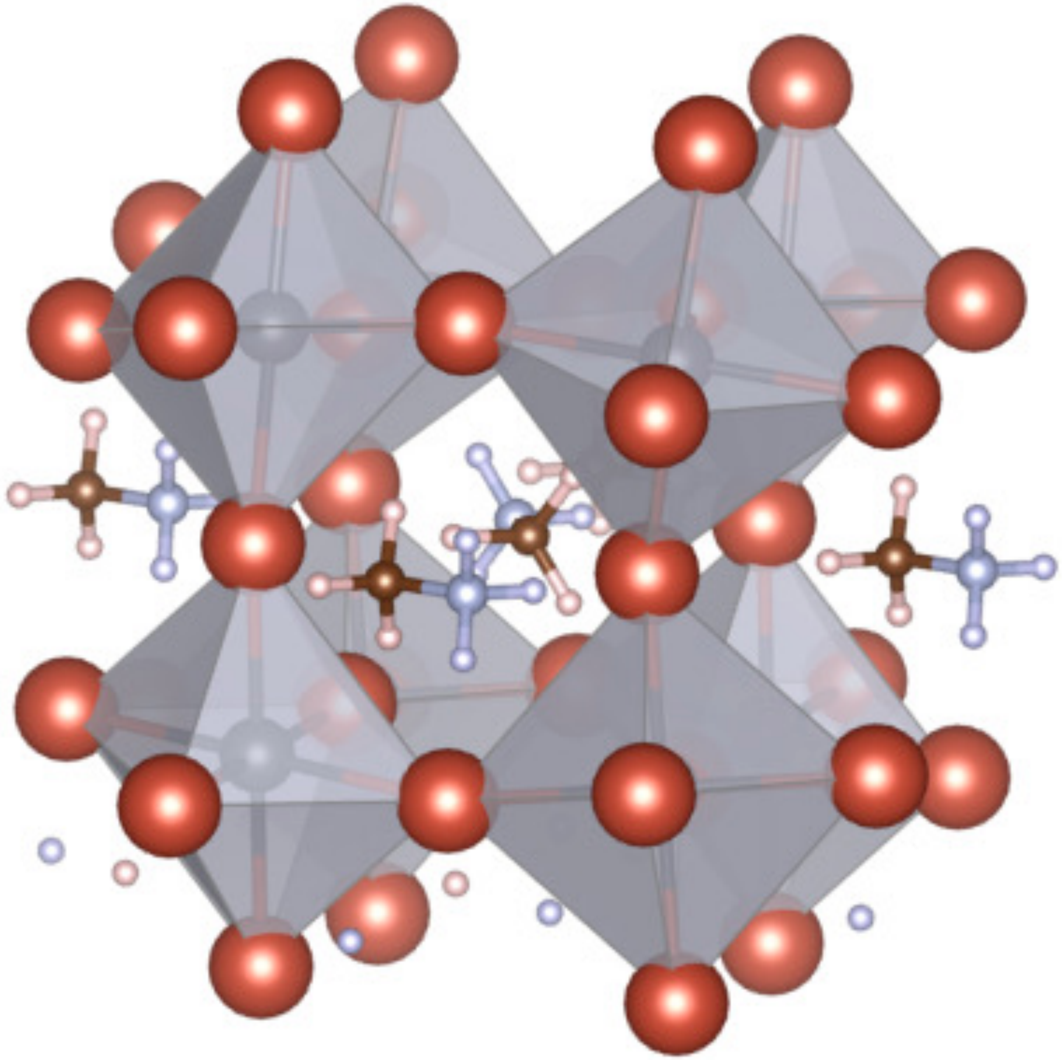


ABX_3 structures

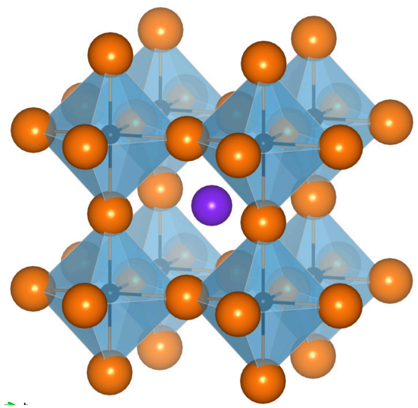
Perovskite structure ABX3:
$CH_3NH_3PbI_3$; orthorhombic structure or tetragonal or…

Methylammonium Lead Iodide
methylammonium trihalogenoplumbates

Distorted octahedra;
Large atom (Pb) in the center of octahedra,



Compare:



Red: I; Black: Pb; Small atoms: H,N,C- CH_3NH_3 molecule

organic molecules are at the place of A-atoms – solar cells

Crystalline symmetry

Macroscopic crystalline symmetry and point groups

Translational symmetry in 3D

$$\vec{t} = p\vec{a}_1 + m\vec{a}_2 + n\vec{a}_3$$

translation vector ($\vec{t}$)

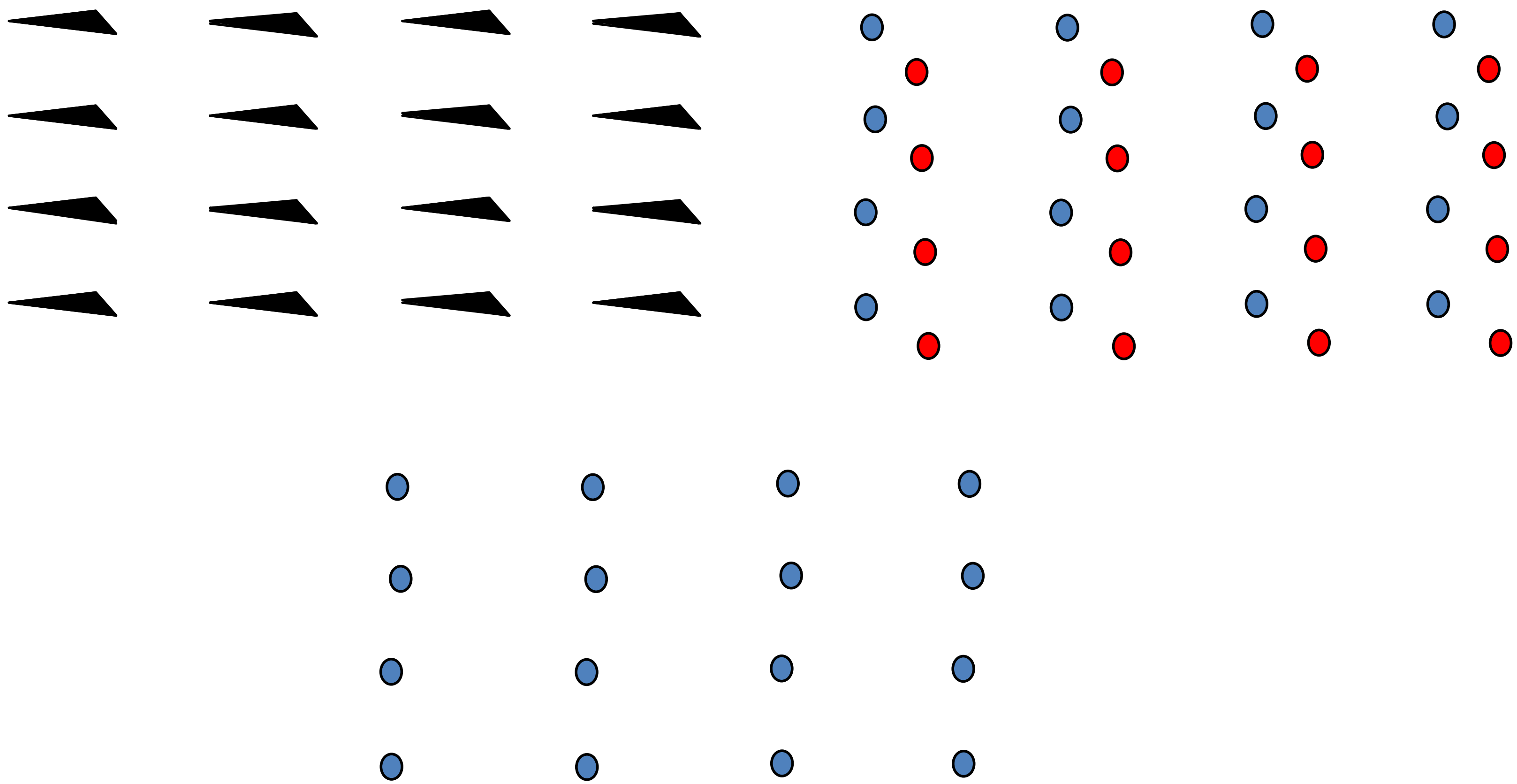
fundamental translation vectors ($\vec{a}_1$, $\vec{a}_2$, $\vec{a}_3$)

p, m, n **integer**

Translation vector makes ***lattice (Bravais Lattice)***

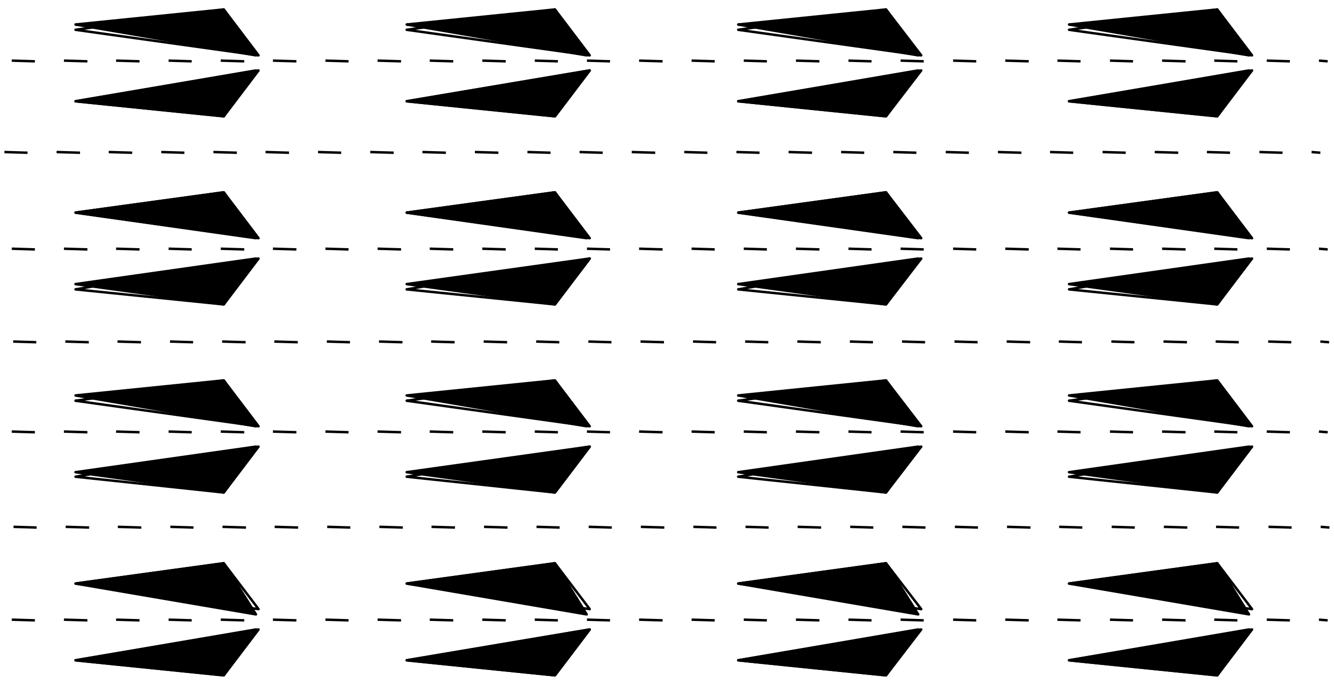
$|\vec{a}_1|\ |\vec{a}_2|\ |\vec{a}_3|$ **lattice constants**

These crystalline structures have the same Bravais lattice



Crystalline Symmetry

Reflections



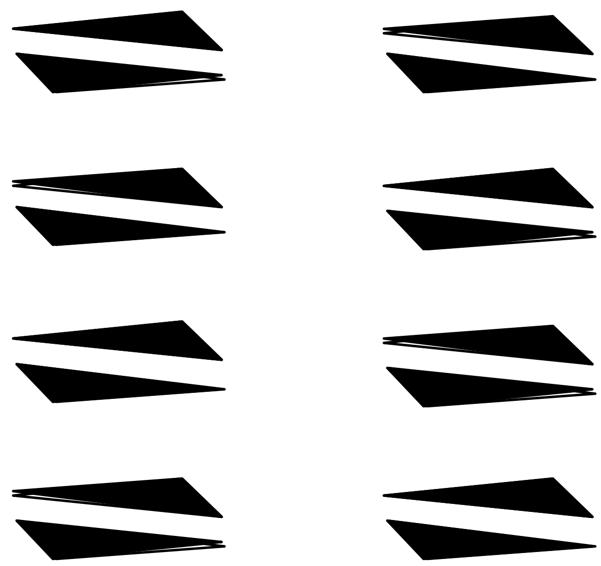
mirror planes

Crystalline Symmetry

rotation axes:

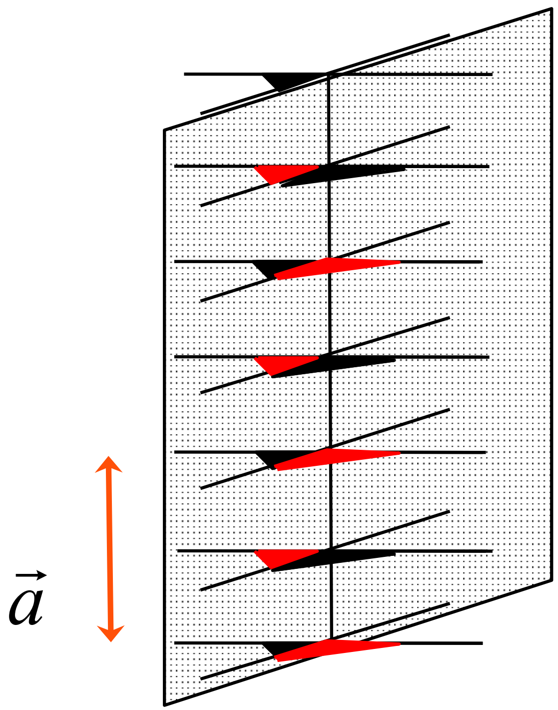
Order 2, 3, 4, 6

2-fold axes:



