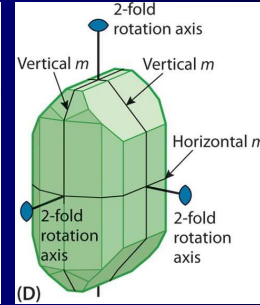
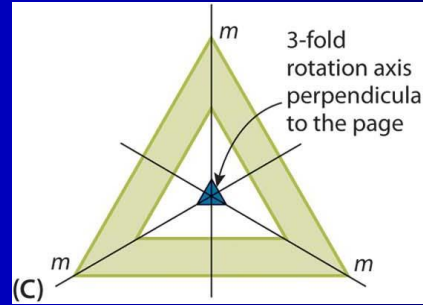
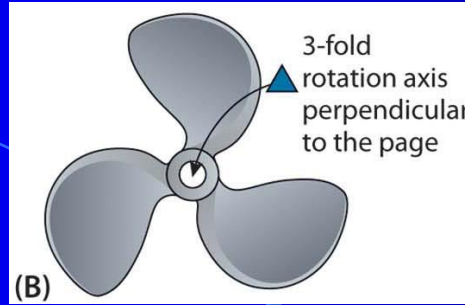
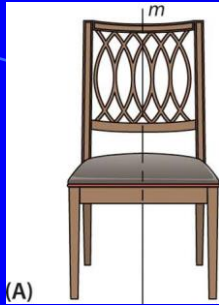


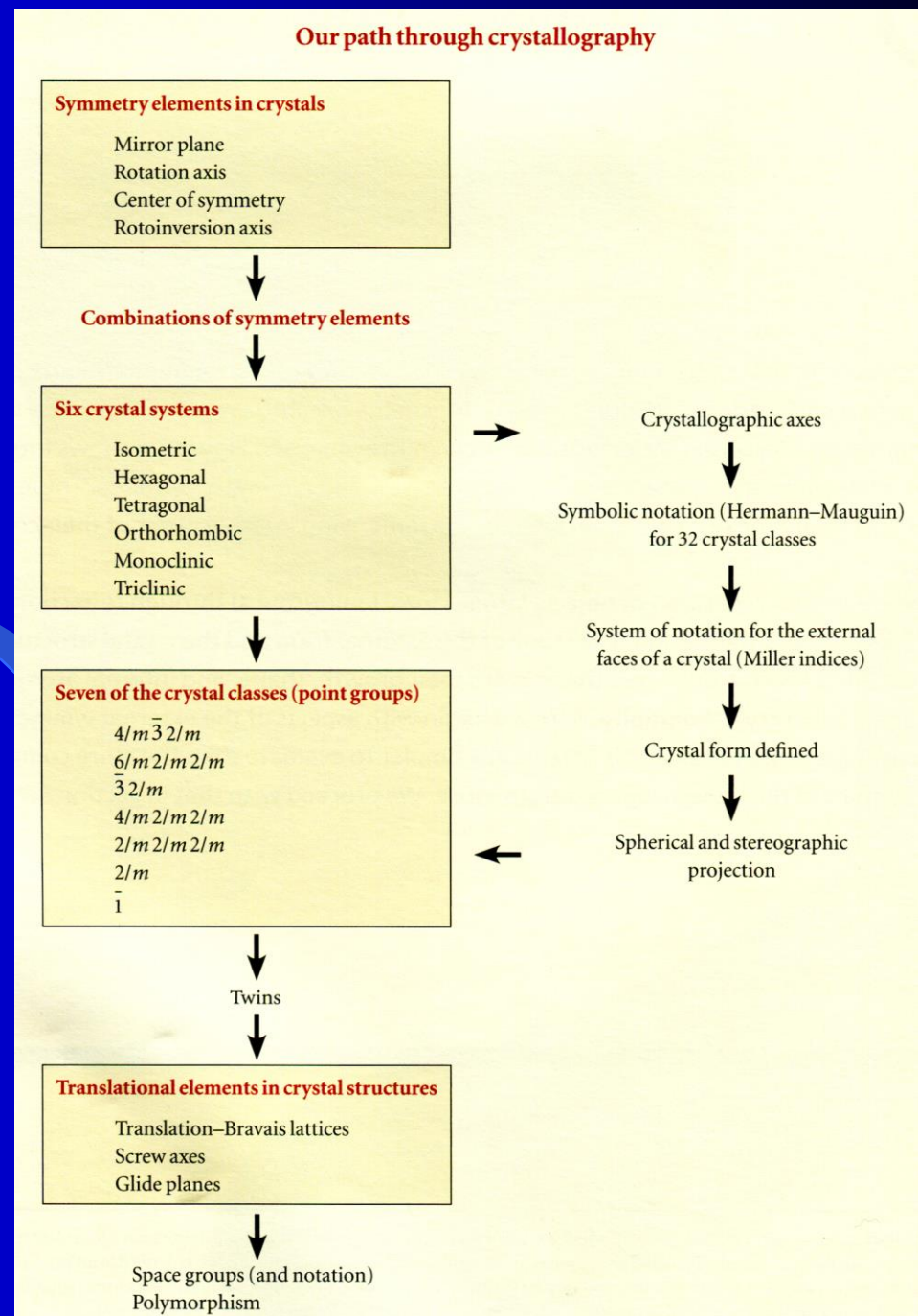
# Earth Materials I

## Crystallography



**Symmetry** – repetition of objects (atoms, ions, ionic groups) through reflection, rotation, inversion, and translation

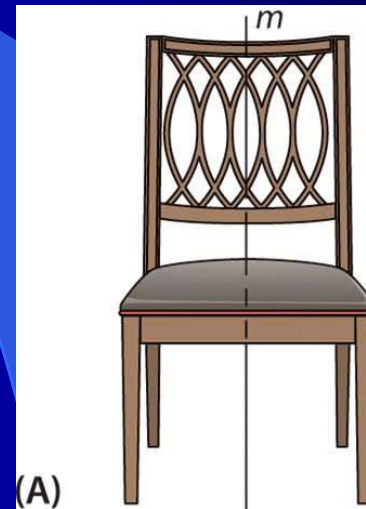
**Crystallography** – study of the external form and the crystal structure of crystalline solids and the principles that govern their growth, shape, and internal atomic arrangement.



**Symmetry Element** – geometric feature that expresses the symmetry of an ordered arrangement.

<b>Element</b>	<b>Operation</b>
<b>Mirror Plane (<math>m</math>)</b>	Reflection through a plane
<b>Rotation axis</b>	Rotation about an axis by some fraction $360^\circ/n$ , where $n = 1, 2, 3, 4,$ or $6$ .
<b>Center of symmetry (<math>i</math>)</b>	Inversion through a point
<b>Rotoinversion axis</b>	Rotation with inversion

**Mirror** – reflect an object, or a specific crystal face, or a unit of structure into its mirror image.



**Rotation axis** – an imaginary line about which an object, or a crystal face, or an atomic arrangement is rotated and repeats itself.

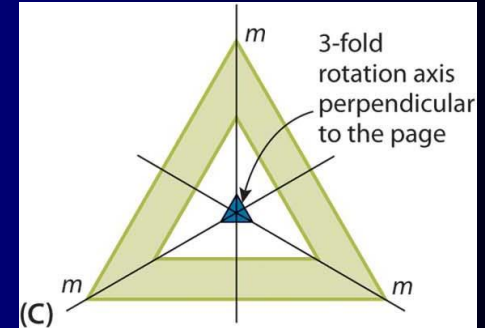
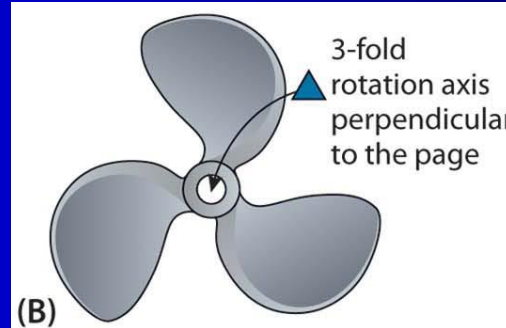
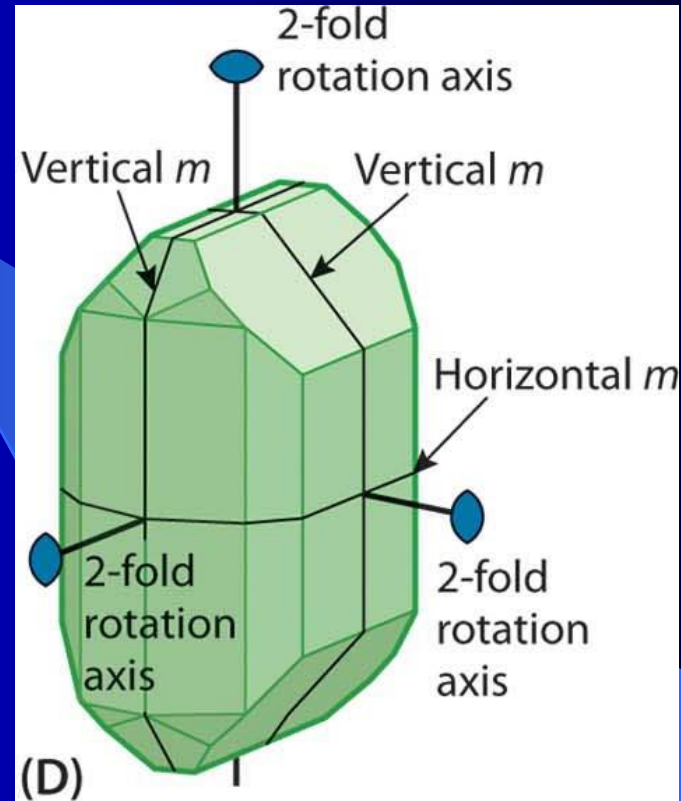
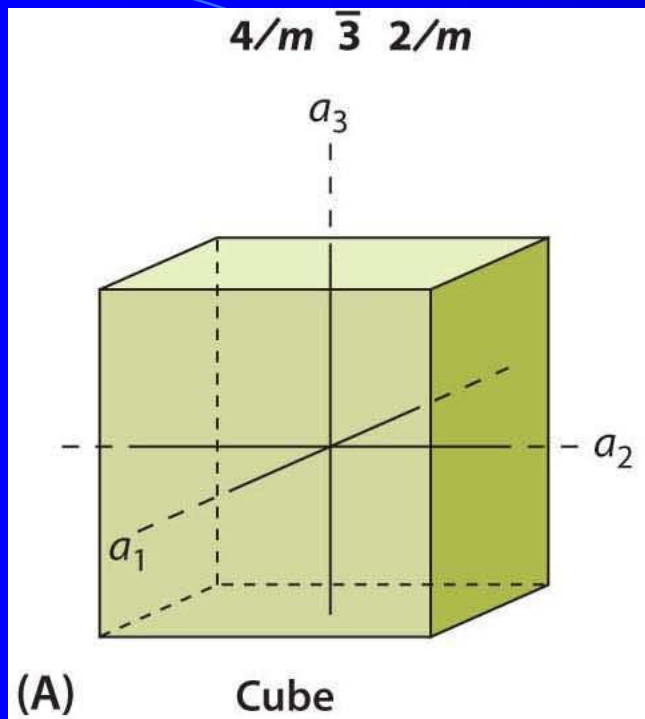