Crystalline Symmetry

Reflection + translation



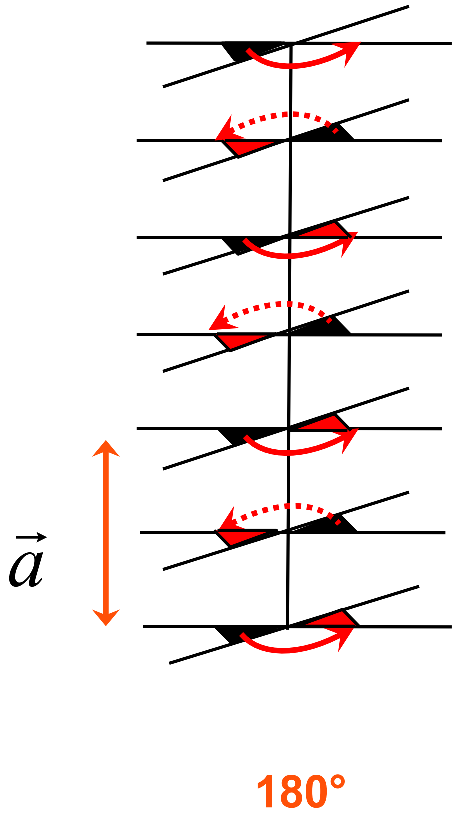
Symmetry element

= reflection + a/2 translation

glide plane

Crystalline Symmetry

rotation + translation



Symmetry element

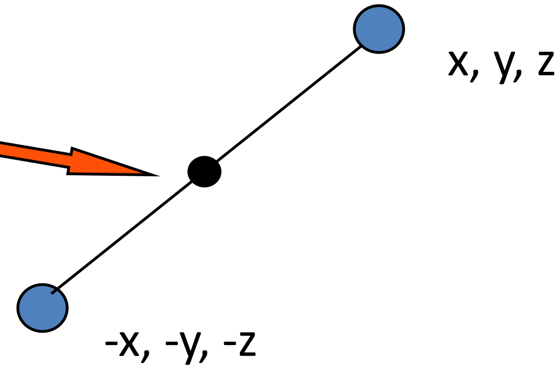
= 180 ° rotation + a/2 translation

2-fold screw axis

Elements of crystalline symmetry

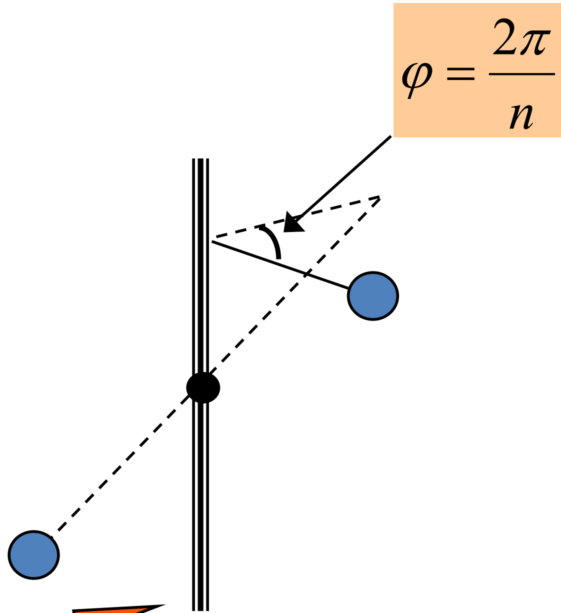
translations

center of symmetry



mirror plane

glide plane



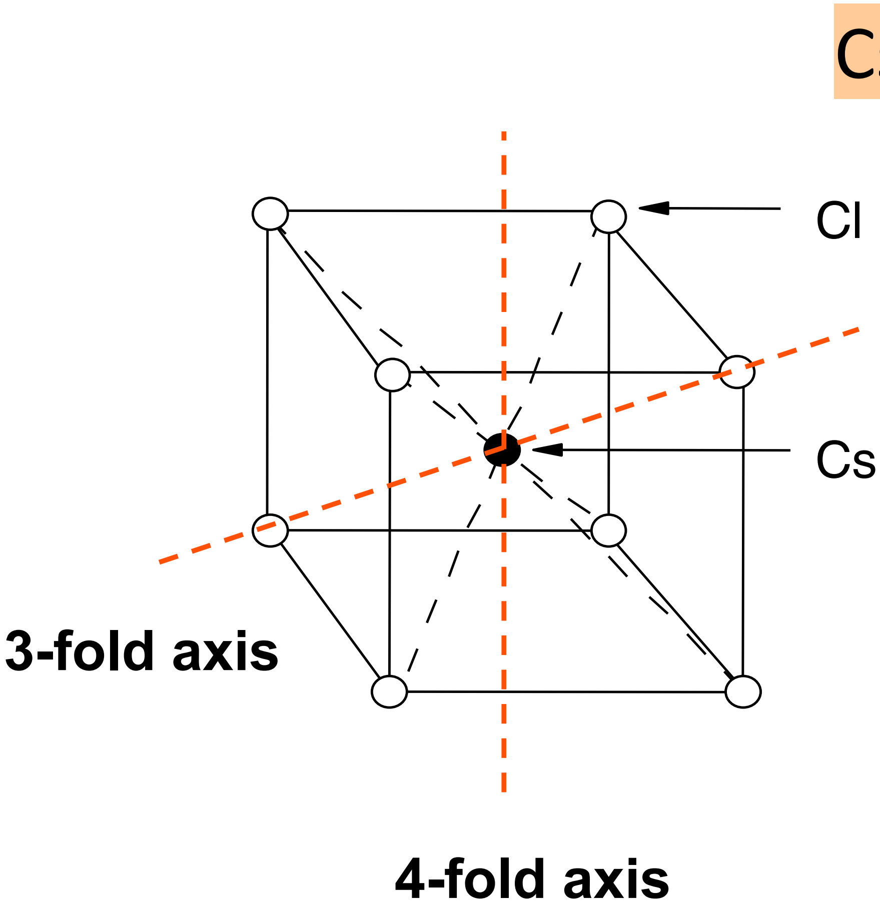
n-fold rotation axis

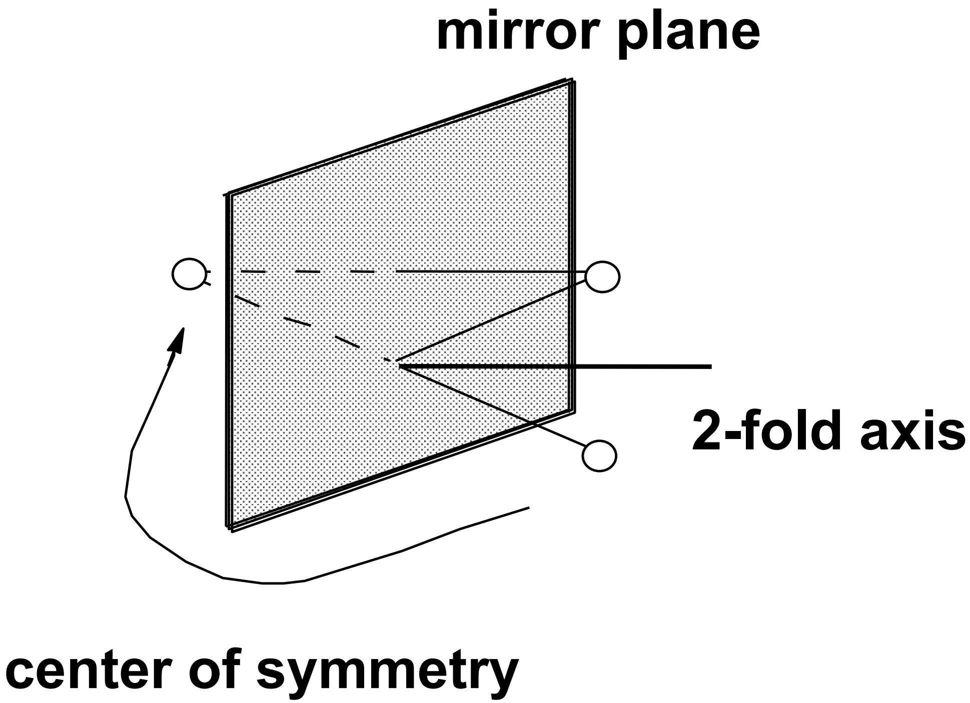
n- fold screw axis

n- fold inversion axis

n = 2, 3, 4, 6

Elements of crystalline symmetry

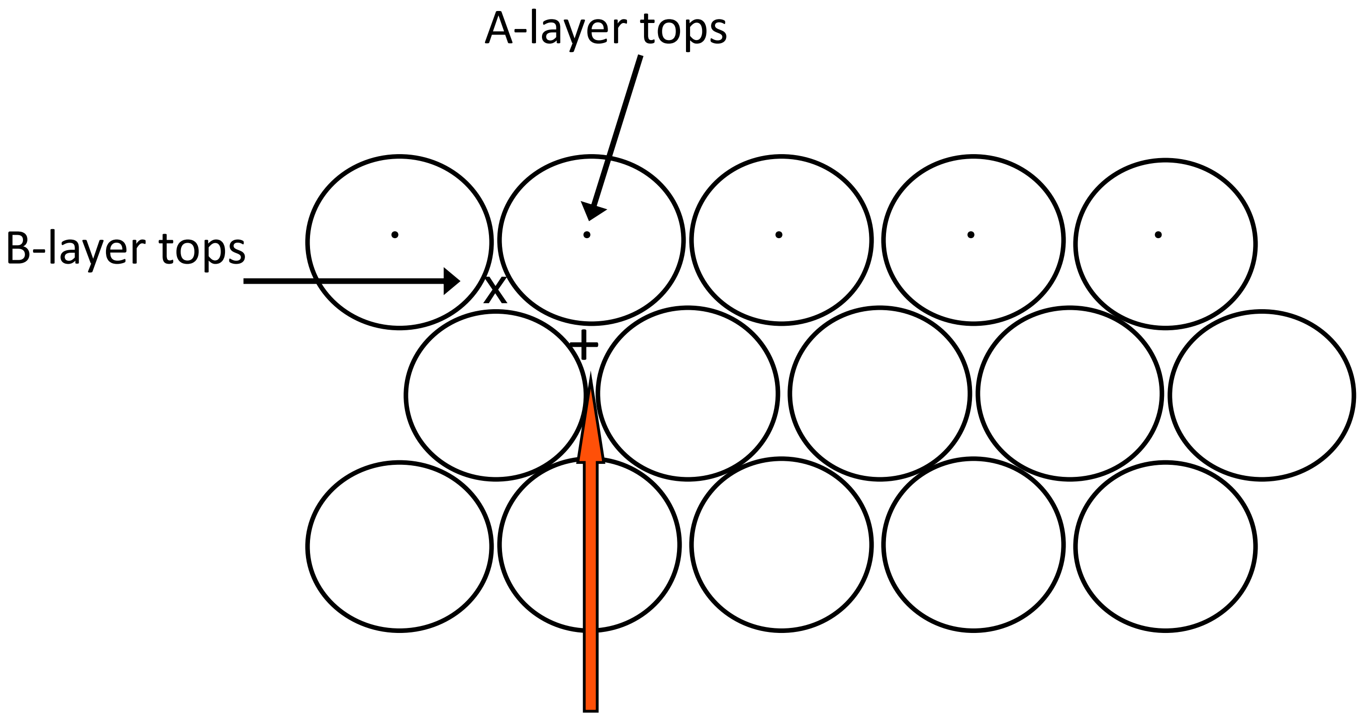




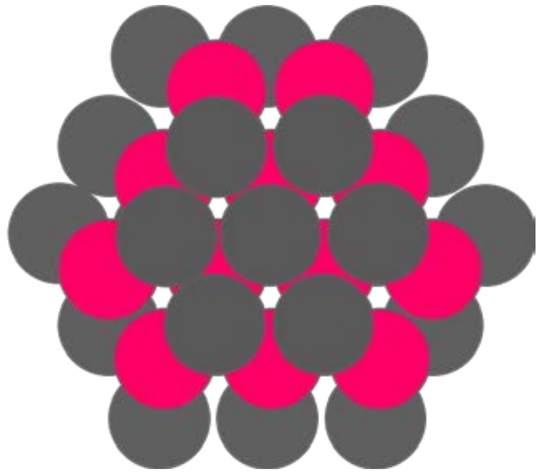
- Not all symmetry elements are independent
- A 2-fold rotoinversion axis is equivalent to a mirror plane , that is why a symbol “bar 2” is rarely used

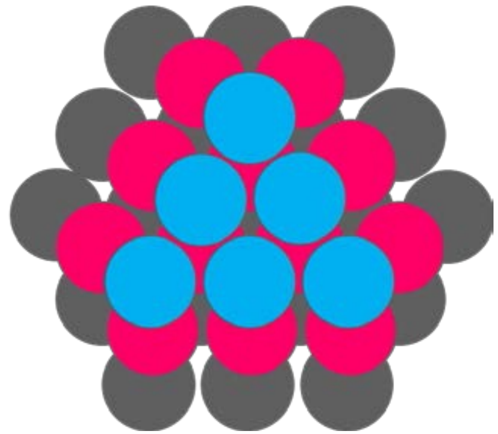
Elements of crystalline symmetry

Hexagonal Close-packed Structure (hcp)



6-fold screw axis





Other symmetry elements:
- mirror planes (passing through atoms)
- glide planes (passing between the atoms)

Elements of MACroscopic crystalline symmetry

Fine symmetry	MACroscopic symmetry
translations	
center of symmetry	center of symmetry
mirror plane	mirror plane
glide plane	
n-fold rotation axis	n-fold rotation axis
n- fold screw axis	
n- fold inversion axis	n- fold inversion axis

Elements of MACroscopic crystalline symmetry

Fine symmetry

230 space groups

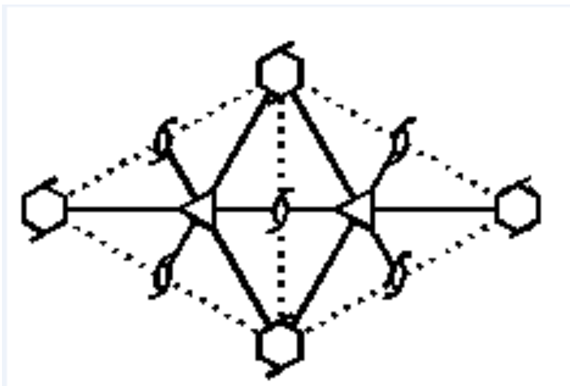
MACroscopic symmetry

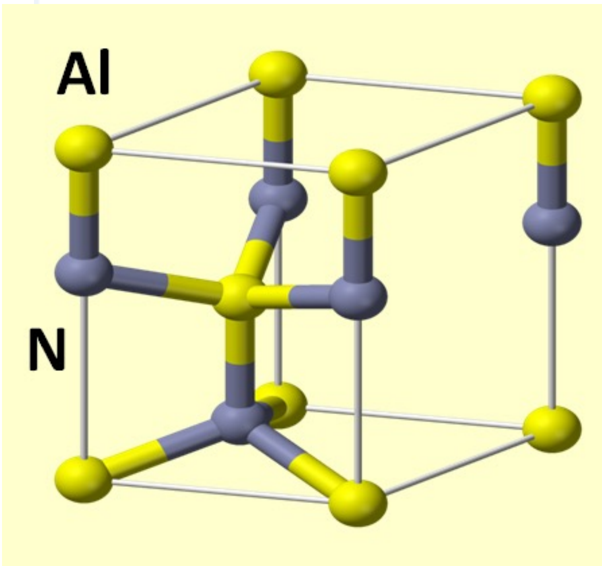
32 point groups

group = set of symmetry elements of an object

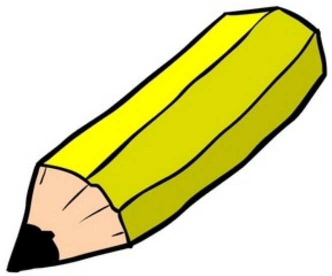
Space group → point group (example)

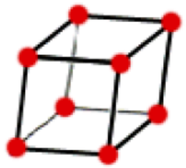
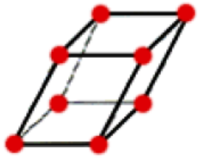
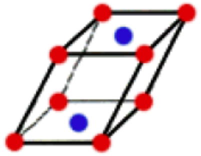
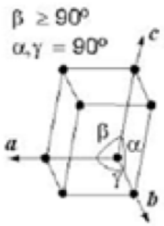
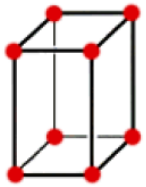
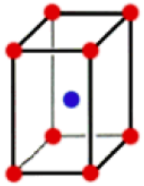
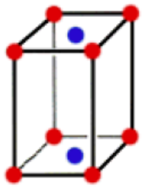
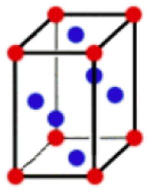
$P6_3mc$ → **6mm**

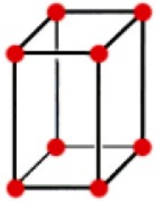
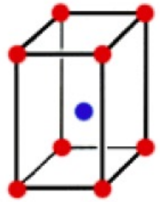
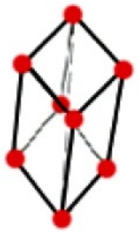
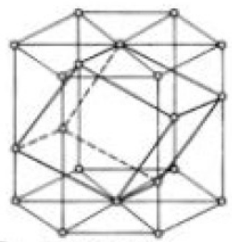
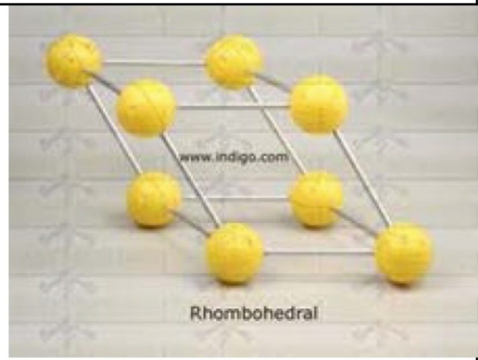
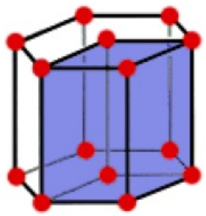
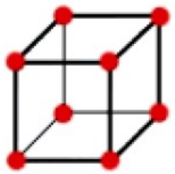
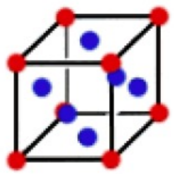
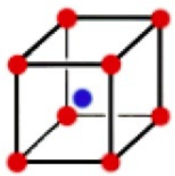




AlN-based filter

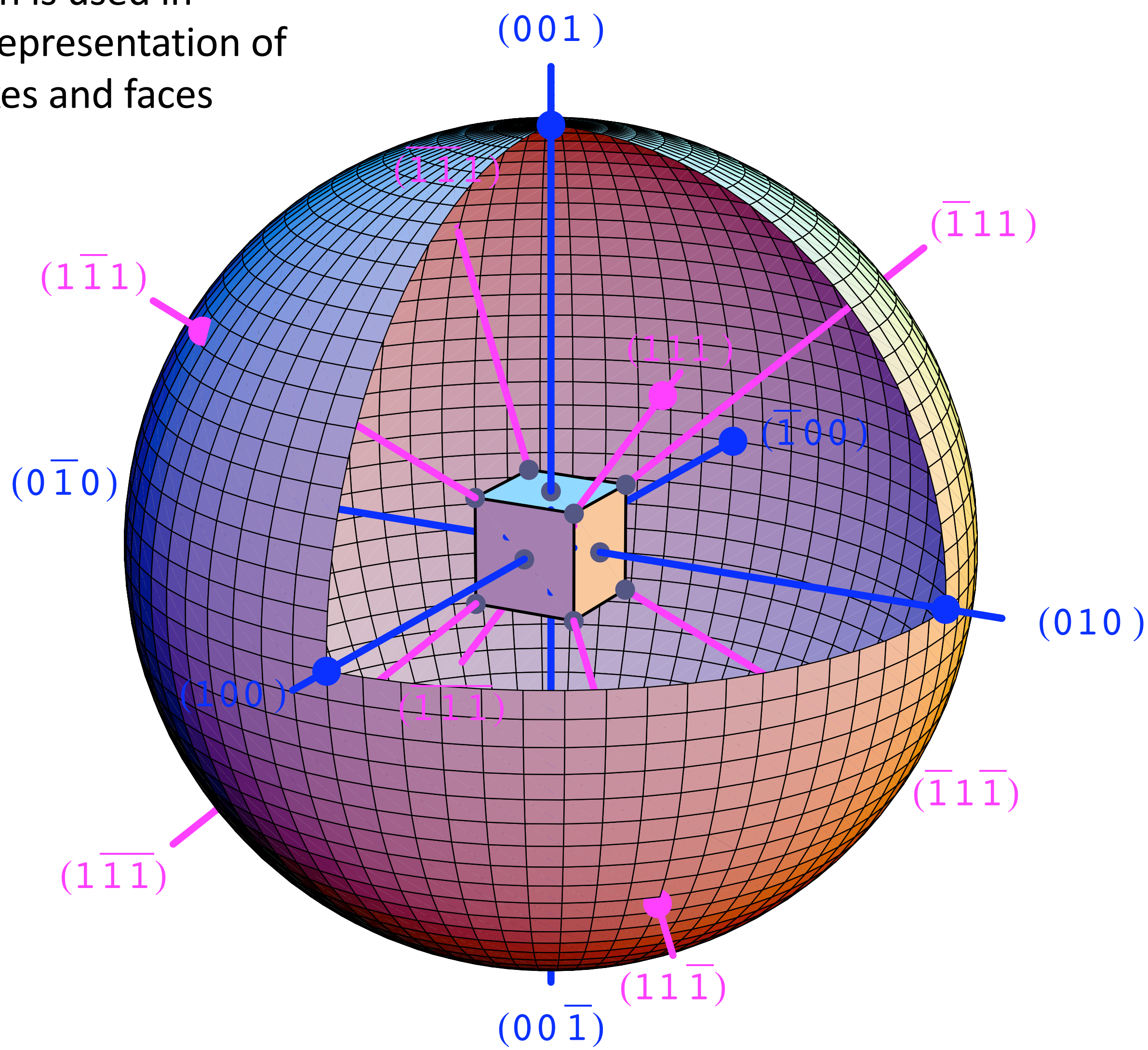


Crystal system	The 14 Bravais lattices	Defining symmetry
Triclinic **a≠ b ≠ c** **α≠β≠γ≠90°**	 **Triclinic**	1-fold axis
Monoclinic **a ≠ b ≠ c ;** **α = γ = 90°; β ≠ 90**	 **Simple Monoclinic**  **Base-centered monoclinic** 	2-fold axis
Orthorhombic **a≠ b ≠ c** **α=β=γ=90°**	 **Simple orthorhombic**  **Body-centered orthorhombic**  **Base-centered orthorhombic**  **Face-centered orthorhombic**	3 x 2 fold axis

Tetragonal **a= b ≠ c** **α=β=γ=90°**	 **Simple tetragonal**  **Body-centered tetragonal**	4-fold axis
Rhombohedral (trigonal) **a= b = c** **α=β=γ≠90°**	 **Rhombohedral**  P Trigonal R  	3-fold axis
Hexagonal **a= b ≠ c** **α=β=90, γ=120°**	 **Hexagonal**	6-fold axis
Cubic **a= b = c** **α=β=γ=90°**	 **Simple cubic**  **Face-centered cubic**  **Body-centered cubic**	4 x 3-fold axis

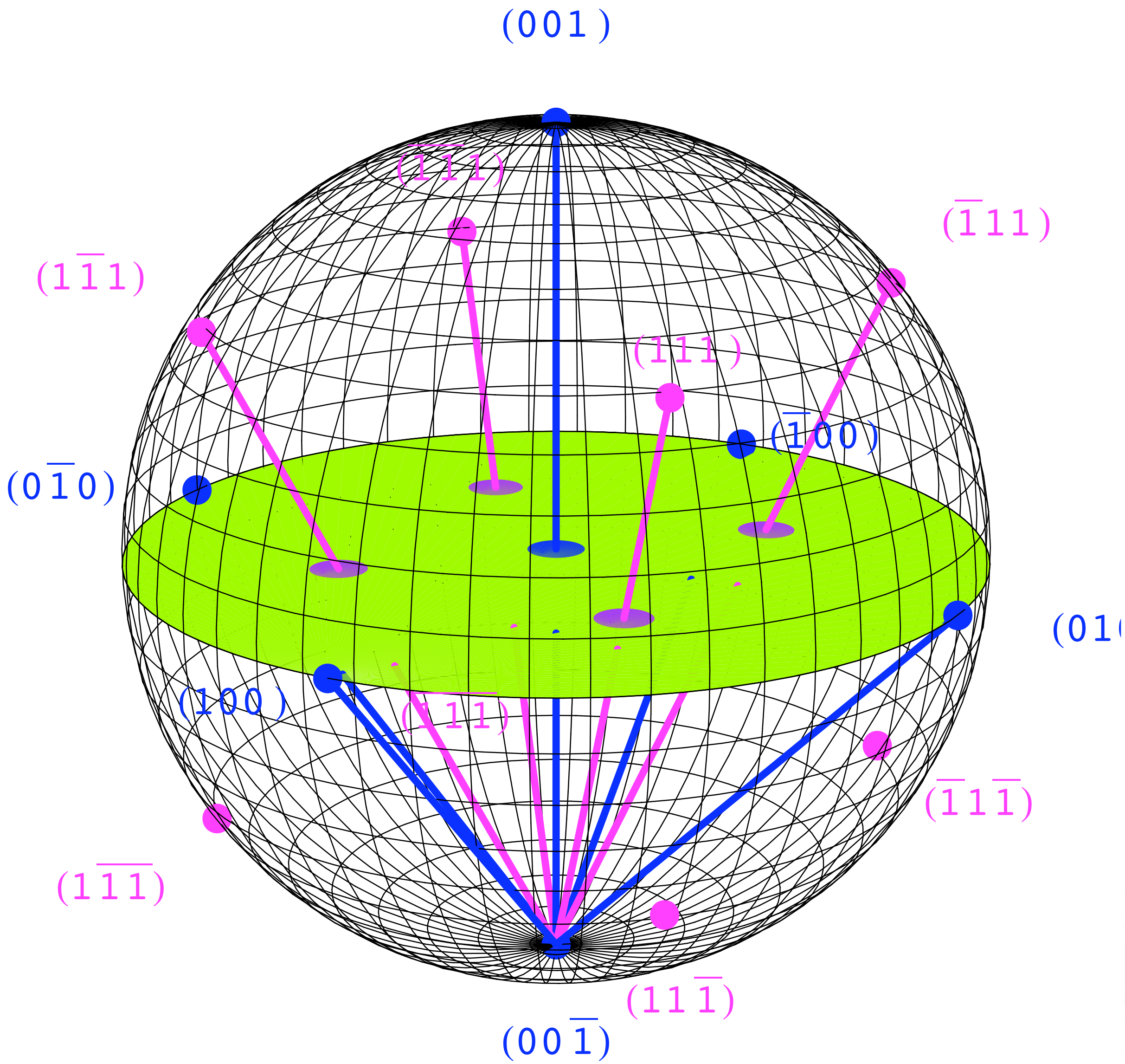
Stereographic Projection

Stereographic projection is used in crystallography for 2D representation of orientation of crystal axes and faces

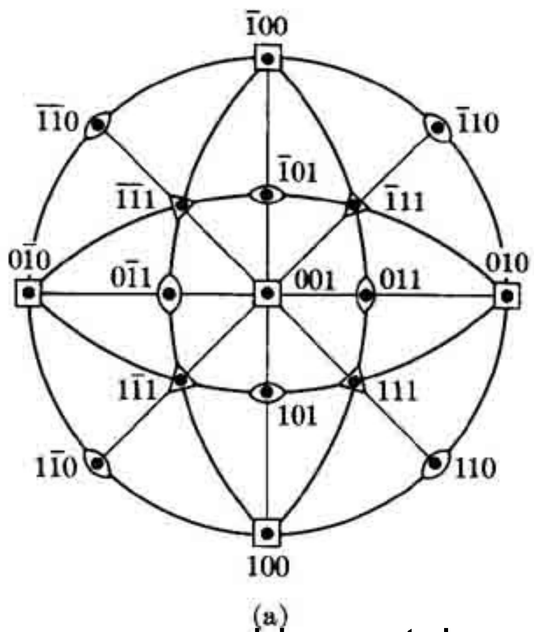


For building up stereographic projection the crystal is imagined to be at the centre of a sphere (called hereafter a stereographic sphere). The normals to the faces are imagined to radiate from the centre and to intersect the sphere in an array of points…

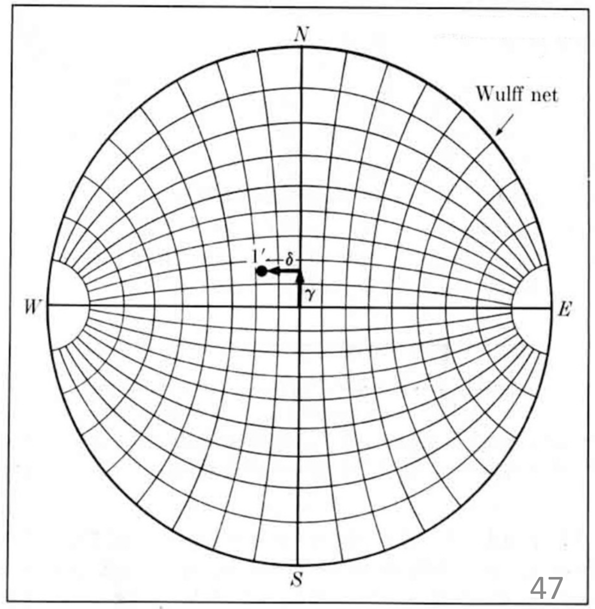
Now to we represent this 3D array of points in 2D as shown below i.e. we project them on the equatorial plane of the stereographic sphere using south pole as a projection center



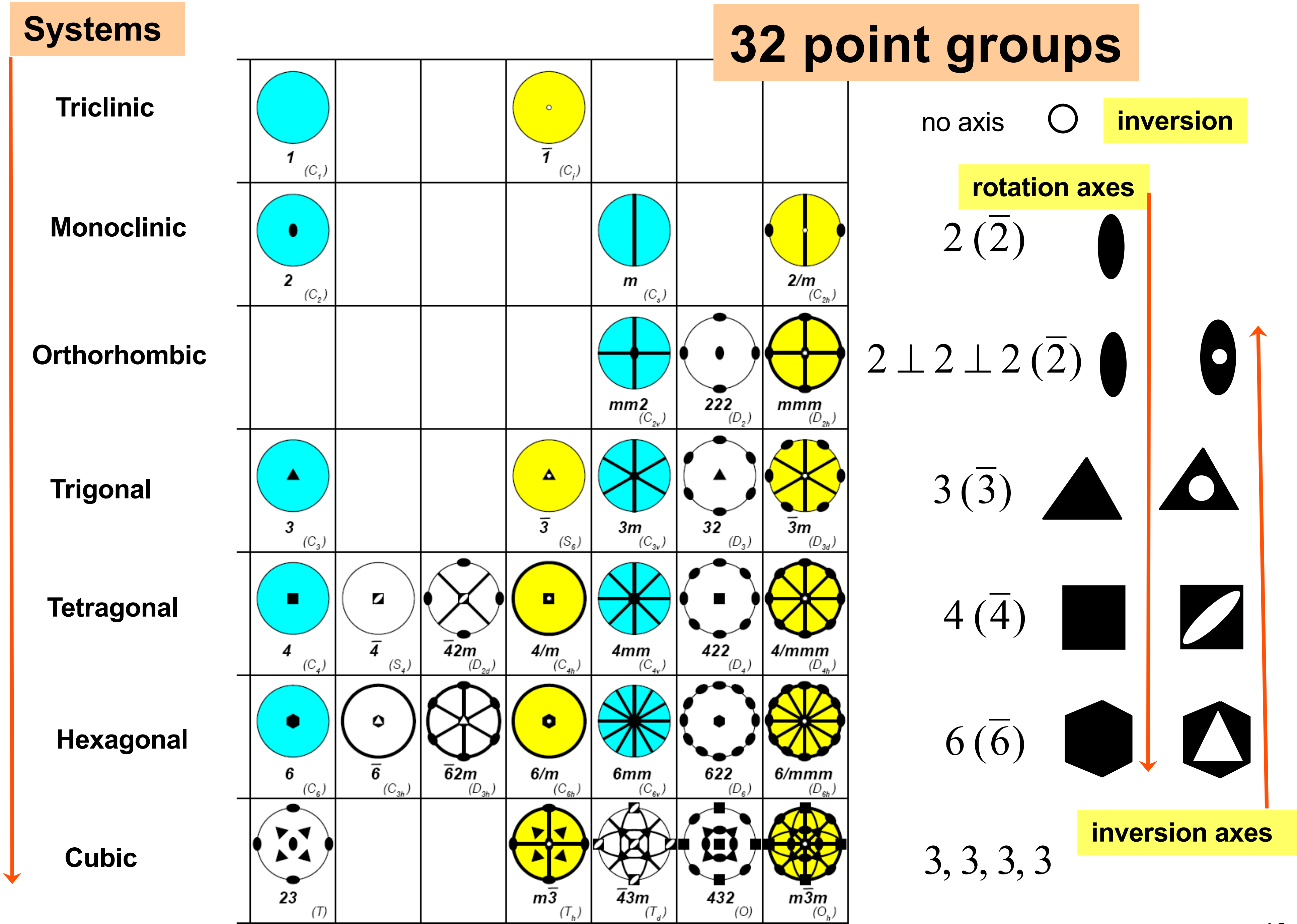
Wulff net is used for measuring angles between the poles