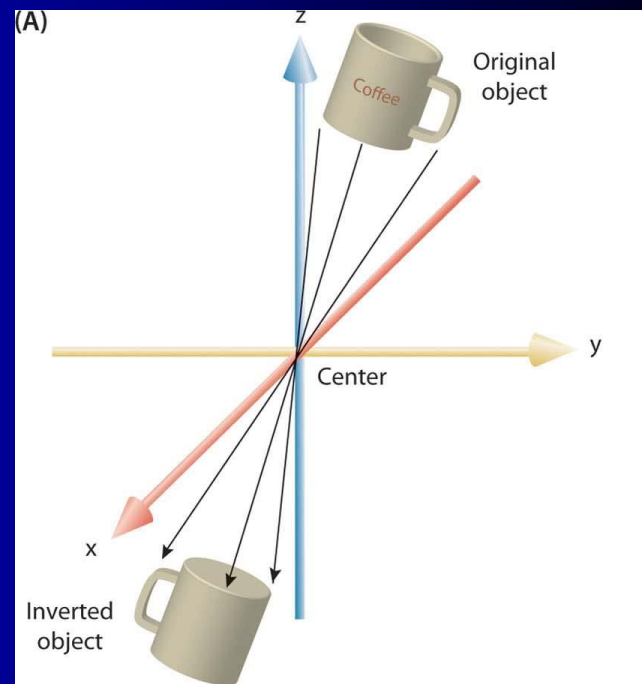
Illustration of mirror planes and rotation axes for a crystalline form.



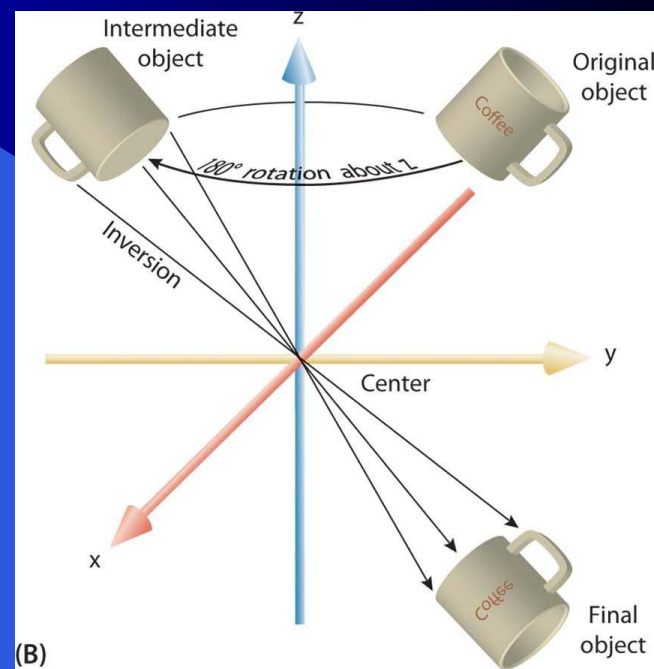
Center of symmetry










Inversion



Rotoinversion



Type of rotation axis	Angle of rotation	Symbol or letter
1-fold rotation = 1	360°	none
2-fold rotation = 2	180°	
3-fold rotation = 3	120°	
4-fold rotation = 4	90°	
6-fold rotation = 6	60°	
1-fold rotoinversion = $\bar{1}^a$	360°	$i^a$
2-fold rotoinversion = $\bar{2}^b$	180°	$m^b$
3-fold rotoinversion = $\bar{3}^c$	120°	
4-fold rotoinversion = $\bar{4}$	90°	
6-fold rotoinversion = $\bar{6}^d$	60°	

<sup>a</sup> $i$  = inversion, which is equivalent to a center of symmetry.

<sup>b</sup> $m$  = mirror;  $m$  is used instead of  $\bar{2}$  in the description of the symmetry of crystals.

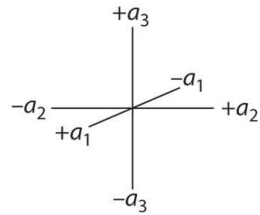
<sup>c</sup> $\bar{3}$  is equivalent to a 3-fold rotation axis in combination with a center of symmetry ( $i$ ).

<sup>d</sup> $\bar{6}$  is equivalent to a 3-fold rotation axis with a mirror perpendicular to it; expressed as  $3/m$ .

**Table 5.1** A listing of all possible symmetry contents (32 of these), their representation in Hermann-Mauguin notation, and their grouping into six crystal systems. The 32 symmetry combinations are known as crystal classes as well as point groups. *R* means rotation axis. The subscript refers to 1, 2, 3, 4, and 6-fold rotation. *m* represents mirrors, and *i* = inversion (center of symmetry).

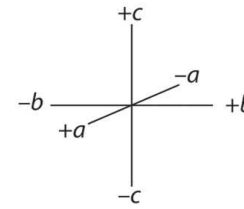
Symmetry content	Crystal class(in Hermann-Mauguin notation; see Box 5.1)	Crystal system	
$3R_4, 4\bar{R}_3, 6R_2, 9m$	$4/m \bar{3} 2/m$	Isometric	
$(1\bar{R}_3 = 1R_3 + i)$			
$\bar{3}\bar{R}_4, 4R_3, 6m$	$\bar{4} 3 m$		
$3R_4, 4R_3, 6R_2$	$4 3 2$		
$3R_2, 3m, 4\bar{R}_3$	$2/m \bar{3}$		
$(1\bar{R}_3 = 1R_3 + i)$			
$3R_2, 4R_3$	$23$		
$1R_6, 6R_2, 7m, i$	$6/m 2/m 2/m$		Hexagonal*
$1\bar{R}_6, 3R_2, 3m$	$\bar{6} m 2$		
$(1\bar{R}_6 = R_3 + m \text{ perpendicular})$			
$1R_6, 6m$	$6 mm$		
$1R_6, 6R_2$	$622$		
$1R_6, 1m, i$	$6/m$		
$1\bar{R}_6 (= 1R_3 + m \text{ perpendicular})$	$\bar{6}$		
$1R_6$	$6$		
$1\bar{R}_3, 3R_2, 3m$	$\bar{3} 2/m$		
$(1\bar{R}_3 = 1R_3 + i)$			
$1R_3, 3m$	$3m$		
$1R_3, 3R_2$	$32$		
$1\bar{R}_3 (= 1R_3 + i)$	$\bar{3}$		
$1R_3$	$3$		
$1R_4, 4R_2, 5m, i$	$4/m 2/m 2/m$	Tetragonal	
$1\bar{R}_4, 2R_2, 2m$	$\bar{4} 2m$		
$1R_4, 4m$	$4mm$		
$1R_4, 4R_2$	$422$		
$1R_4, m, i$	$4/m$		
$1\bar{R}_4$	$\bar{4}$		
$1R_4$	$4$		
$3R_2, 3m, i$	$2/m 2/m 2/m$	Orthorhombic	
$1R_2, 2m$	$m m 2$		
$3R_2$	$2 2 2$		
$1R_2, 1m, i$	$2/m$	Monoclinic	
$1m$	$m$		
$1R_2$	$2$	Triclinic	
$i$	$\bar{1}$		
$R_1$	no symmetry		

### Isometric



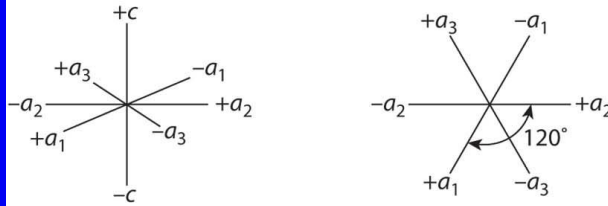
$a_1 = a_2 = a_3$ ; all axes  
at  $90^\circ$  to each other

### Orthorhombic



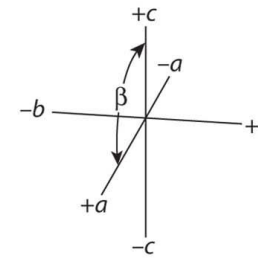
$a \neq b \neq c$ ;  
all axes at  $90^\circ$  to each other

### Hexagonal



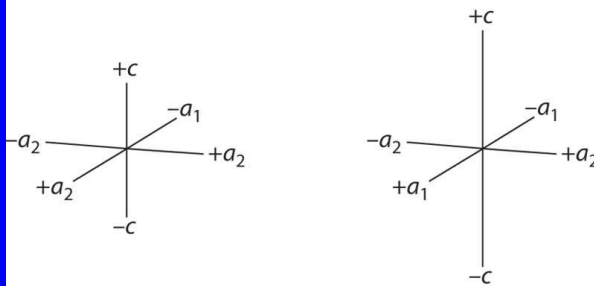
$a_1 = a_2 = a_3$ ; intersecting at  $120^\circ$   
c perpendicular to plane with  $a_1, a_2, a_3$

### Monoclinic



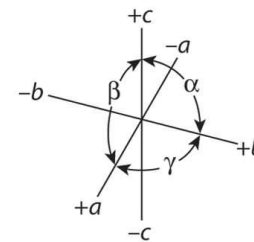
$a \neq b \neq c$   
 $\beta > 90^\circ$ ;  $\alpha = \gamma = 90^\circ$

### Tetragonal



$a = b \neq c$ ;  $a = a_1$ ;  $b = a_2$ ;  
all axes at  $90^\circ$  to each other