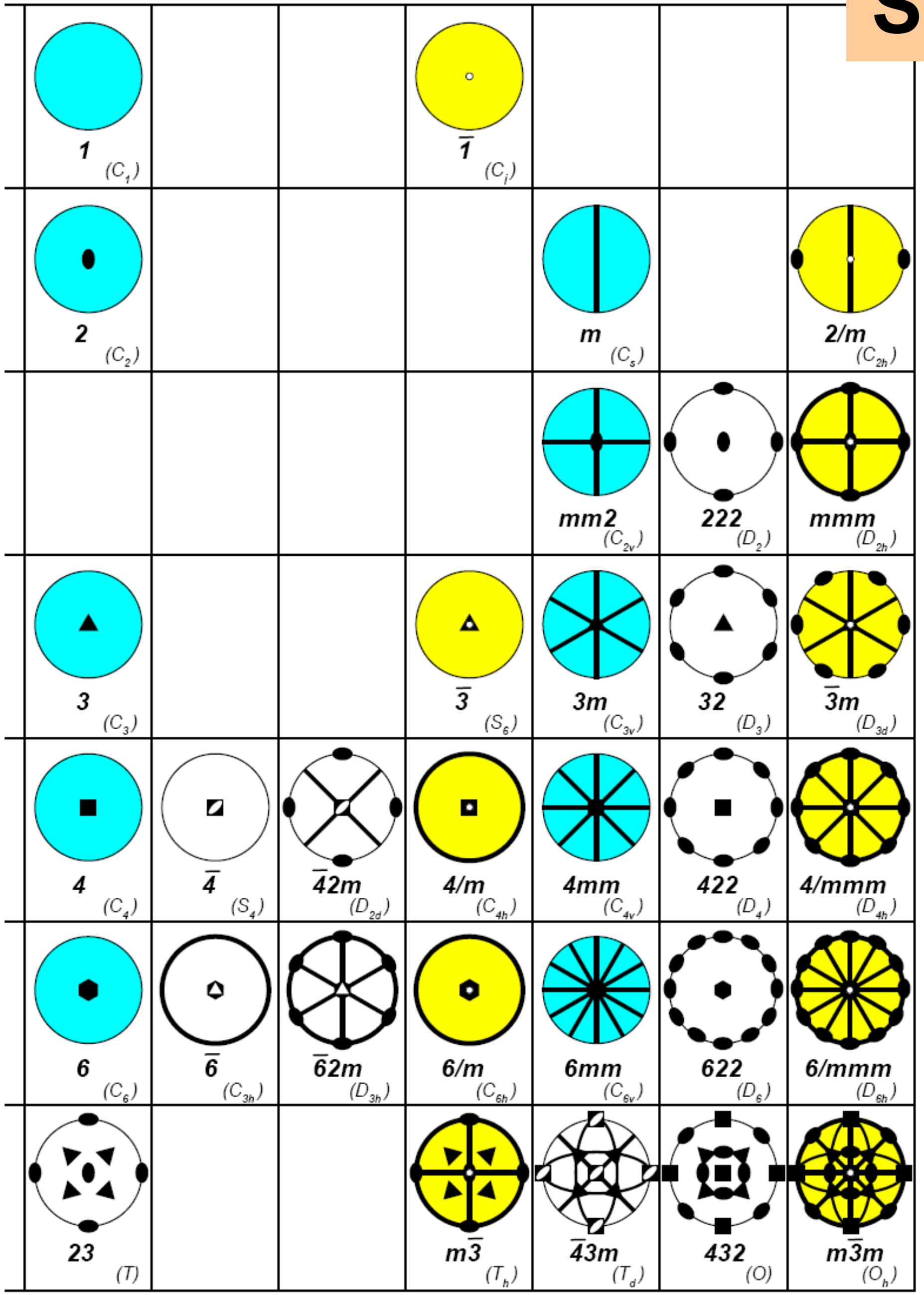
cubic crystal:

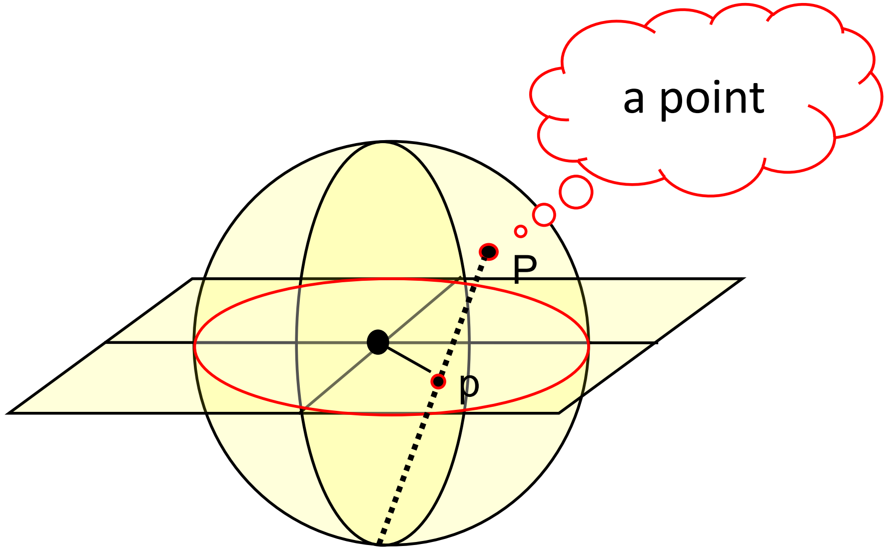


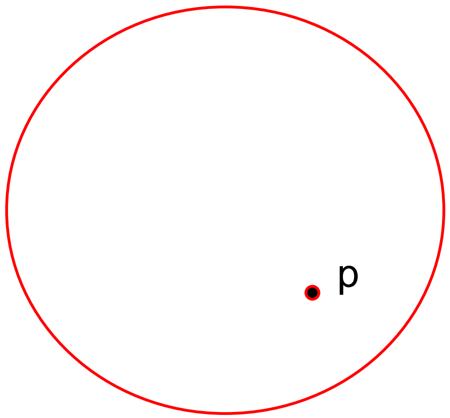
32 point groups



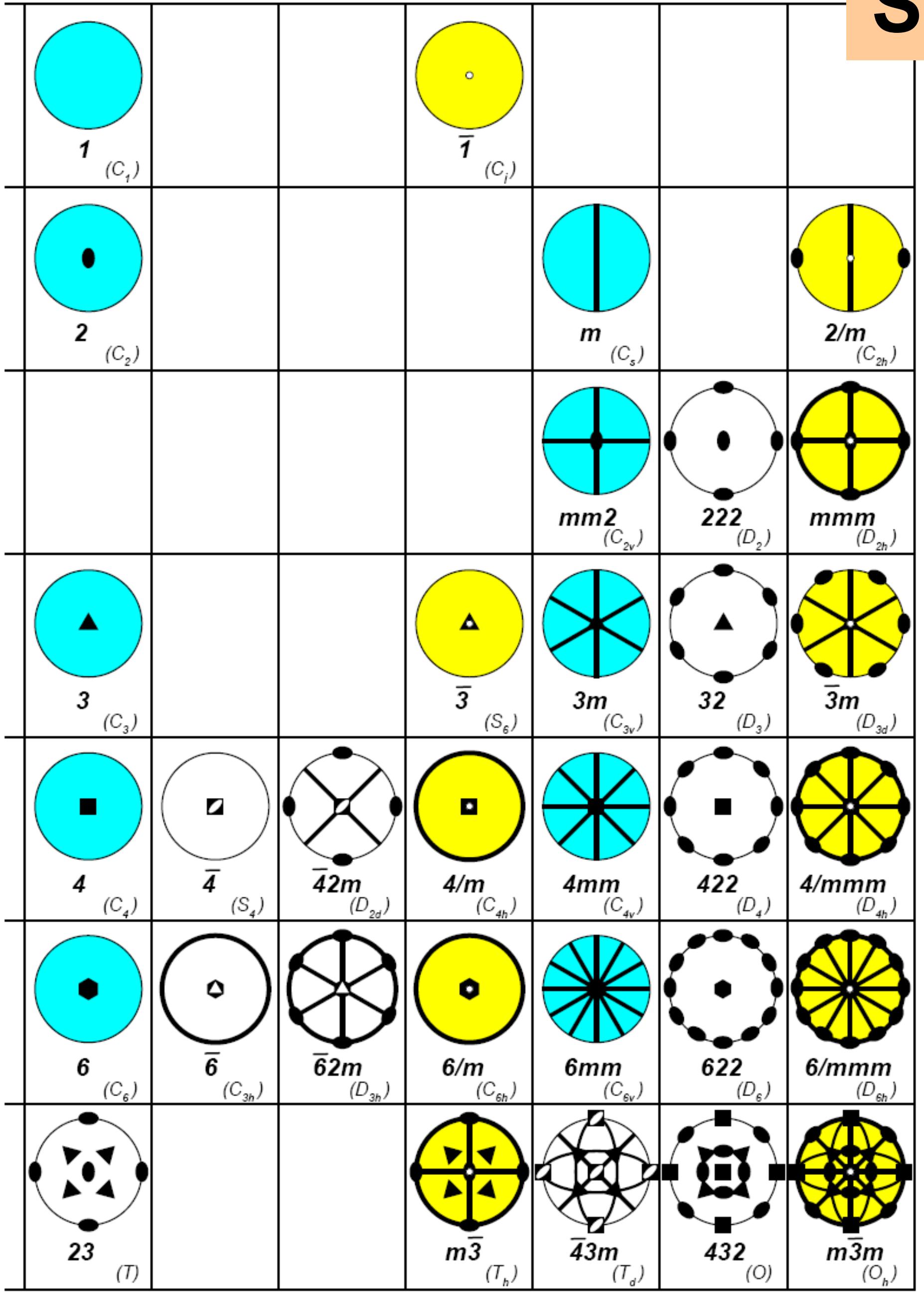
Stereographic projections

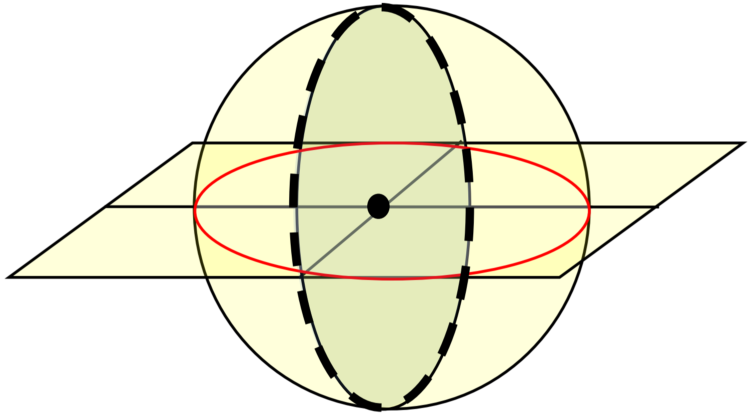


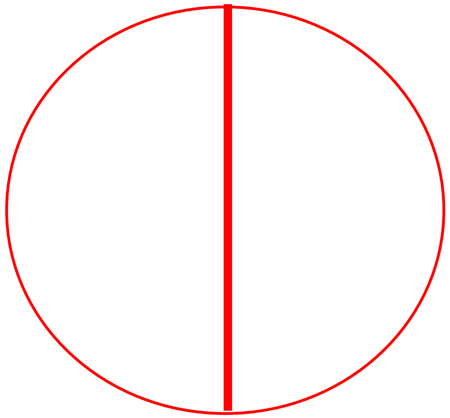




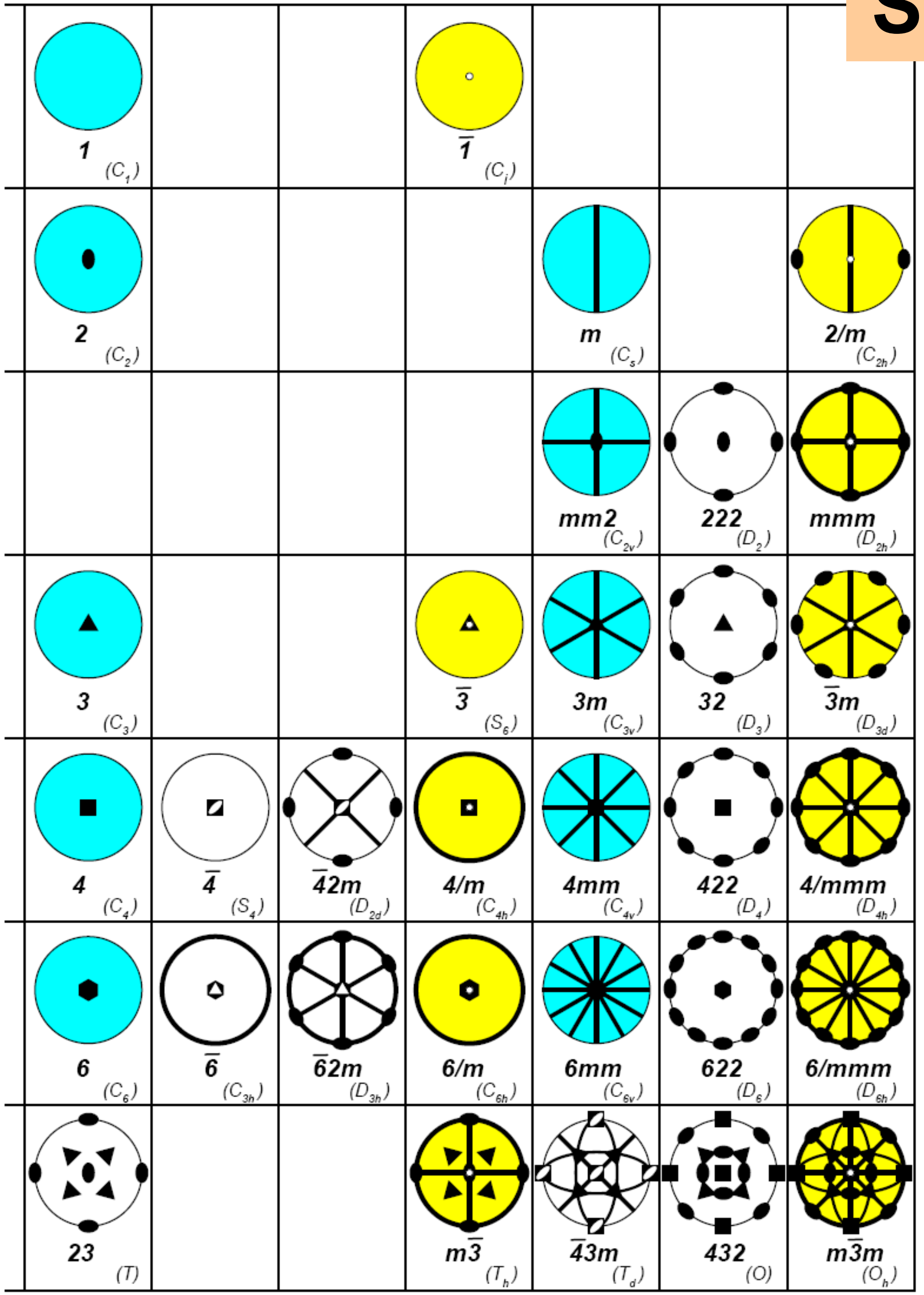
Stereographic projections

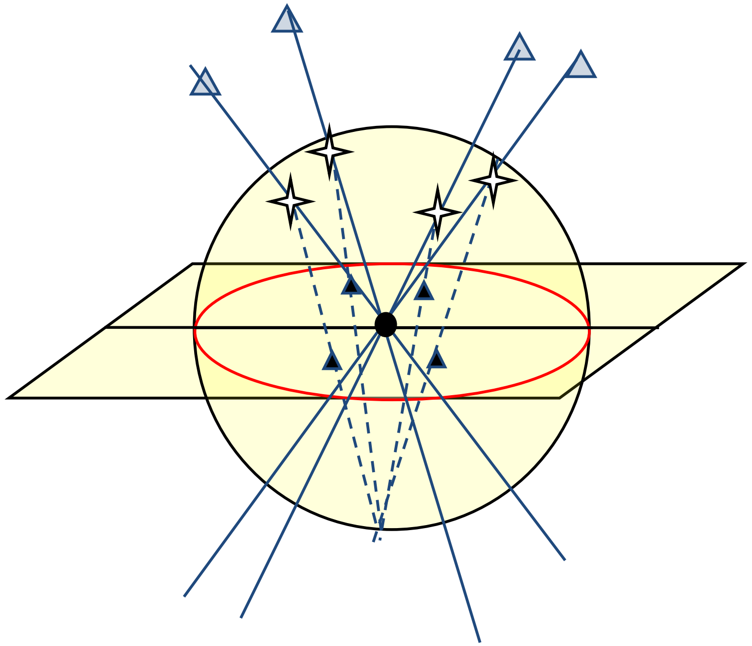


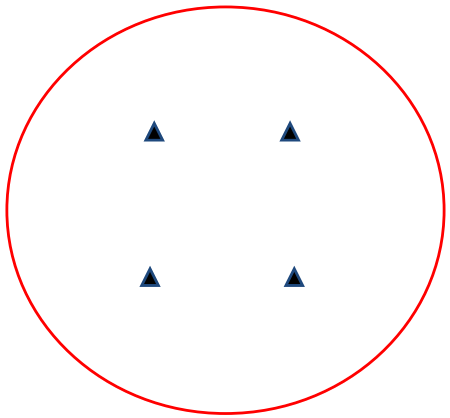




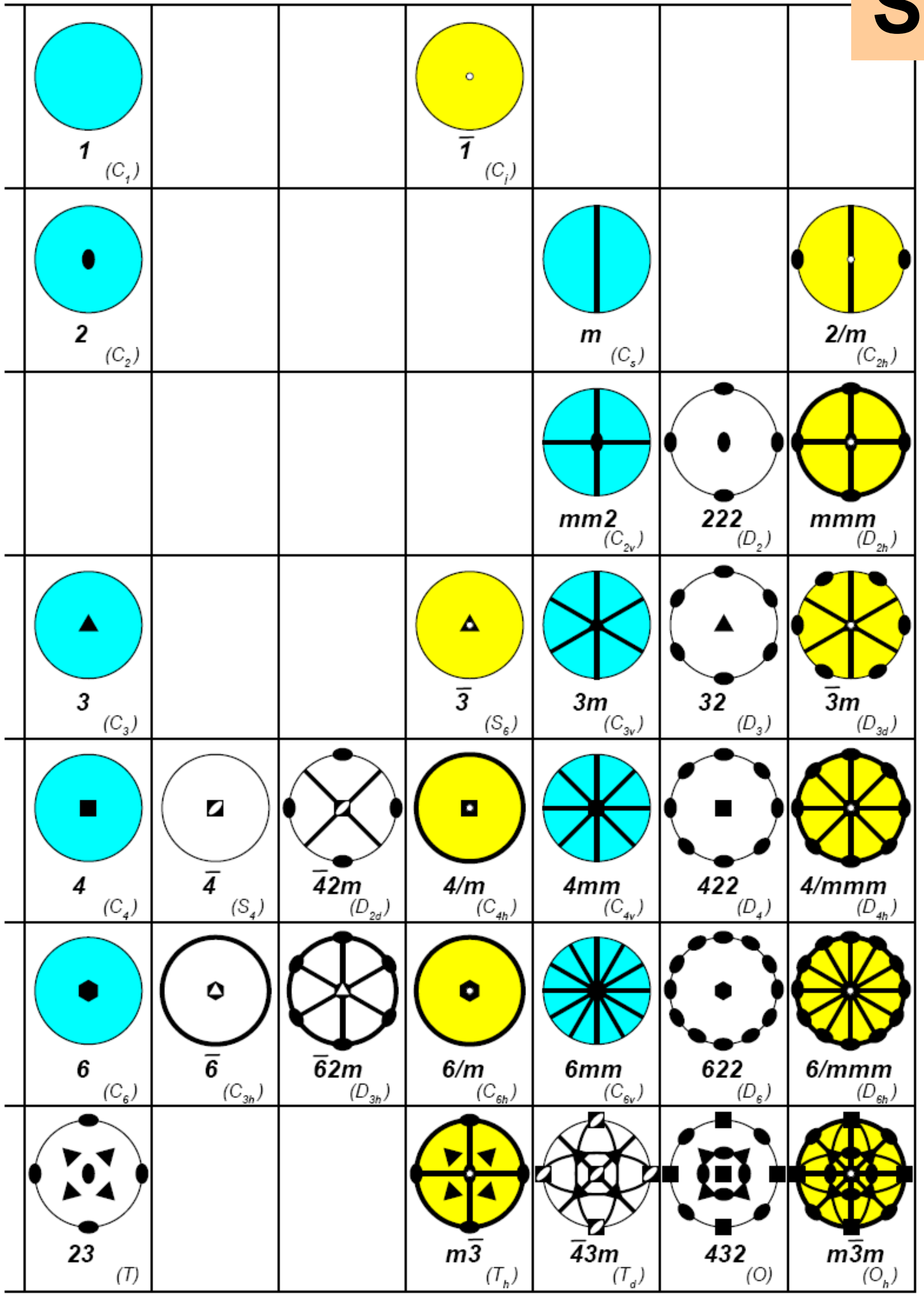
Stereographic projections



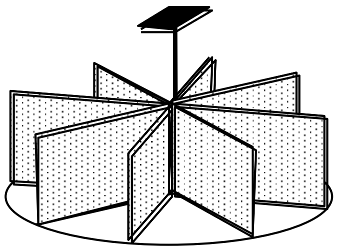




Stereographic projections



4mm, C_{4v}



Systems ↓ / Types →	Si	R/I	R/I-P	In	P	Ro	Su
Triclinic	1 (C_1)			$\bar{1}$ (C_i)			
Monoclinic	2 (C_2)				m (C_s)		2/m (C_{2h})
Orthorhombic					mm2 (C_{2v})	222 (D_2)	mmm (D_{2h})
Trigonal	3 (C_3)			$\bar{3}$ (S_6)	3m (C_{3v})	32 (D_3)	$\bar{3}m$ (D_{3d})
Tetragonal	4 (C_4)	$\bar{4}$ (S_4)	$\bar{4}2m$ (D_{2d})	4/m (C_{4h})	4mm (C_{4v})	422 (D_4)	4/mmm (D_{4h})
Hexagonal	6 (C_6)	$\bar{6}$ (C_{3h})	$\bar{6}2m$ (D_{3h})	6/m (C_{6h})	6mm (C_{6v})	622 (D_6)	6/mmm (D_{6h})
Cubic	23 (T)			$m\bar{3}$ (T_h)	$\bar{4}3m$ (T_d)	432 (O)	$m\bar{3}m$ (O_h)