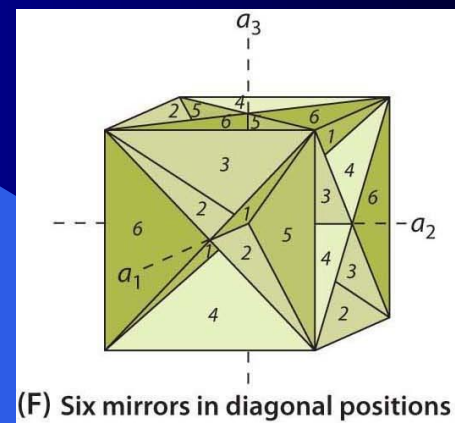
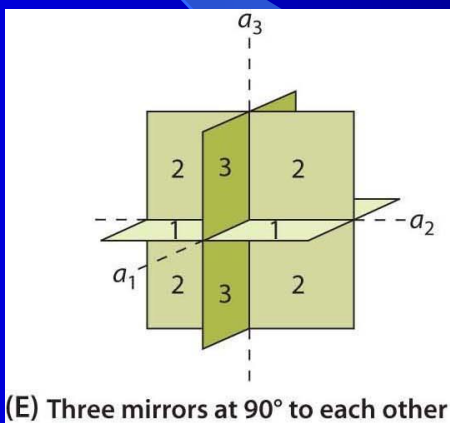
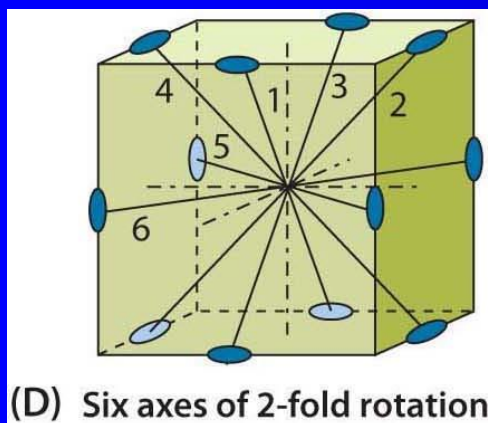
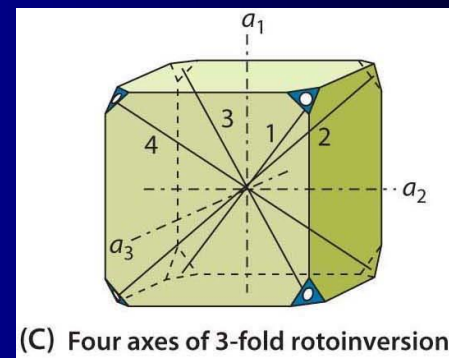
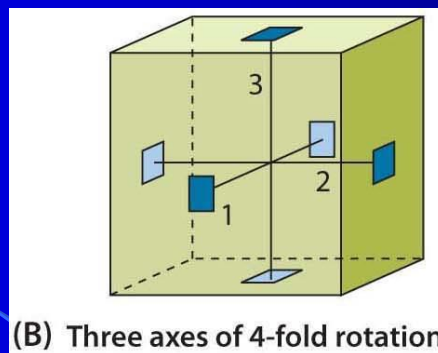
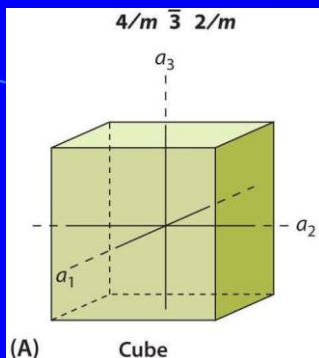
### Triclinic



$a \neq b \neq c$   
 $\alpha \neq \beta \neq \gamma \neq 90^\circ$

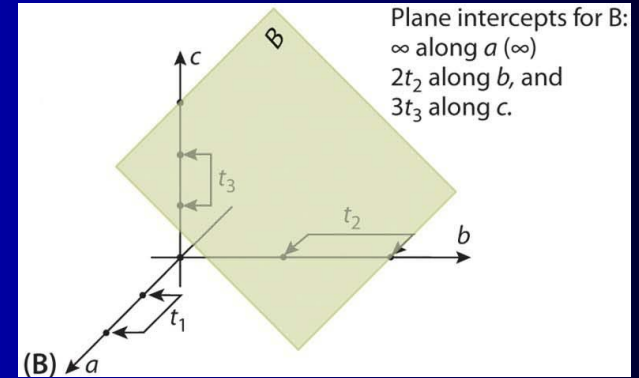
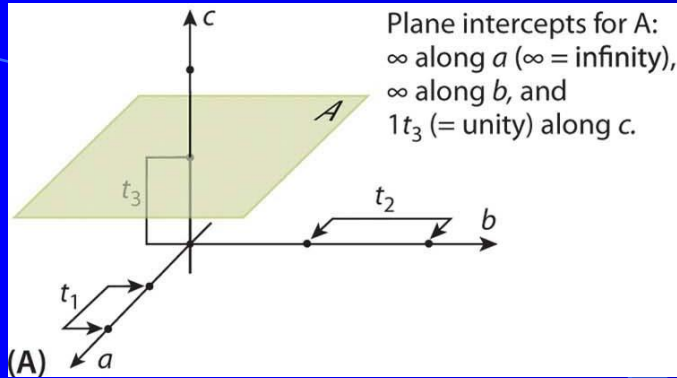


# Hermann-Mauguin notation explained



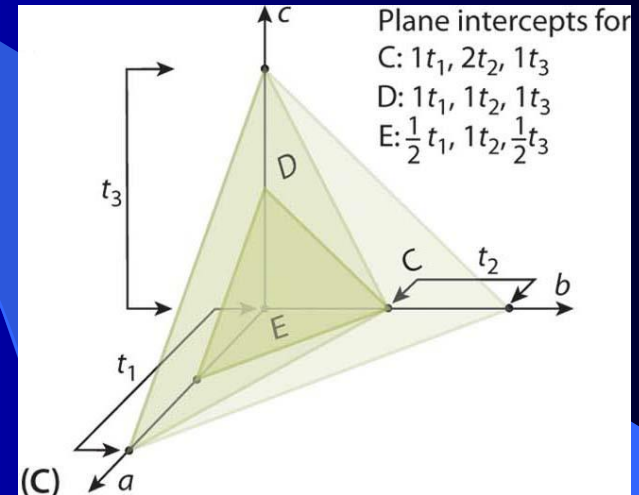
# Miller Indices

Three integers identifying a type of crystal plane; the intercepts of a plane on the three crystallographic axes are expressed as fractions of the crystal parameters; the reciprocals of these fractions, reduced to integral proportions, are the Miller indices. Also known as crystal indices.

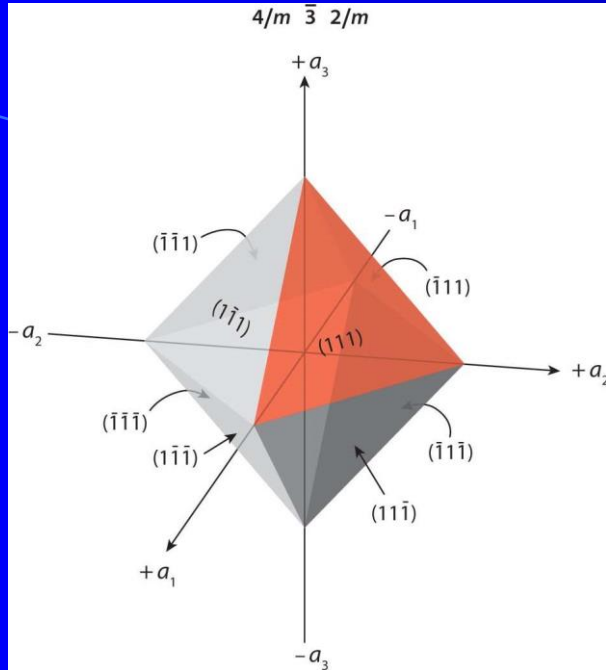


**Table 5.2** Conversion of intercept values (Fig. 5.5) to Miller indices by inversion and clearing of fractions, if necessary.

Plane	Intercepts	Inversion	Miller index
A	$\infty a, \infty b, 1c$	$\frac{1}{\infty}, \frac{1}{\infty}, \frac{1}{1}$	(001)
B	$\infty a, 2b, 3c$	$\frac{1}{\infty}, \frac{1}{2}, \frac{1}{3} \times 6$	(032)
C	$1a, 2b, 1c$	$\frac{1}{1}, \frac{1}{2}, \frac{1}{1} \times 2$	(212)
D	$1a, 1b, 1c$	$\frac{1}{1}, \frac{1}{1}, \frac{1}{1}$	(111)
E	$\frac{1}{2}a, 1b, \frac{1}{2}c$	$\frac{1}{1/2}, \frac{1}{1}, \frac{1}{1/2}$	(212)

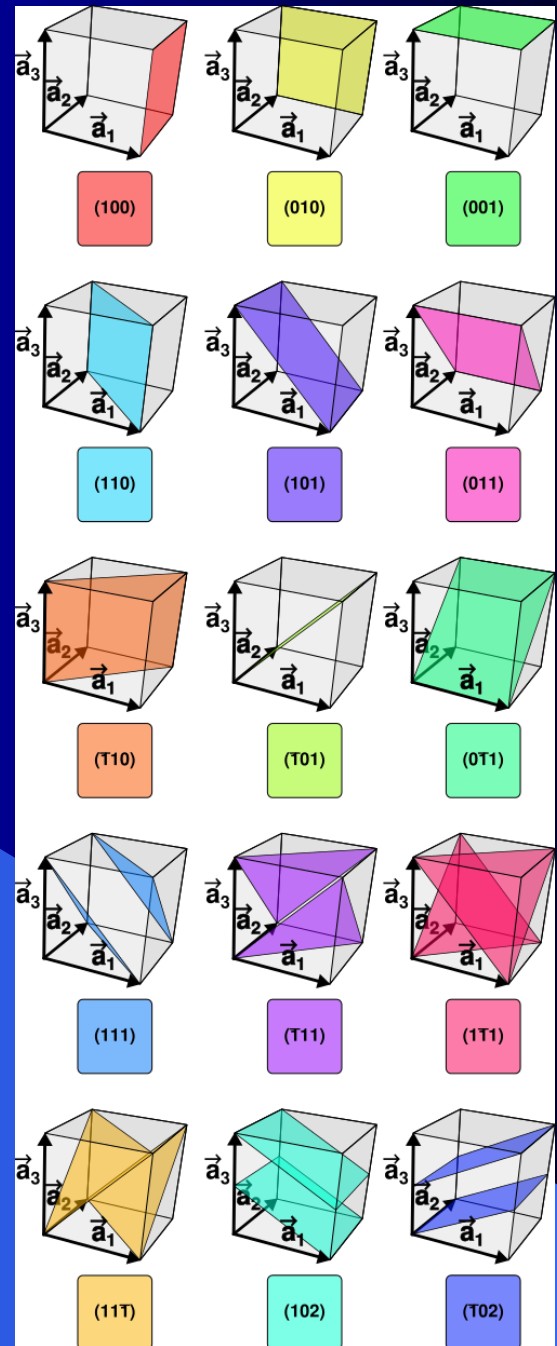


# Miller Indices for various planes in a cube.



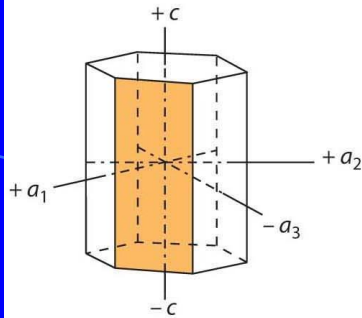
For further information about Miller Indices and a nice animation go to

<http://chemistry.bd.psu.edu/jircitano/Miller.html>

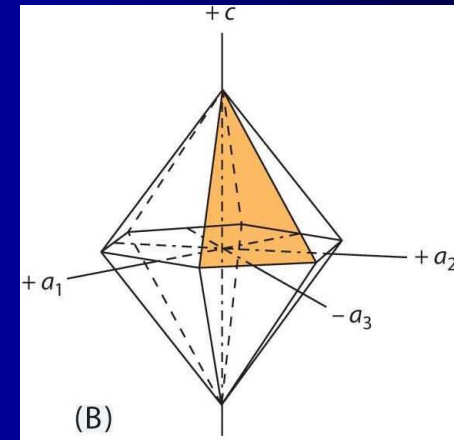


# Miller-Bravais Index in the hexagonal system

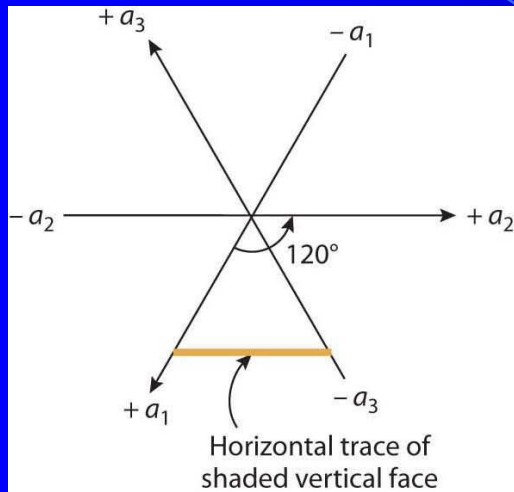
6/m 2/m 2/m



(A)



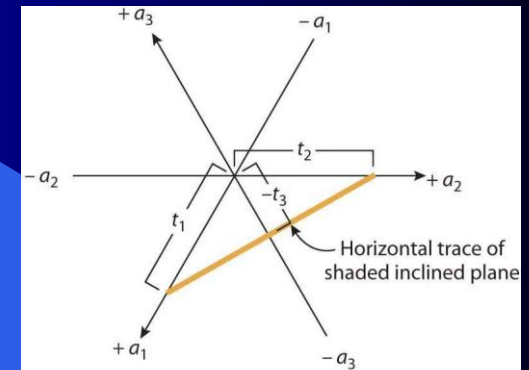
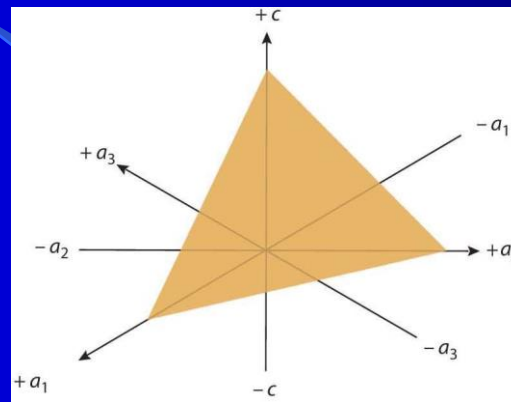
(B)



Intercepts of face:  
 $1a_1, \infty a_2, 1a_3(-), \infty c$

Inversion:  
 $\frac{1}{1} \frac{1}{\infty} \frac{1}{\bar{1}} \frac{1}{\infty}$

Index:  
 $(10\bar{1}0)$



Intercepts of face:  $1a_1, 1a_2, \frac{1}{2}a_3(-), 1c$

Inversion:  $\frac{1}{1} \frac{1}{1} \frac{1}{\frac{1}{2}} \frac{1}{1}$

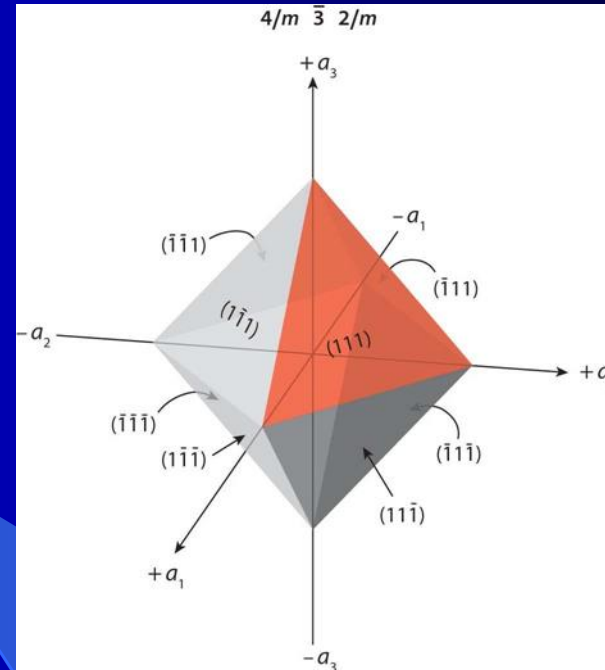
Index:  $(11\bar{2}1)$

**Form** – a group of like crystal faces, all of which have the same relation to the symmetry elements.

A form includes the whole set of crystal faces. Using the illustration to the right

form  $\{hkl\} = \{111\}$

For a specific crystal face in the form: (111). Note the difference, it is important.



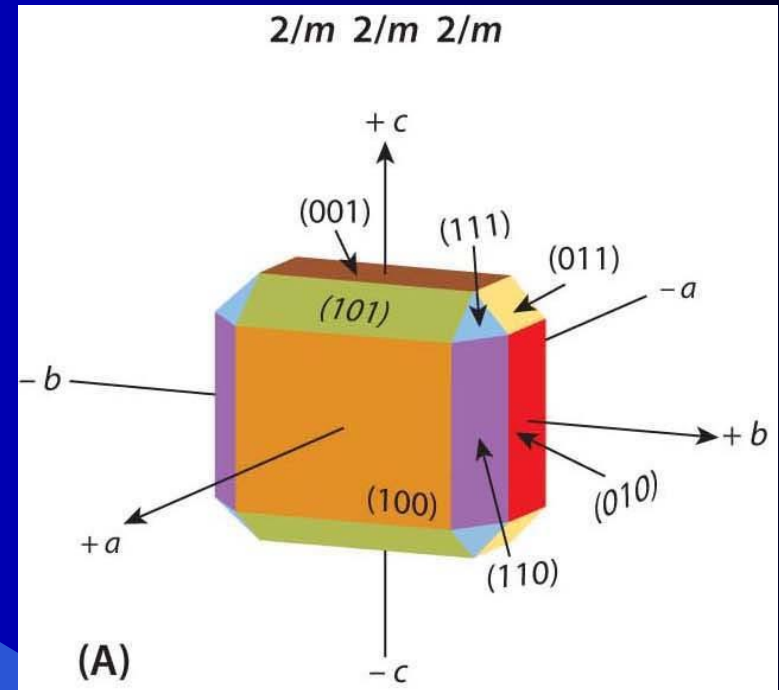
In the case of a **general form**, designated  $\{hkl\}$ , the faces intersect the crystallographic axes at different lengths.

**Open form** – doesn't enclose space

**Closed form** – encloses space

### Types of Open forms

- **Pinacoids** – two parallel faces  $\{100\}$ ,  $\{010\}$ ,  $\{001\}$
- **Prisms** – four parallel faces  $\{110\}$ ,  $\{101\}$ ,  $\{011\}$



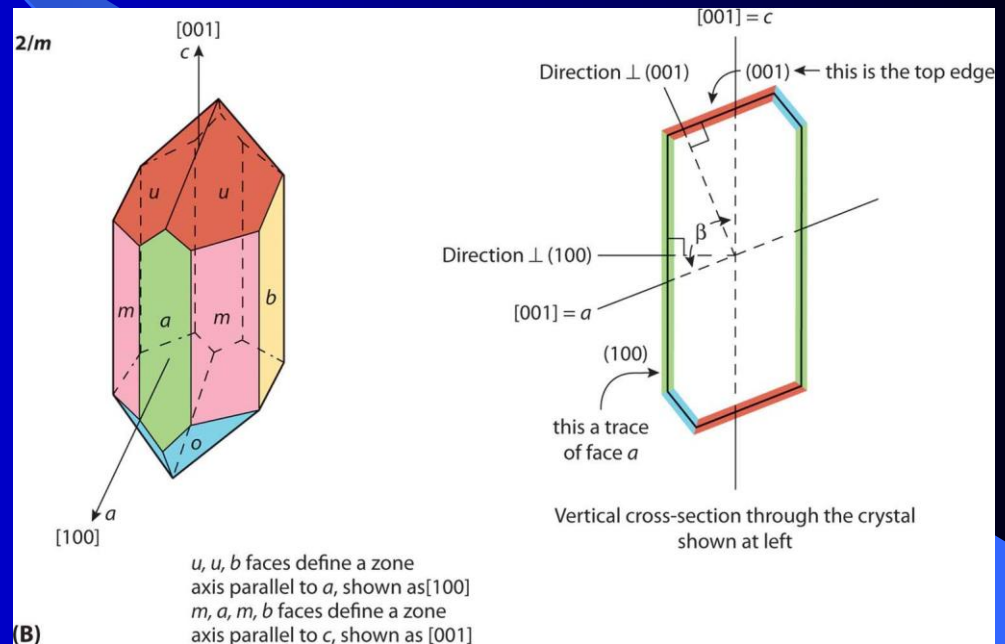
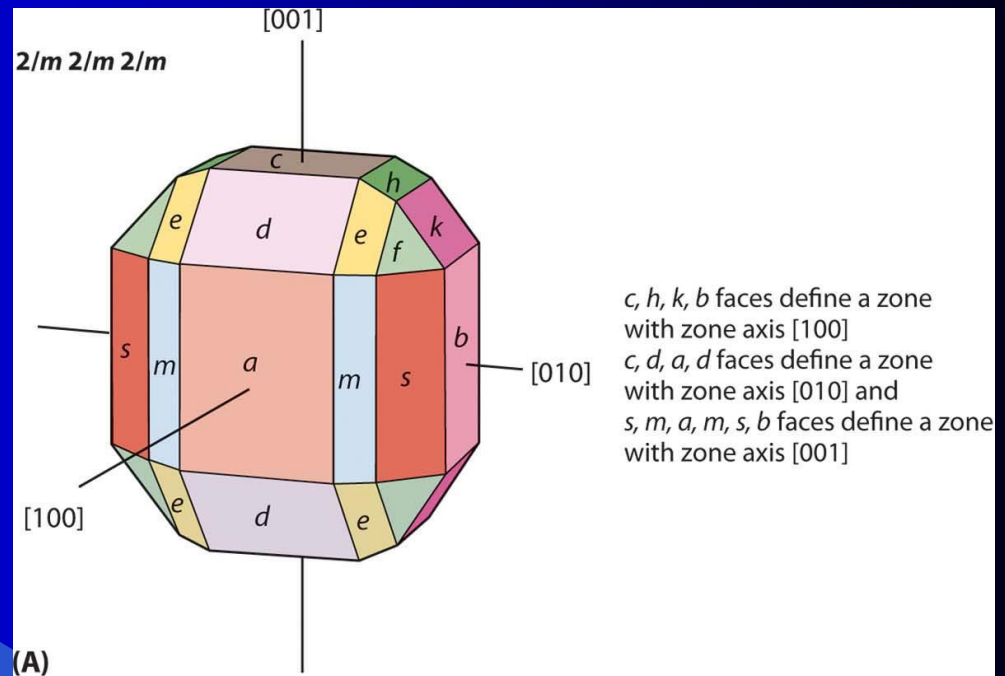
### Some examples of closed forms

- **Rhombic dipyramid**  $\{111\}$  – eight inclined corner faces
- **Octahedron**  $\{111\}$  – eight triangular faces
- **Dodecahedron**  $\{011\}$  – 12 rhomb-shaped faces
- **Tetrahexahedron**  $\{0k1\}$  – consists of 24 isosceles triangular faces

**Zone** – a collection of crystal faces with parallel edges.

In crystal classes with orthogonal axes (isometric, tetragonal, orthorhombic) zone axes correspond with crystallographic axes. For example, zone  $[001]$  is perpendicular to face  $(001)$ .