Si = simple

R/I = inversion axes

R/I - P = inversion axes + planes

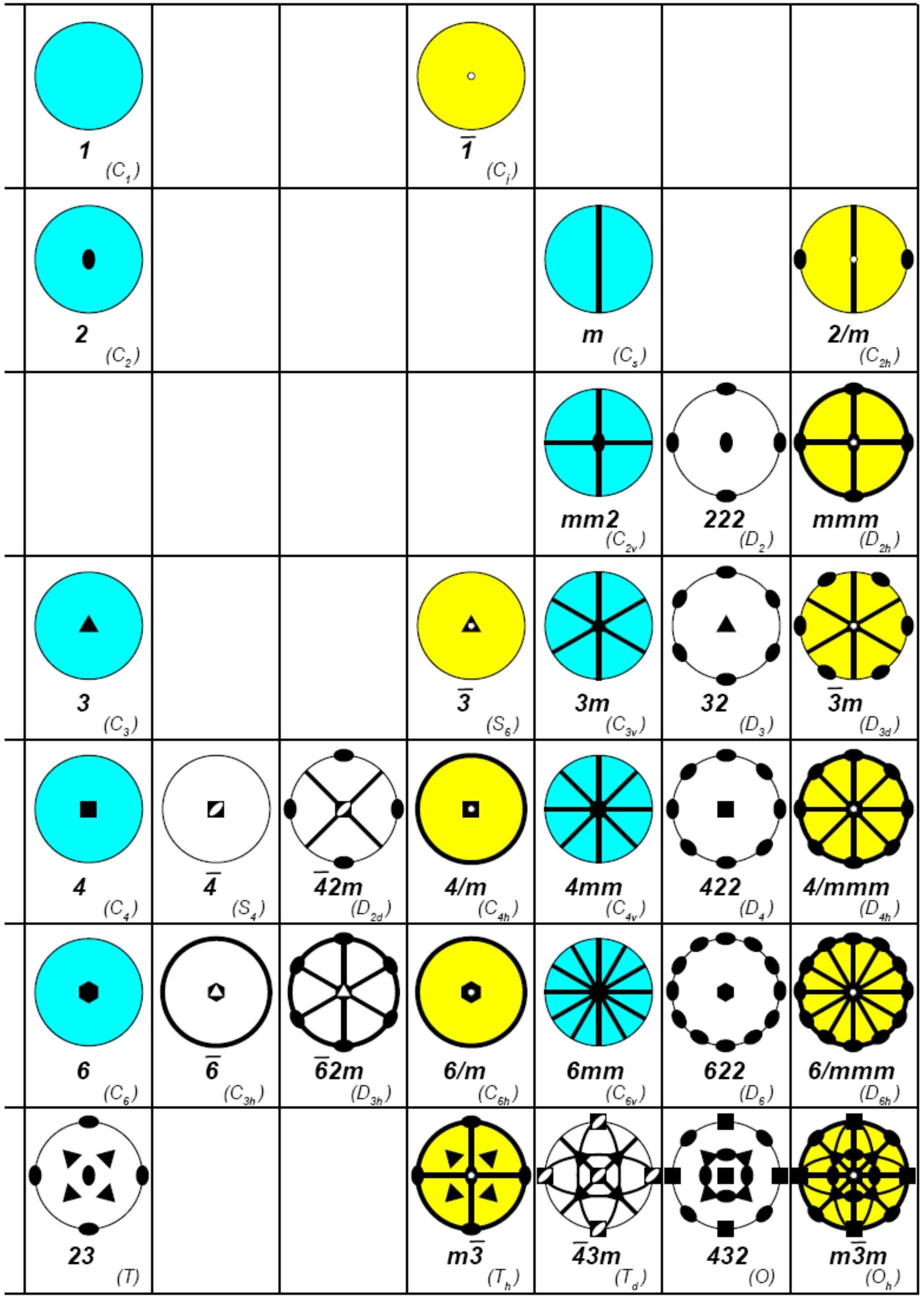
I = inversion

P = planes

Ro = rotations only

Su = super

Polarity

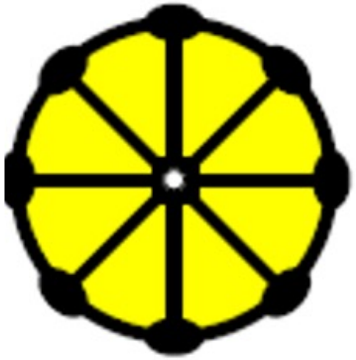


Centrosymmetric

Non-centrosymmetric
Non-polar

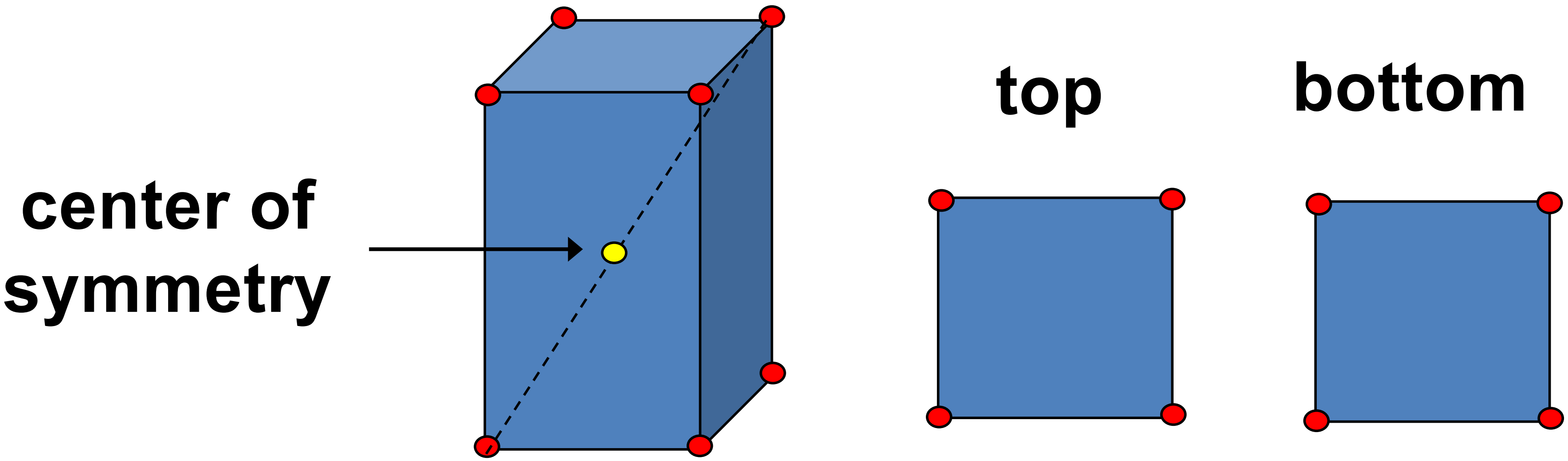
Non-centrosymmetric
Polar

4/mmm, D_{4h}

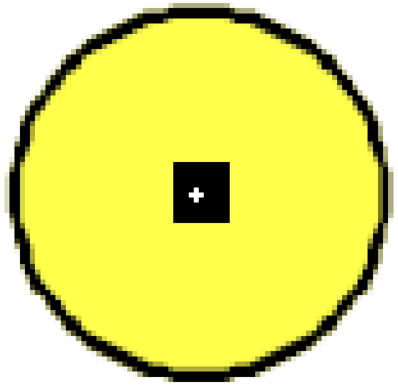


Tetragonal

Centrosymmetric

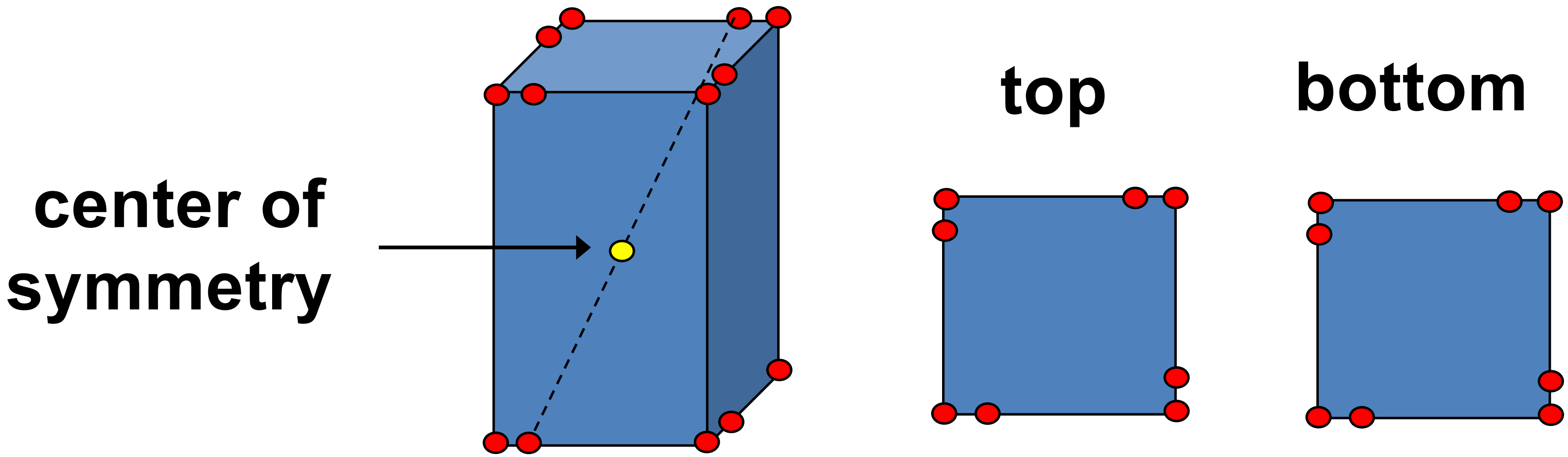


$4/m$, C_{4h}



Tetragonal

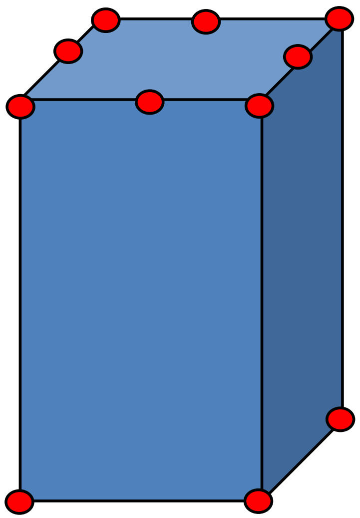
Centrosymmetric



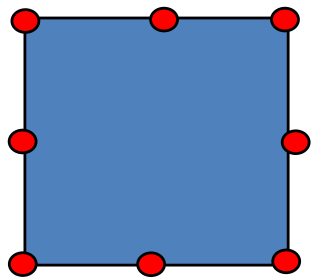
4mm, C_{4v}

Tetragonal

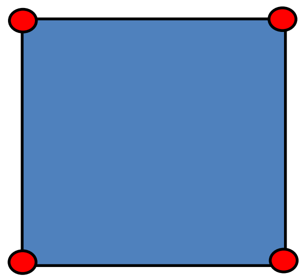
Non-centrosymmetric



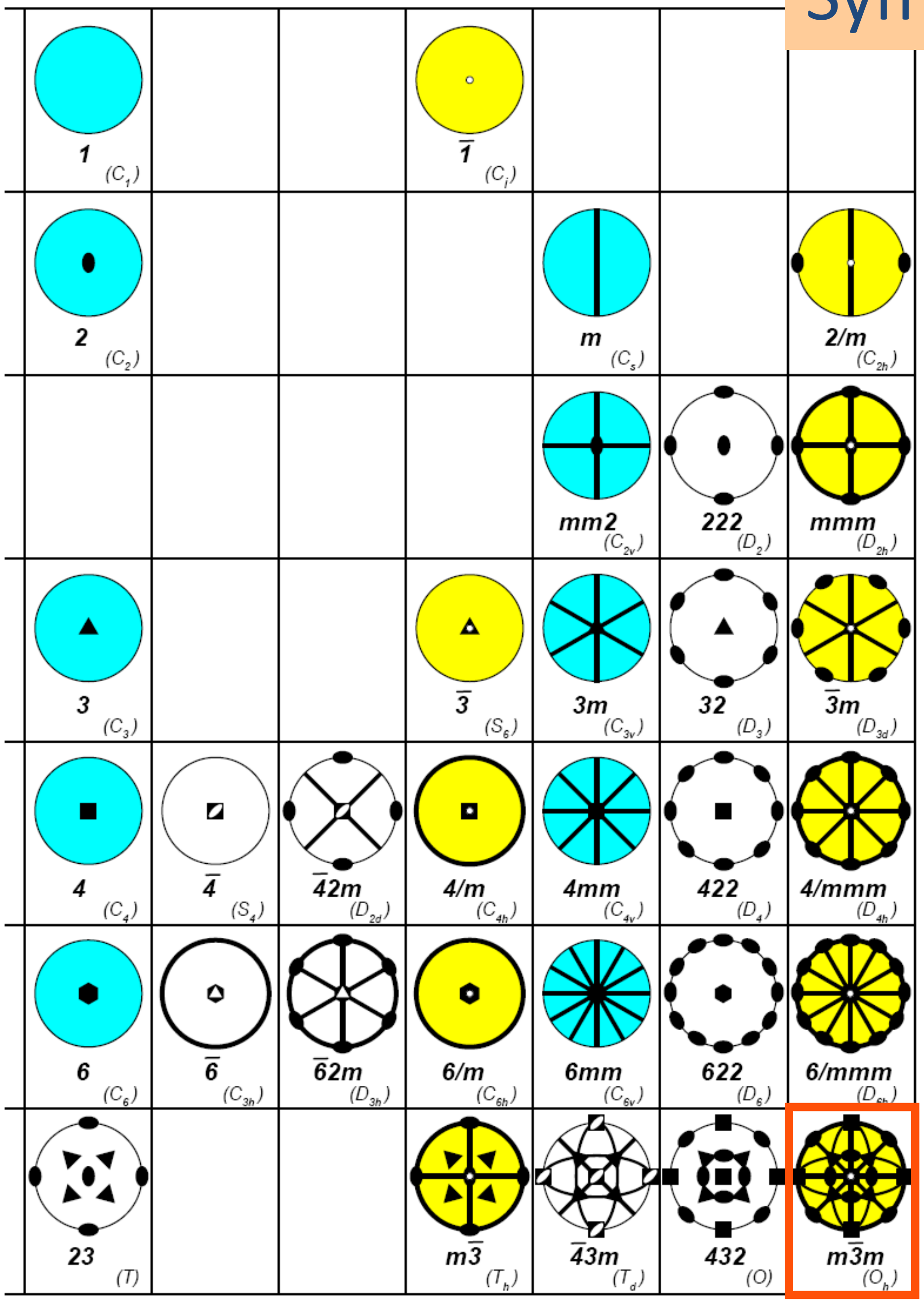
top

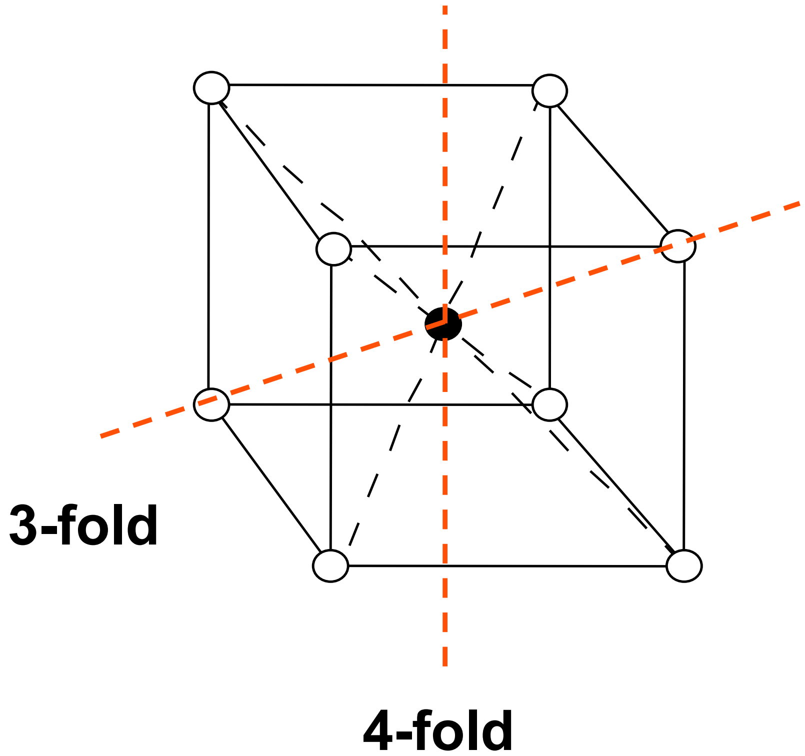


bottom



Symmetry of CsCl structure

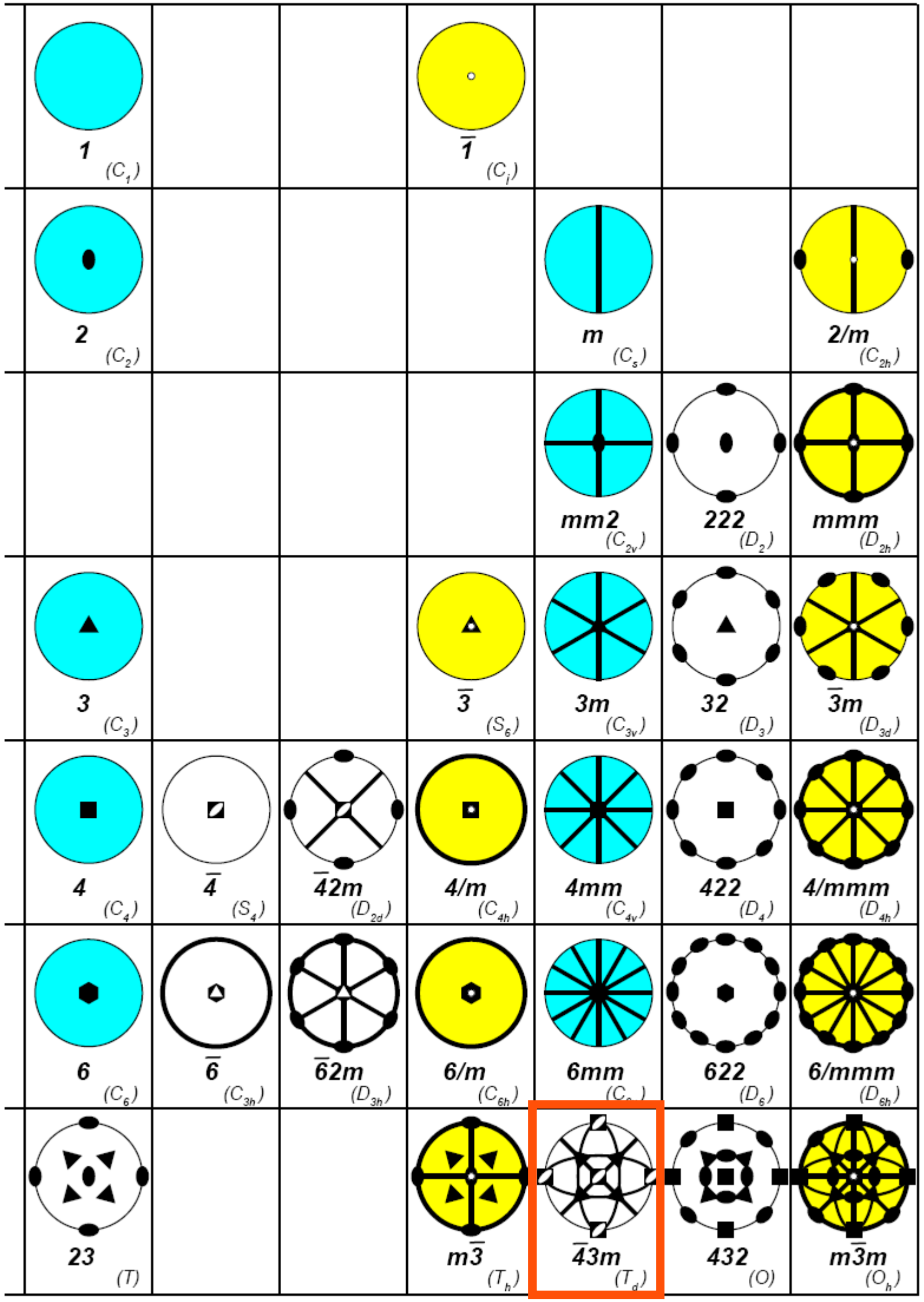


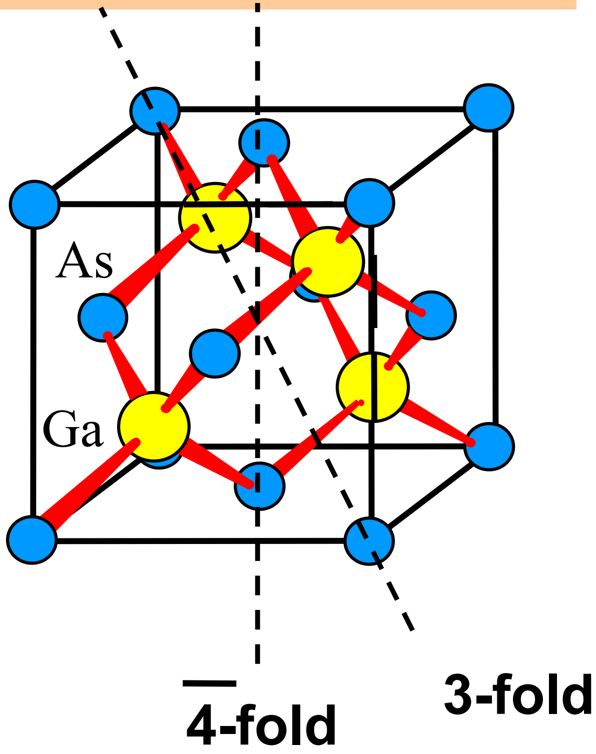


Cubic $m\bar{3}m$

Centrosymmetric

Symmetry of ZnS zinc blende structure





Cubic $\bar{4}3m$

Non-centrosymmetric

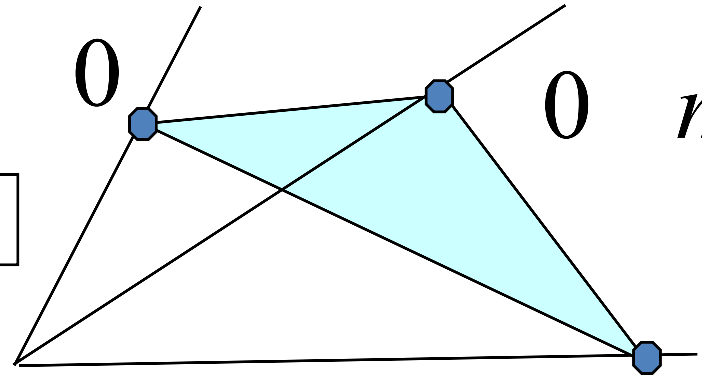
Miller indices for planes

Plane passing through points

$$\left(pa_1 \quad 0 \quad 0\right)$$

$$\left(0 \quad ma_2 \quad 0\right)$$

$$\left(0 \quad 0 \quad na_3\right)$$

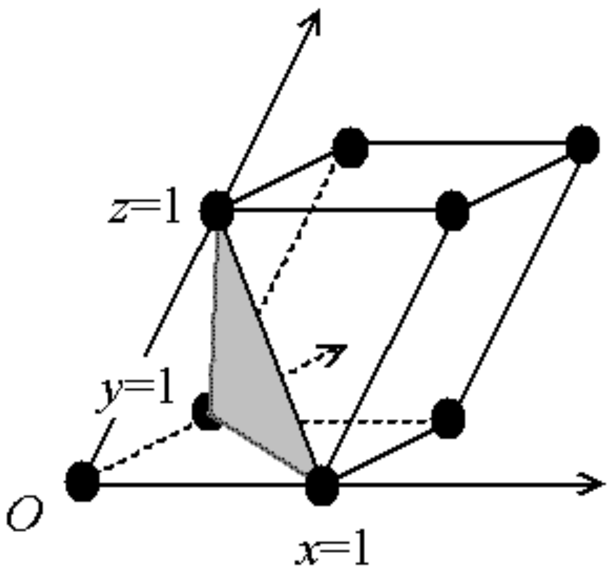


$$\left(h \quad k \quad l\right) = \left(\frac{b}{p} \quad \frac{b}{m} \quad \frac{b}{n}\right)$$

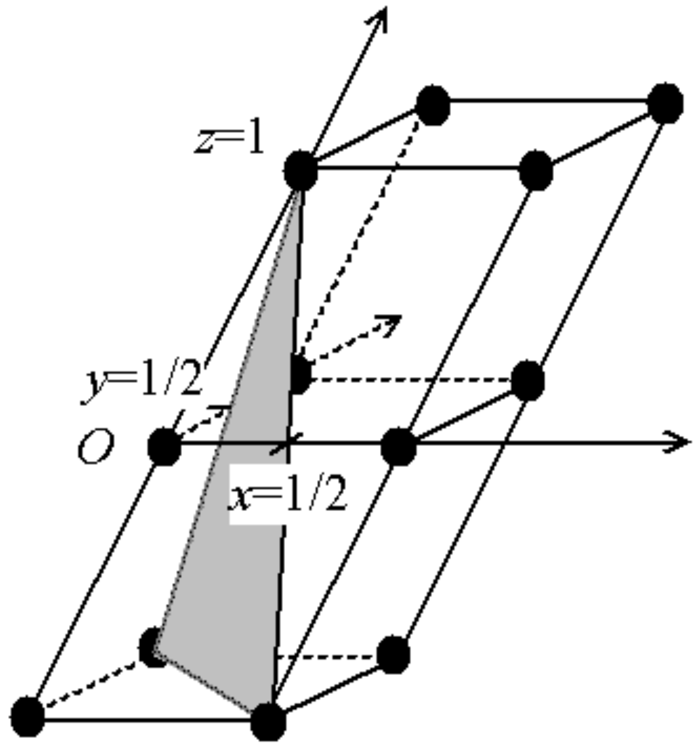
with <u>minimal</u> possible *b*

Miller indices for planes

plan (111)



plan (221)



Miller indices for directions

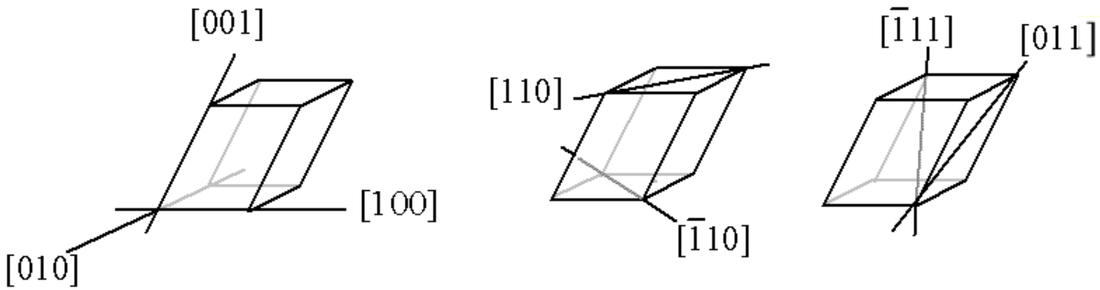
$$\vec{t} = p\vec{a}_1 + m\vec{a}_2 + n\vec{a}_3$$

$$\begin{bmatrix} h & k & l \end{bmatrix} = \begin{bmatrix} \frac{p}{b} & \frac{m}{b} & \frac{n}{b} \end{bmatrix}$$

$$-1 \Rightarrow \bar{1}$$