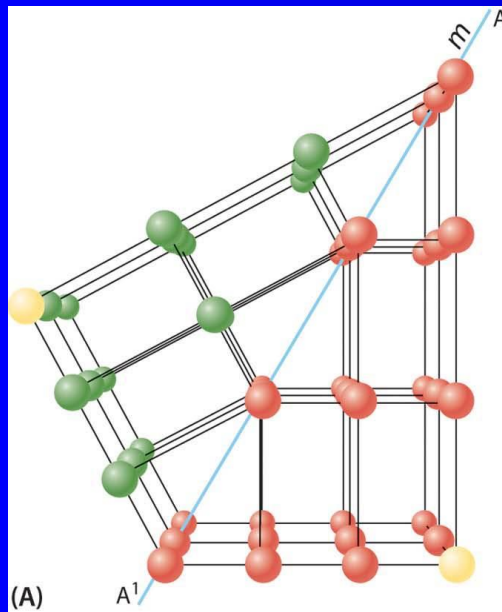
In crystal classes where all axes are not orthogonal, the zone axes do not correspond to some or all of the crystallographic axes.



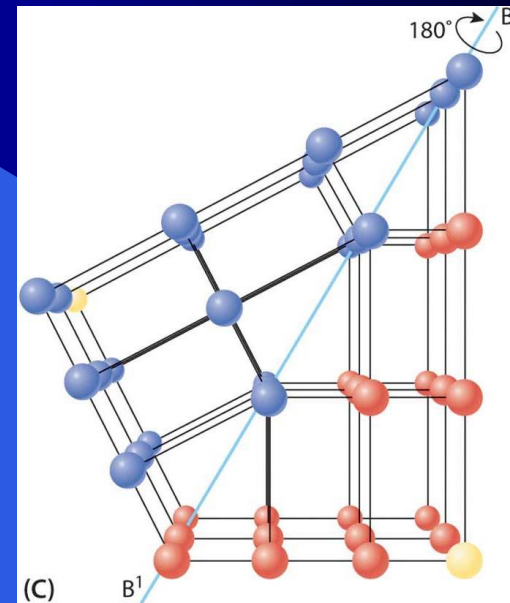
**Twins** – rational, symmetrical intergrowths of two or more crystals of the same substance.

The two or more individuals are related by a **new** symmetry element that was **not already present** in the untwinned single crystal. Twin laws -

- A **mirror plane** or twin plane
- A **rotation axis** or twin axis
- An **inversion** about a point or twin center



Mirror plane



Rotation axis



**Primary twins** (growth twins) are due to nucleation errors that occur during crystal growth. The original pattern of the crystal is interrupted in a regular way.

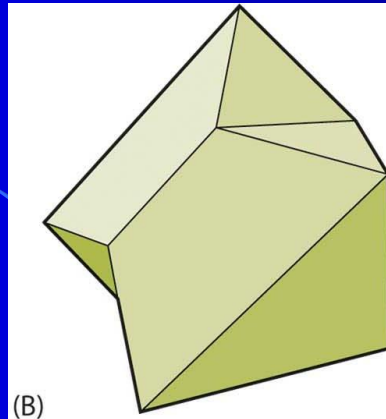
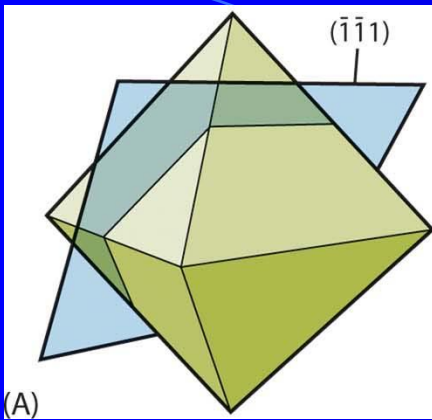
**Secondary twins** – modification of a crystal after its formed. Result of mechanical deformation or displacive transformation of one polymorph into another.

Twins are classified as

- **Contact twins** – a regular composition plane joins the two individuals
- **Penetration twins** – appear to be intergrown. Usually produced by rotation and defined by an axis of rotation.
- **Multiple twins** – three or more individual crystals are twinned according to the same twin law. **Polysynthetic** twin if all the composition faces are parallel

Example:

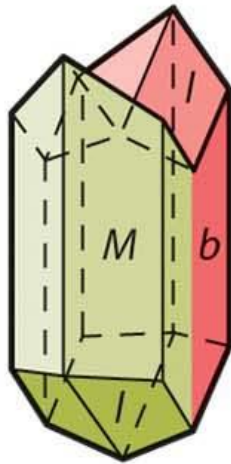
**Spinel twin** – twin plane is  $\{111\}$  which is not a mirror plane in the isometric point group  $4/m\bar{3}2/m$ .



# Examples of Contact twins

## Gypsum

Monoclinic:  $2/m$



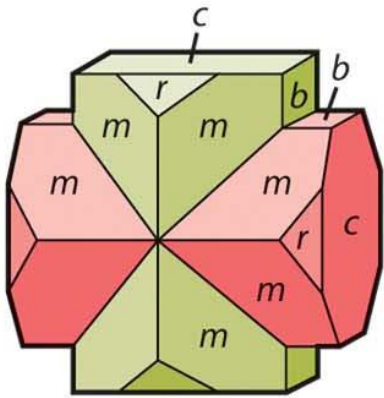
(C) Swallowtail twin on  $\{100\}$



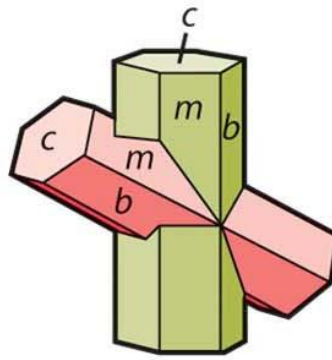
The mirror plane is perpendicular to  $b$  and therefore is  $(010)$