p, m, n, h, k, l, b **with <u>maximal</u> possible *b***

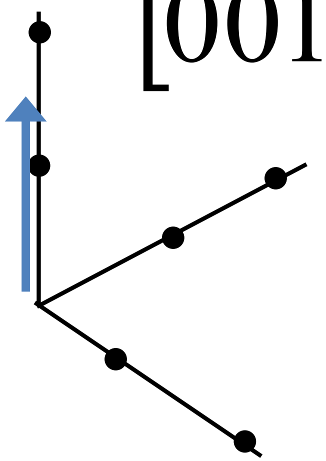
integer



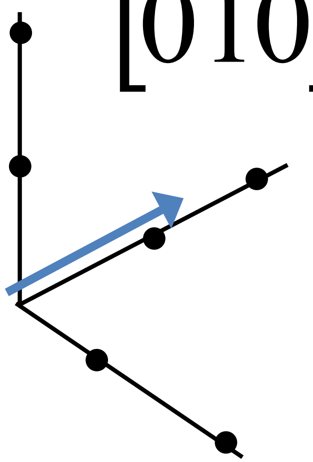
Miller indices for directions

***Directions equivalent by symmetry* =**
Directions that can be obtained from a given direction by application of the point symmetry operations of the structure

$[001]$



$[010]$



symmetry $m\bar{3}m$

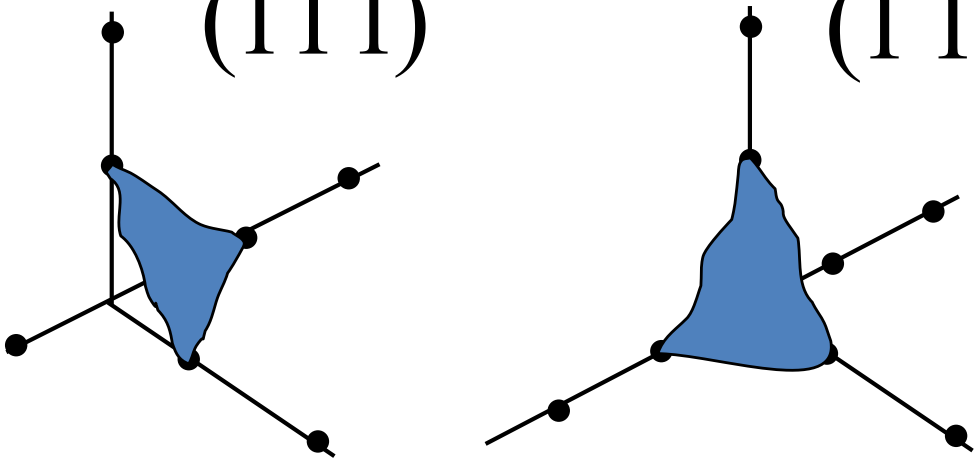
$[001]$
$[00\bar{1}]$
$[010]$
$[0\bar{1}0]$
$[100]$
$[\bar{1}00]$

$\langle 100 \rangle$

Miller indices for planes

Planes equivalent by symmetry **=**
Planes that can be obtained from a given plane by application of the point symmetry operations of the structure

(111) $(1\bar{1}1)$

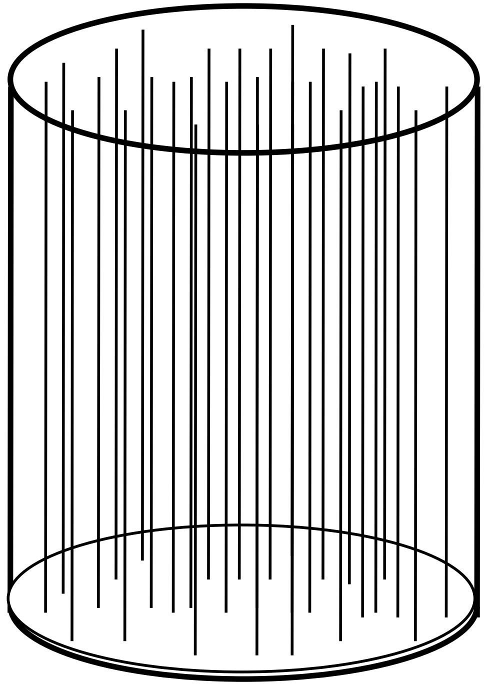


symmetry $m\bar{3}m$

(111)
$(1\bar{1}1)$
$(11\bar{1})$
$(\bar{1}11)$
$(\bar{1}\bar{1}1)$
$(\bar{1}1\bar{1})$
$(1\bar{1}\bar{1})$
$(\bar{1}\bar{1}\bar{1})$

$\{111\}$

Macroscopic symmetry of non-crystalline materials

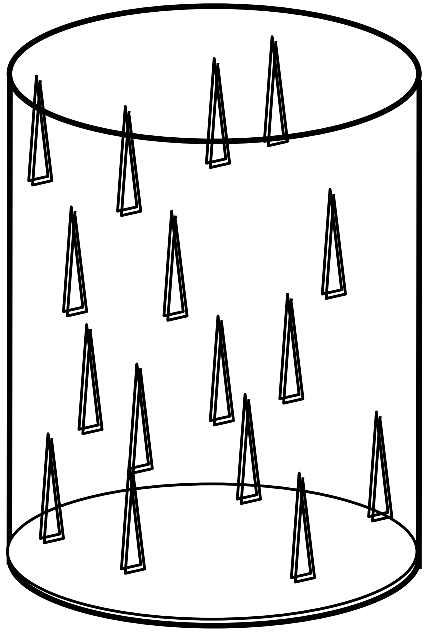


$$\frac{\infty}{m}m$$

Curie group

Symmetry operations link macroscopically indistinguishable states

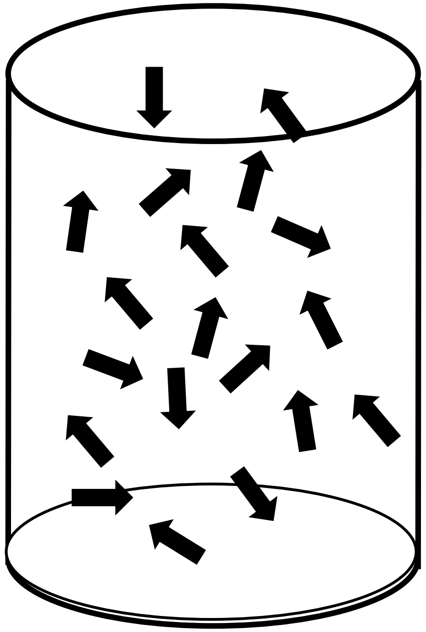
Macroscopic symmetry of non-crystalline materials



∞m **Curie group**

Symmetry operations link macroscopically indistinguishable states

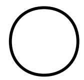
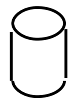
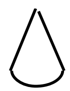
Macroscopic symmetry of non-crystalline materials



$\infty\infty m$ **Curie group**

Symmetry operations link macroscopically indistinguishable states

Macroscopic symmetry of non-crystalline materials

Curie group	**Geometrical bodies**	
$\infty\infty m$		**sphere**
∞ / mm		**cylinder**
∞m		**cone**

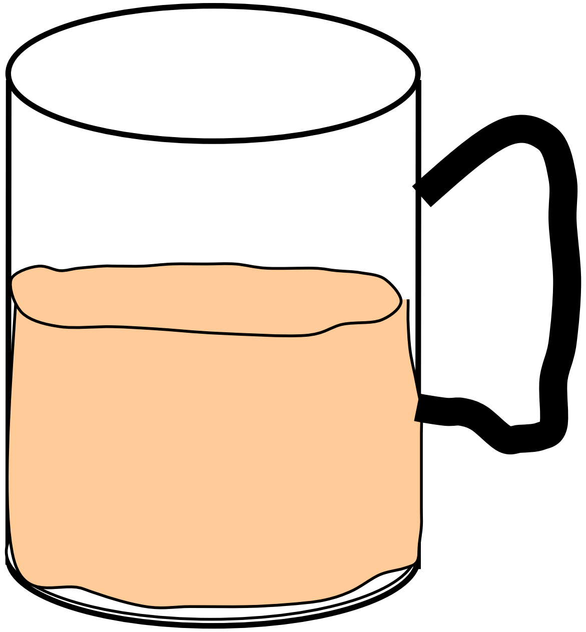
$\infty\infty$ ∞

$\infty 2$ ∞ / m

?