## Staurolite

Pseudo-orthorhombic (monoclinic with  $\beta \sim 90^\circ$ ):  $2/m$



(B) Twin on {031}

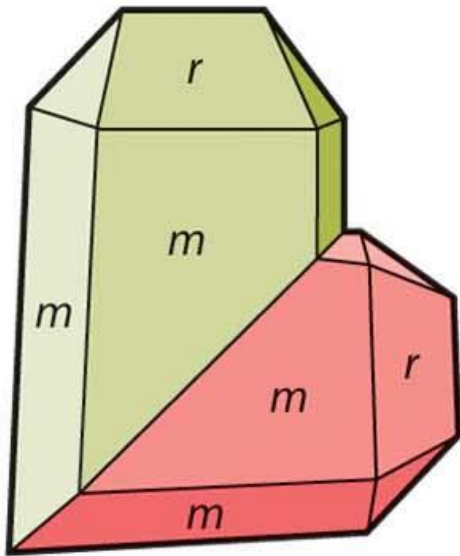


Twin on {231}



# Quartz

Hexagonal: 32

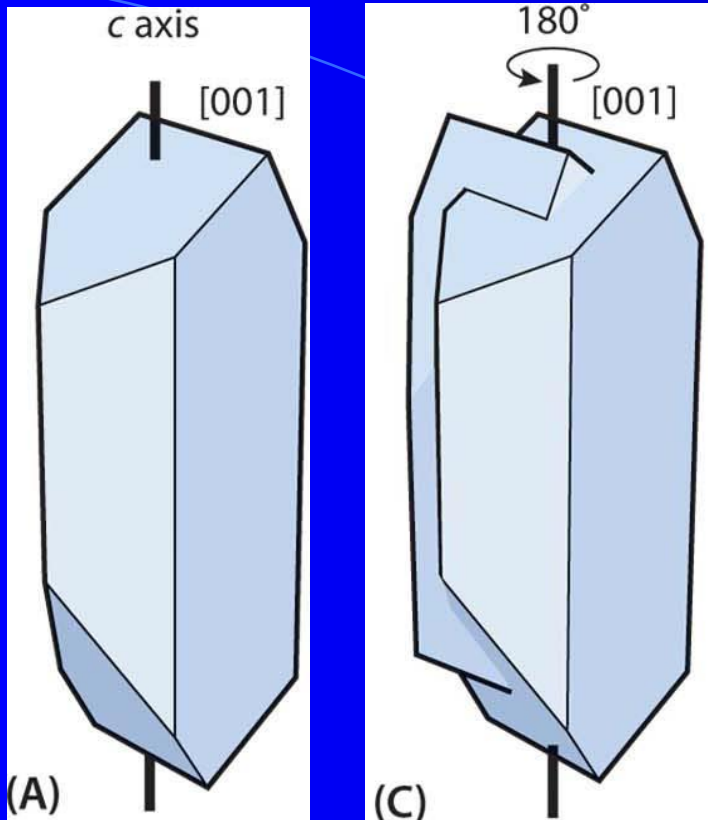


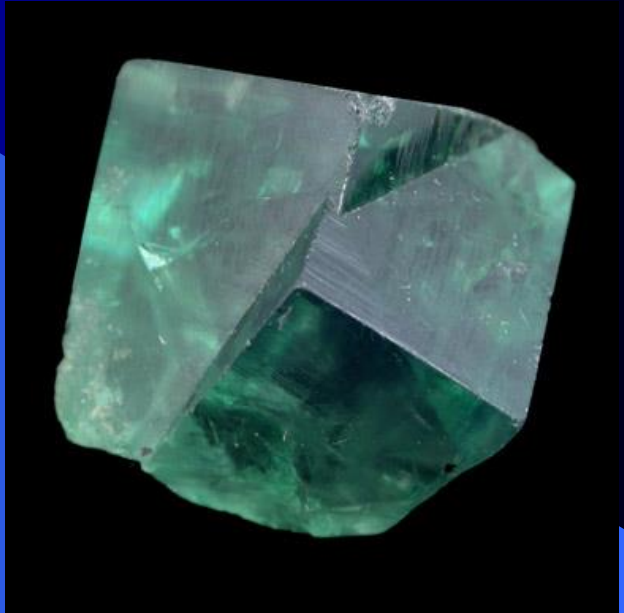
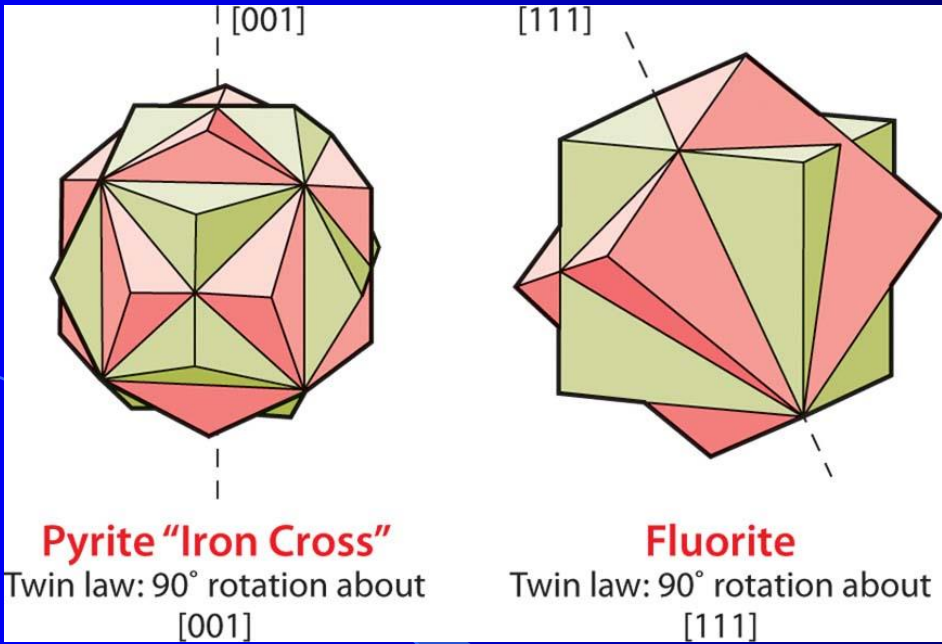
(A) Japan twin on  $\{11\bar{2}2\}$



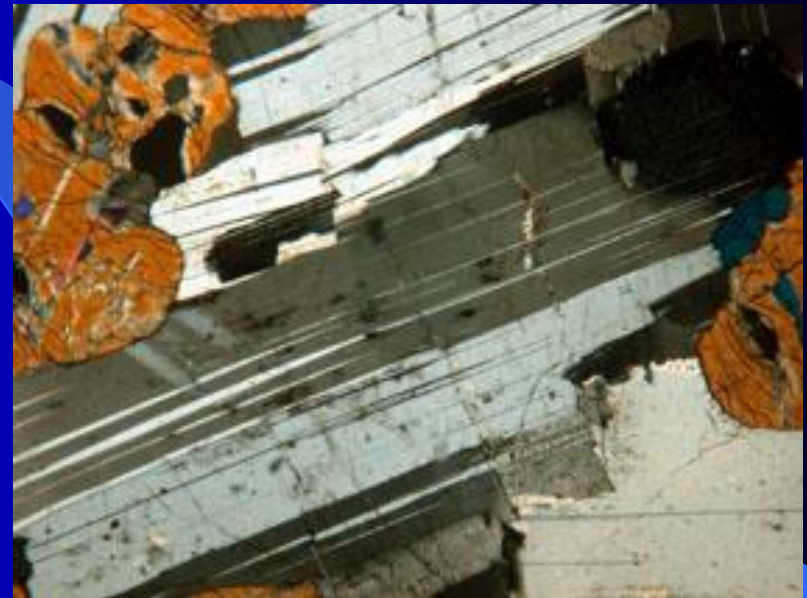
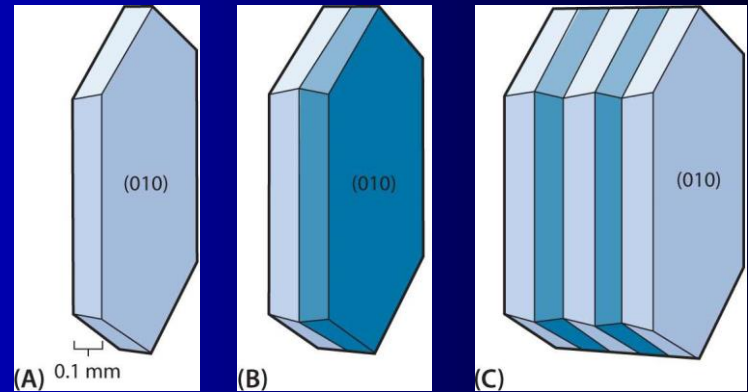
Penetration twin – twinning of monoclinic orthoclase  $2/m$

2-fold rotation axis is parallel to  $b$ .





Development of a polysynthetic (albite) twin. Mirror reflection parallel to (010). This example is for a triclinic crystal and the only symmetry element is  $i$ .





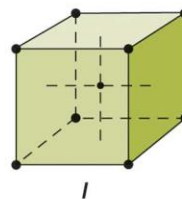
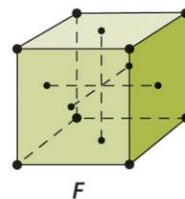
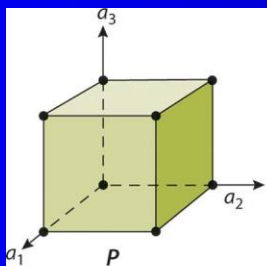
In the case of the **32 point groups** all the symmetry elements intersect at one point in the center of the crystal. There isn't any translation.

In the case of the **space groups** we add an additional symmetry element which is translation. This gives rise to the 230 space groups.

These new elements are

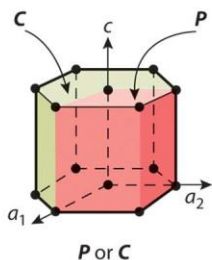
- **Translation** – this element leads to the 14 Bravais Lattices. These are three dimensional arrays of nondimensional points.
- **Screw axes** - a rotation axis combined with translation
- **Glide planes** – a mirror plane combined with translation

# The Bravais Lattices

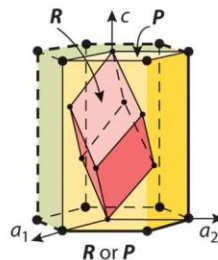


Isometric  
 $\alpha = \beta = \gamma = 90^\circ$   
 $a = b = c$

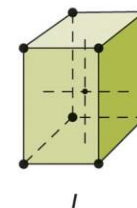
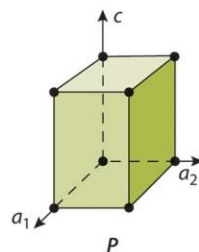
**P** = Primitive  
**F** = All-face centered  
**I** = Body-centered (from the German innenzentriert)



Hexagonal  
 $\alpha = \beta = 90^\circ; \gamma = 120^\circ$   
 $a = b (\neq c)$

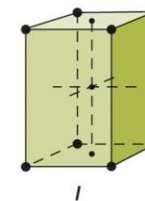
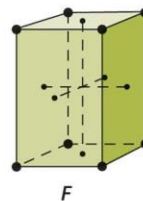
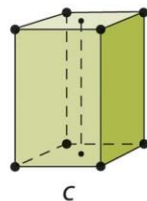
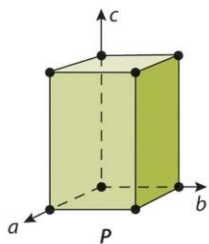


Rhombohedral

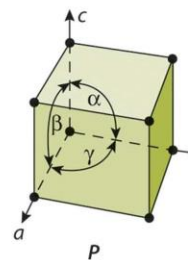
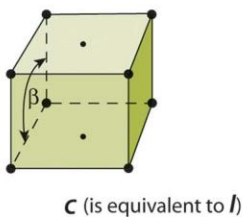
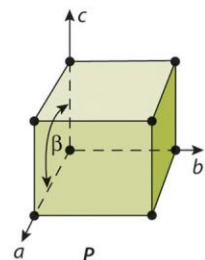


Tetragonal  
 $\alpha = \beta = \gamma = 90^\circ; a = b (\neq c)$

**C** = c- face centered  
**R** = rhombohedral in the trigonal division of the hexagonal system



Orthorhombic  
 $\alpha = \beta = \gamma = 90^\circ (a \neq b \neq c)$



Monoclinic  
 $\alpha = \gamma = 90^\circ (\neq \beta; a \neq b \neq c)$

Triclinic  
 $(\alpha \neq \beta \neq \gamma; a \neq b \neq c)$   
 no symmetry imposed restrictions

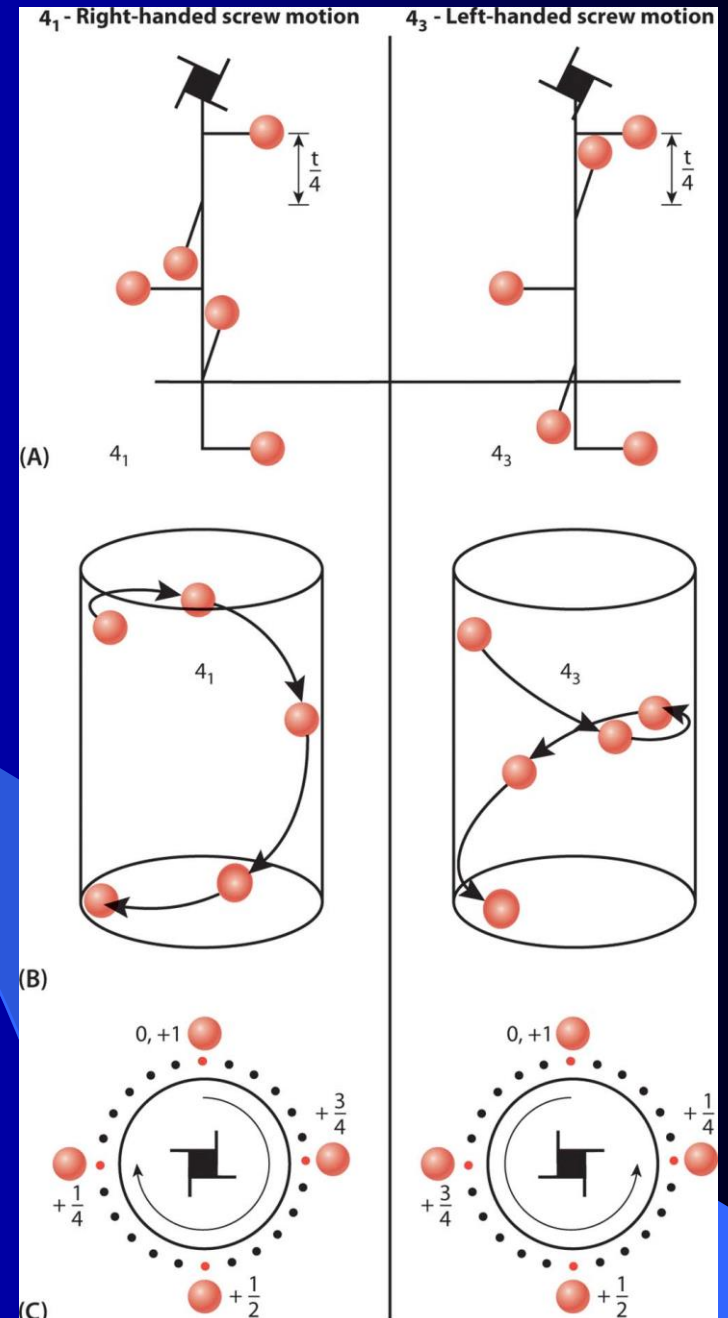
**Screw axis** – rotational operation with a translation ( $t$ ) parallel to the axis of rotation.

Nomenclature

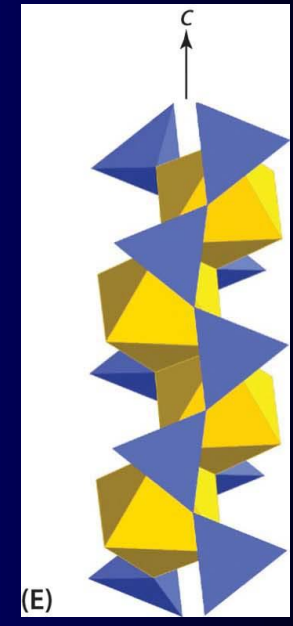
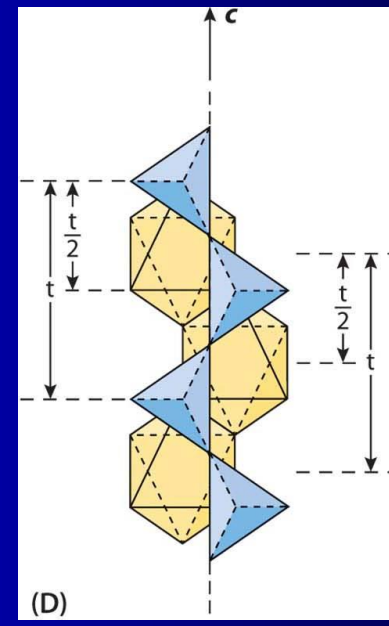
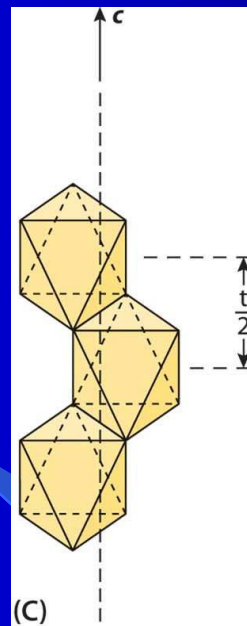
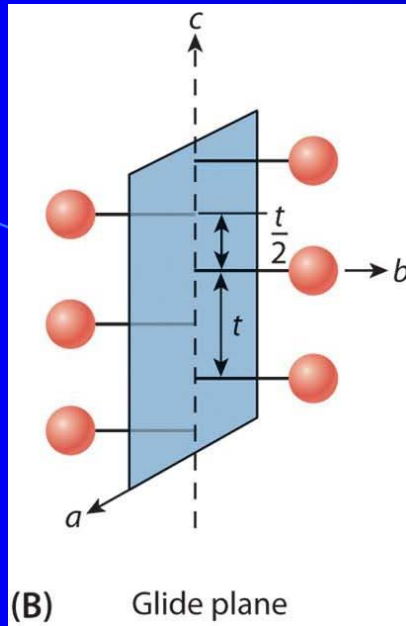
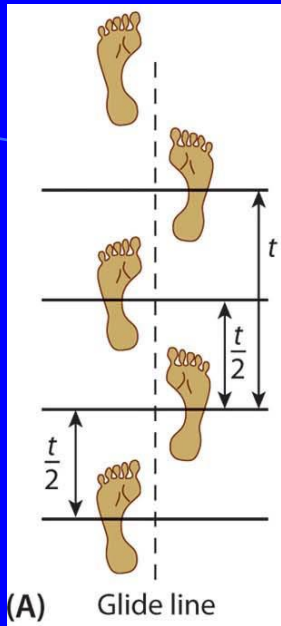
$2_1$  = 2-fold rotation with a translation of  $\frac{1}{2} t$   
 Subscript over the main axis symbol yields translation

$4_1$  and  $4_3$  = 4-fold rotation with a translation of  $\frac{1}{4} t$ . Subscript less than  $\frac{1}{2}$  right handed screw operation (CW). Subscript greater than  $\frac{1}{2}$  left handed screw operation (CCW).

When the ratio is exactly  $\frac{1}{2}$  the screw operation is neutral. It doesn't matter which direction, the atoms end up in the same place.



**Glide operation** – a combination of a mirror reflection with a translation ( $t/2$  or  $t/4$ ) parallel to the mirror. (B) to (E), glide operation is parallel to c-axis.



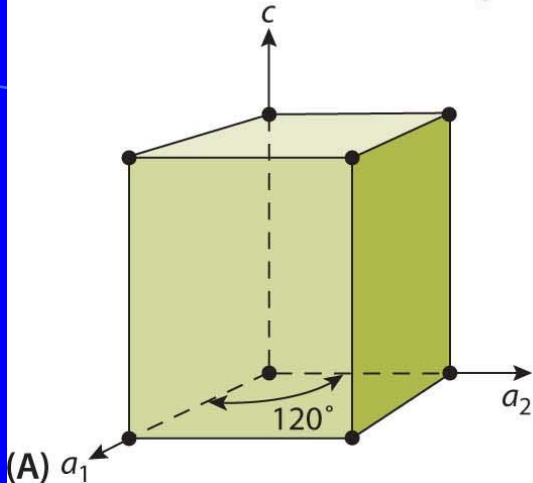
## Glide plane nomenclature

Symbol	Symmetry Plane	Direction and distance of glide translation	Graphical symbol
			Glide plane normal to plane of projection
$m$	Mirror	none	—————
$a, b$	Axial glide plane (Parallel to one of three axial directions)	$a/2$ along [100] or $b/2$ along [010]*	-----
$c$		$c/2$ along the $c$ axis	.....
$n$	Diagonal glide plane	$a/2 + b/2$ ; $a/2 + c/2$ ; $b/2 + c/2$ ; or $a/2 + b/2 + c/2$ (tetragonal and isometric)*	-----
$d$	Diamond glide plane	$a/4 + b/4$ ; $b/4 + c/4$ ; $a/4 + c/4$ ; or $a/4 + b/4 + c/4$ (tetragonal and isometric)*	----- ← ----- →

\* Axial directions and crystal systems are discussed in Section 5.3

# Examples of Crystallographic Descriptions

## Low quartz $\text{SiO}_2$

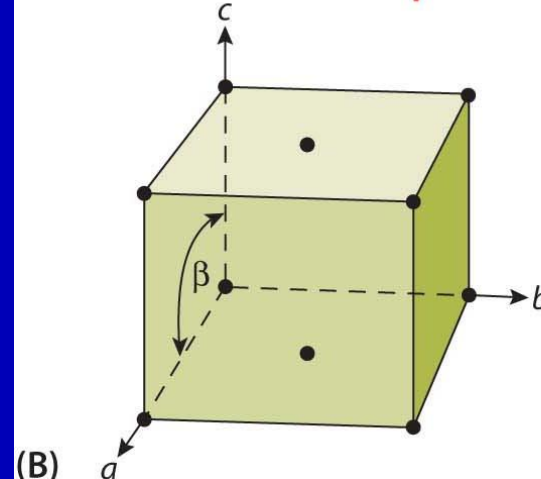


Hexagonal  
 Space group:  $P 3_2 21$  or  $P 3_1 21$   
 Point group:  $32$   
 Unit cell dimensions:  
 $a = 4.91 \text{ \AA}$   
 $c = 5.41 \text{ \AA}$   
 $Z = 3$

Primitive cell, 3-fold rotation axis with  $1/3$  translation.  
 Rotation axis can be CW ( $3_1$ ) or CCW ( $3_2$ ). 2-fold rotation axis.  
 "1" means there is no symmetry element in this position.  
 $Z = \#$  formula units in unit cell

Centered cell. 2-fold rotation axis.  
 Glide plane in the "c" direction with  $1/2$  t.

## Diopside $\text{Ca Mg Si}_2\text{O}_6$

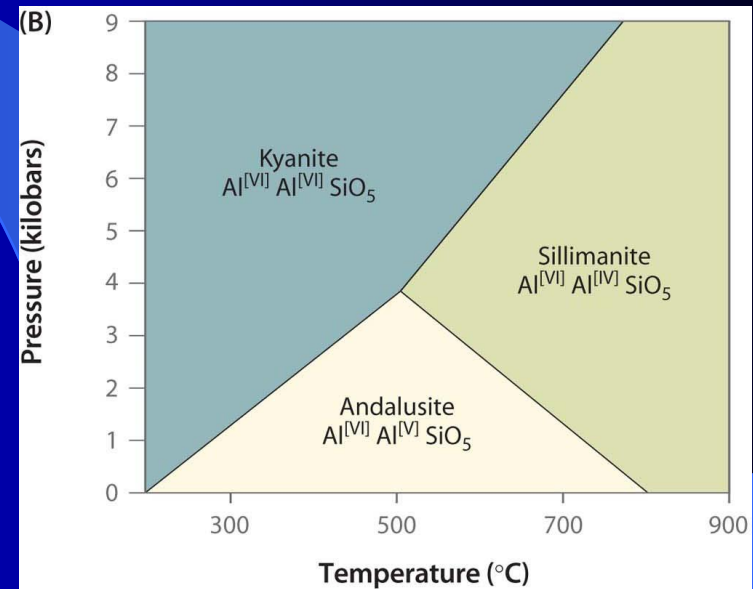
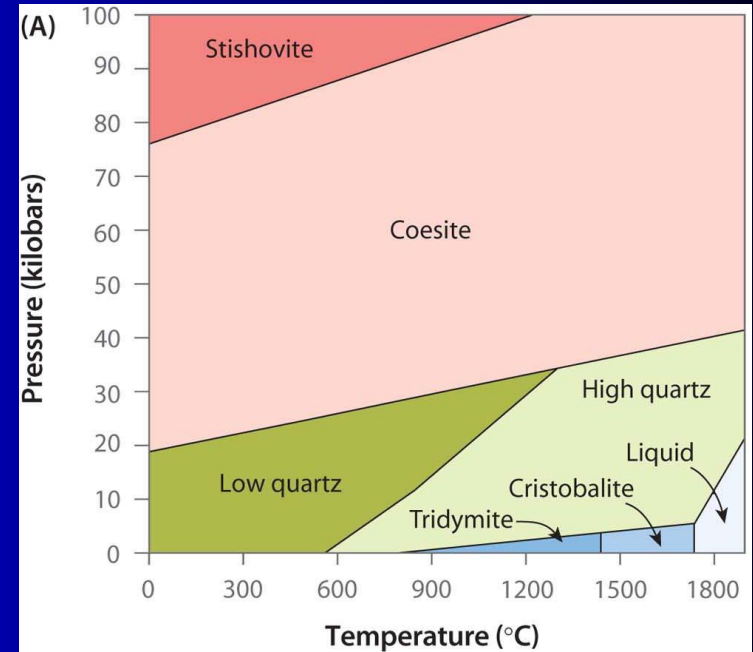


Monoclinic  
 Space group:  $C 2/c$   
 Point group:  $2/m$   
 Unit cell dimensions:  
 $a = 9.73 \text{ \AA}$   
 $b = 8.91 \text{ \AA}$   
 $c = 5.25 \text{ \AA}$   
 $\beta = 105^\circ 30'$   
 $Z = 4$

**Polymorphism** - the ability of a substance to adopt different internal structures and external forms, in response to different conditions of temperature and/or pressure

### Types of polymorphism

- **Reconstructive** – extensive rearrangement of the crystal structure involving breaking of bonds and reassembly of structural units into different arrangements.
- **Displacive** – slight rearrangement of crystal structure. No bonds are broken.
- **Order-disorder** – ordering of individual elements in different structural sites in a mineral.
- **Polytypism** – different structural arrangements due to different stacking of sheets in three dimensions (sheet silicates).