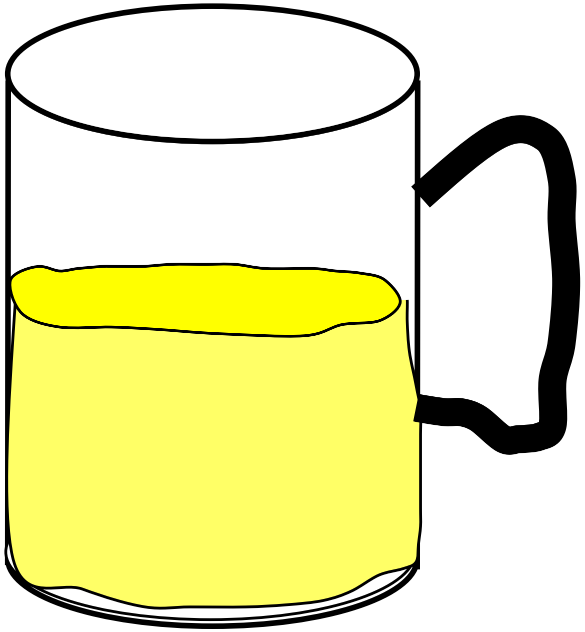
Macroscopic symmetry of non-crystalline materials

$\infty\infty m$



tee without sugar

$\infty\infty$



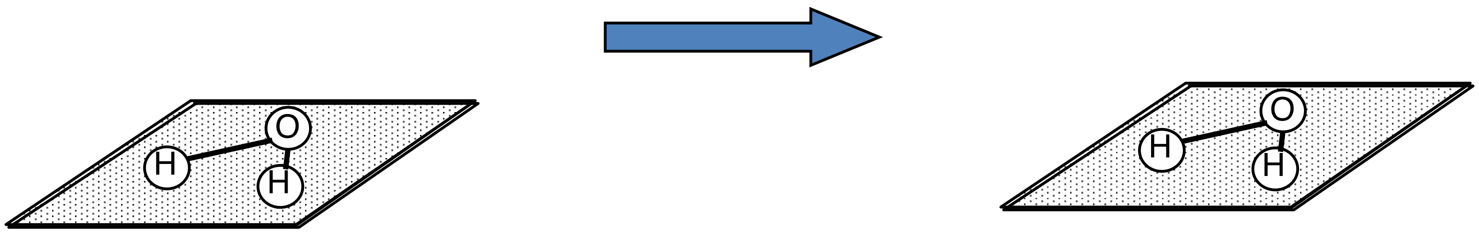
tee with sugar

Macroscopic symmetry of non-crystalline materials

molecular water

H_20

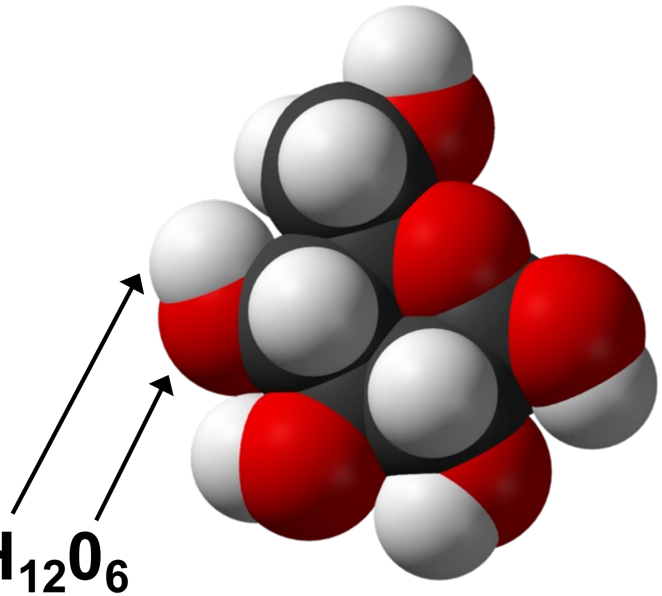
mirror image



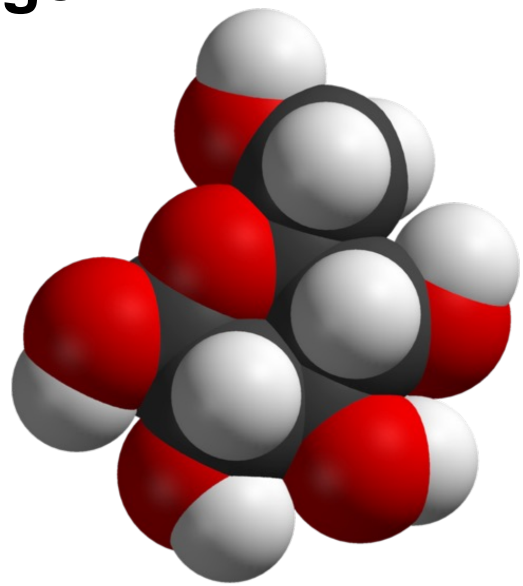
water **water**

Sugar (D-glucose)

mirror image



$C_6H_{12}0_6$



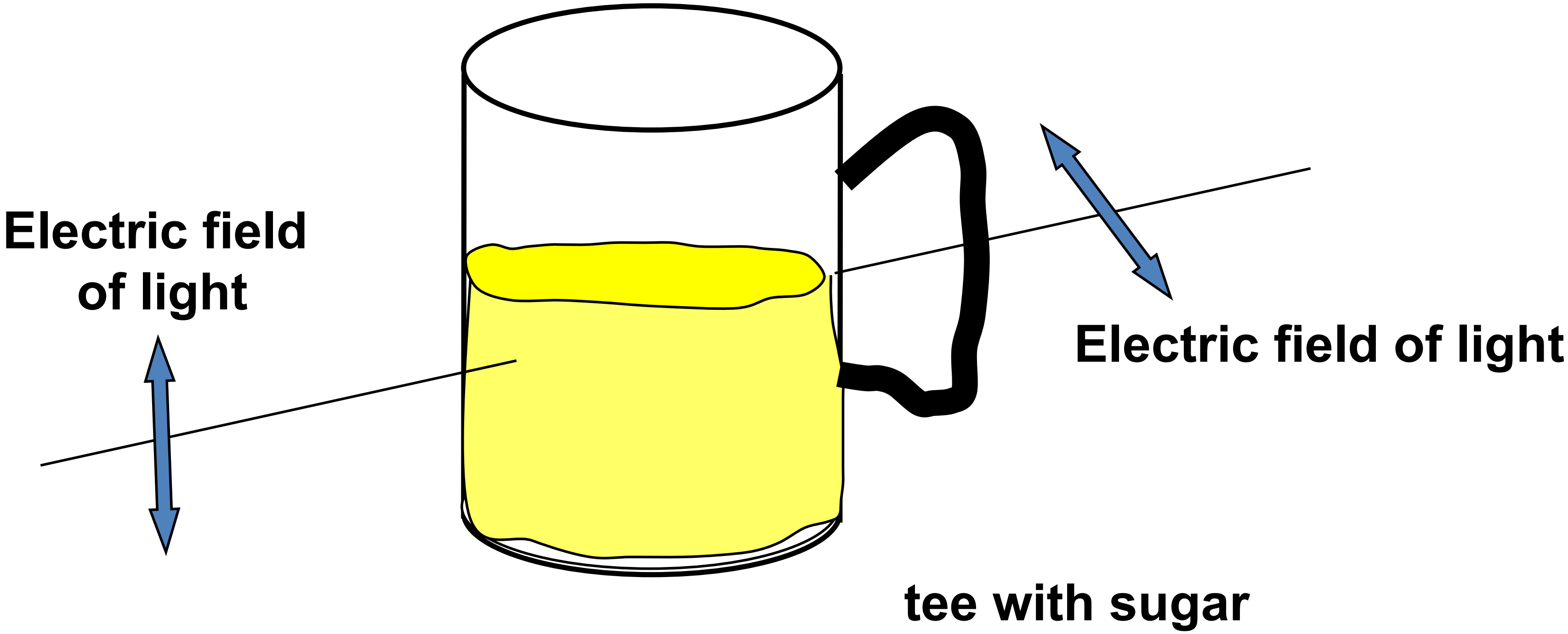
D-glucose sweet

L-glucose bitter

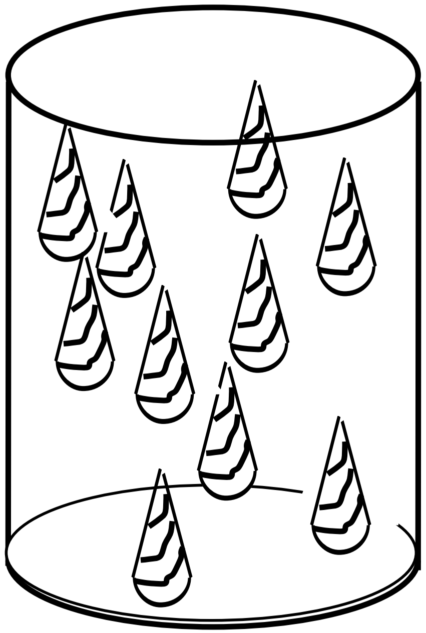
Macroscopic symmetry of non-crystalline materials

$\infty\infty m - \infty\infty$ **difference may have important consequences**

$\infty\infty$ **materials are optically active**

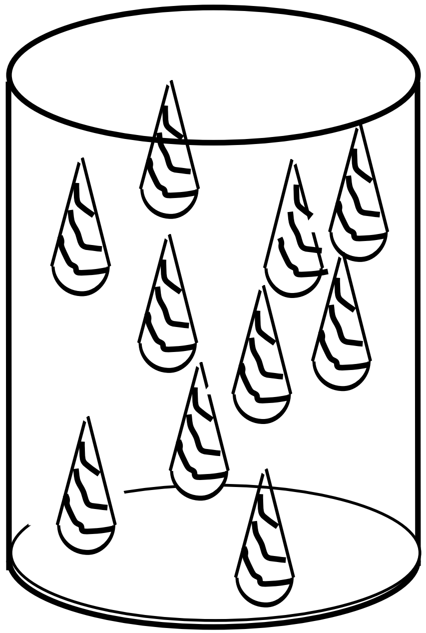


Macroscopic symmetry of non-crystalline materials



∞_R

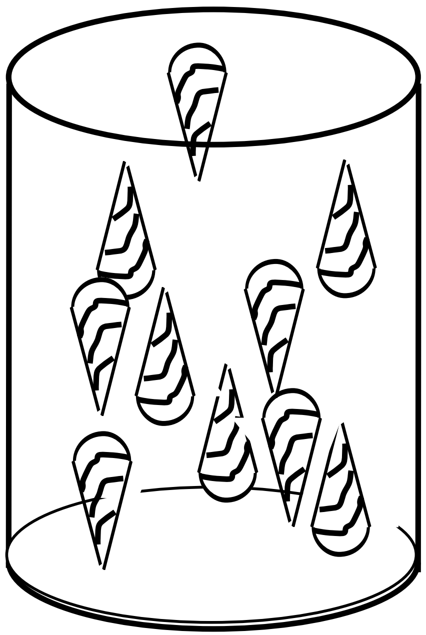
Right-handed screws, tips up



∞_L

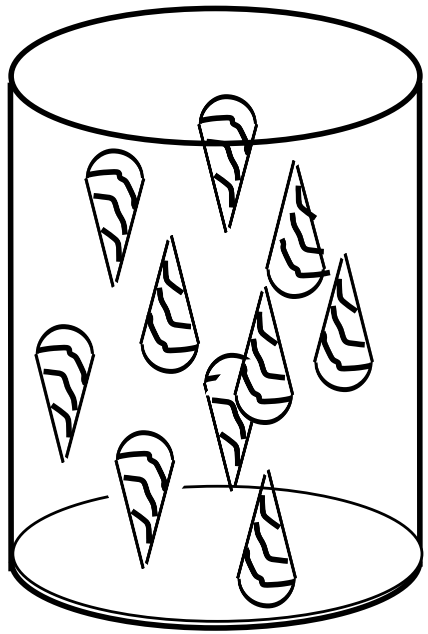
left-handed screws, tips up

Macroscopic symmetry of non-crystalline materials



$\infty 2_R$

Right-handed screws,
50% tips up+ 50% tips down



$\infty 2_L$

Left-handed screws,
50% tips up+ 50% tips down

Macroscopic symmetry of non-crystalline materials

Crystalline vs. non-crystalline group relation

$$2, 3, 4, 6 \quad \Rightarrow \quad \infty$$

$$222, 32, 422, 622 \quad \Rightarrow \quad \infty 2$$

$$mm2, 3m, 4mm, 6mm \quad \Rightarrow \quad \infty m$$

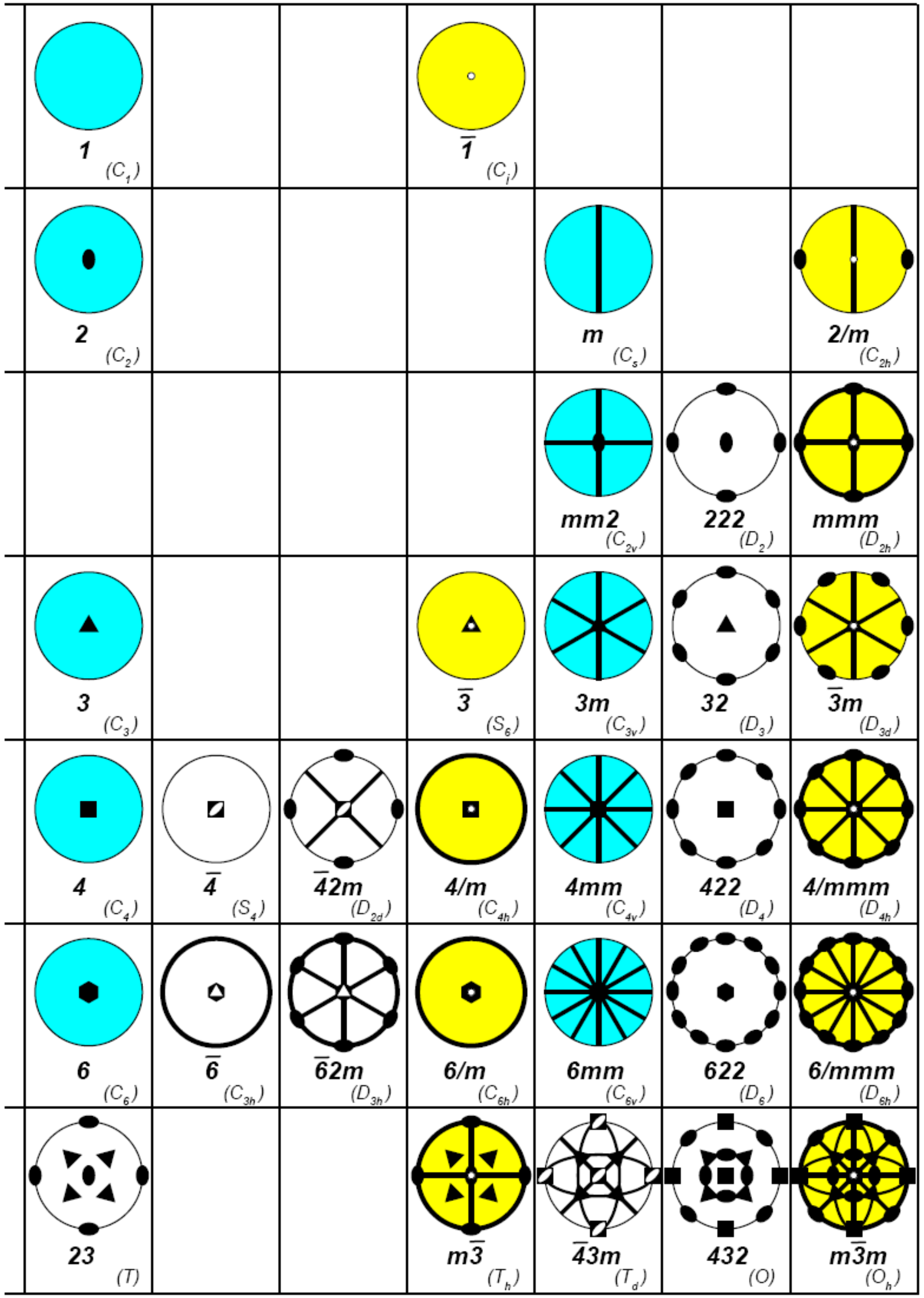
$$2/m, \bar{6}, 4/m, 6/m \quad \Rightarrow \quad \infty / m$$

$$mmm, 4/mmm, 6/mmm \quad \Rightarrow \quad \infty / mm$$

Essential I

MICroscopic symmetry	MACroscopic symmetry
230 space groups	**32 point crystallographic groups** **+** **7 Curie groups**

-Additional literature for basics of crystallography: “The basics of Crystallography and Diffraction” (Ch. Hammond)



Essential II

Centrosymmetric

Non-centrosymmetric
Non-polar

Non-centrosymmetric
Polar