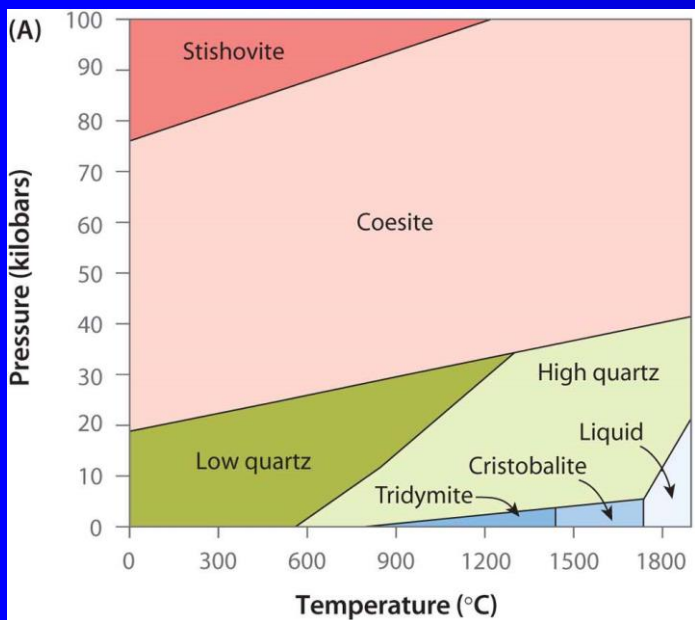


**Table 5.4** Common polymorphous minerals.

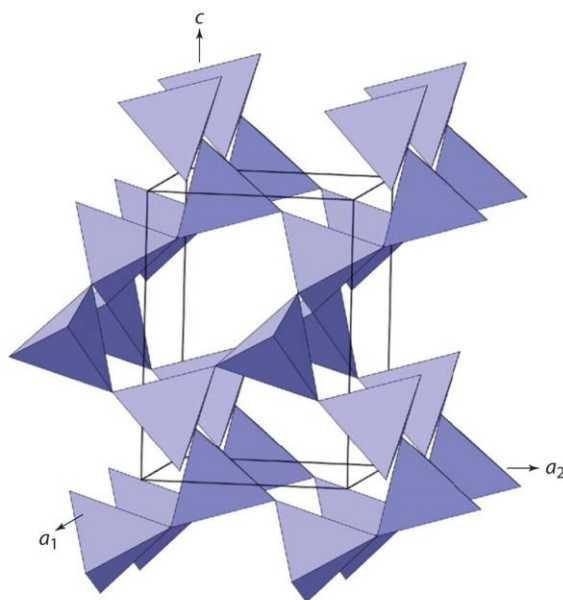
Composition	Mineral Name	Crystal system and space group	G	Average refractive index
SiO <sub>2</sub>	Low ( $\alpha$ ) quartz	Hexagonal – $P3_221$ (or $P3_121$ )	2.65	1.55
	High ( $\beta$ ) quartz	Hexagonal – $P6_222$ (or $P6_422$ )	2.53	1.54
	Tridymite	Monoclinic – $Cc$	2.27	1.47
	Cristobalite	Tetragonal – $P4_12_12$	2.32	1.48
	Coesite	Monoclinic – $C2/c$	2.92	1.59
	Stishovite	Tetragonal – $P4_2/m2_1/n2/m$	4.29	1.81
	Al <sub>2</sub> SiO <sub>5</sub>	Andalusite	Orthorhombic – $P2_1/n2_1/n2/m$	3.15
Sillimanite		Orthorhombic – $P2_1/n2_1/m2_1/a$	3.24	1.66
Kyanite		Triclinic – $P\bar{1}$	3.65	1.72
KAlSi <sub>3</sub> O <sub>8</sub>	Microcline	Triclinic – $C\bar{1}$	2.58	1.52
	Orthoclase	Monoclinic – $C2/m$	2.57	1.52
	Sanidine	Monoclinic – $C2/m$	2.57	1.52
C	Diamond	Isometric – $F4_1/d\bar{3}2/m$	3.52	2.42
	Graphite	Hexagonal – $P6_3/m2/m2/c$	2.23	
CaCO <sub>3</sub>	Calcite	Hexagonal (rhombohedral) – $R\bar{3}2/c$	2.71	1.57
	Aragonite	Orthorhombic – $P2/m2/n2_1/a$	2.94	1.63
FeS <sub>2</sub>	Pyrite	Isometric – $P2_1/a\bar{3}$	5.02	
	Marcasite	Orthorhombic – $P2_1/n2_1/n2/m$	4.89	

Example of reconstructive polymorphism – the high T and or P SiO<sub>2</sub> polymorphs

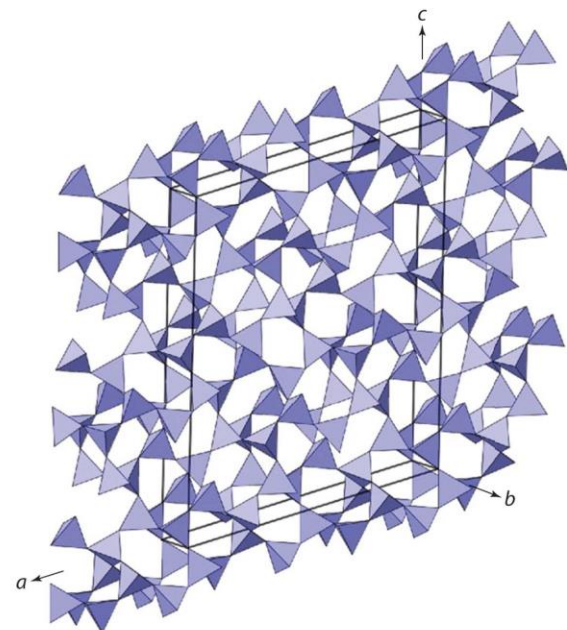
In the high pressure Stishovite polymorph the Si is in 6-fold coordination with oxygen.



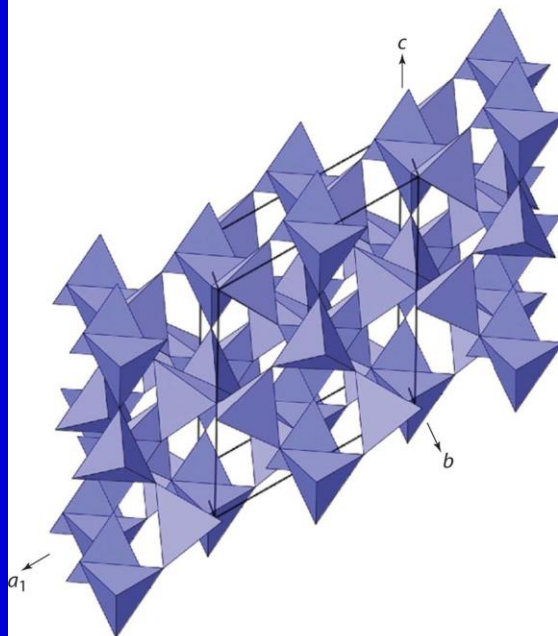
**Cristobalite**  
Tetragonal  $P4_12_12$



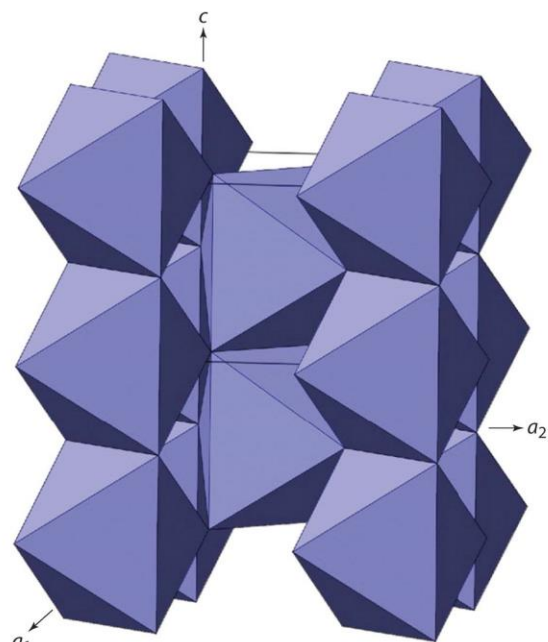
**Tridymite**  
Monoclinic  $Cc$



**Coesite**  
Monoclinic  $C2/c$

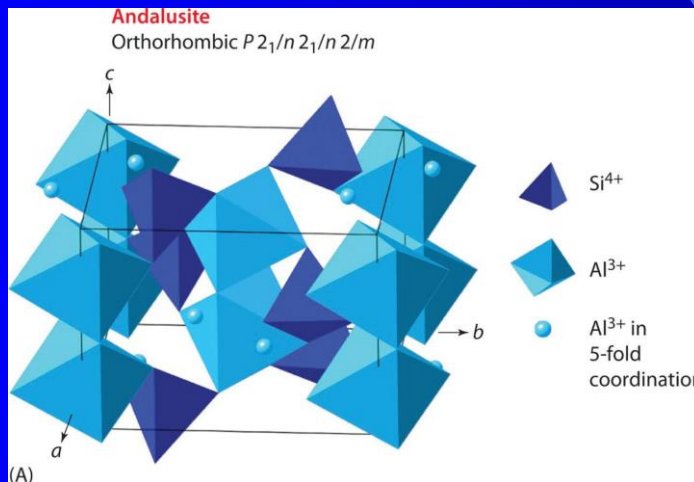
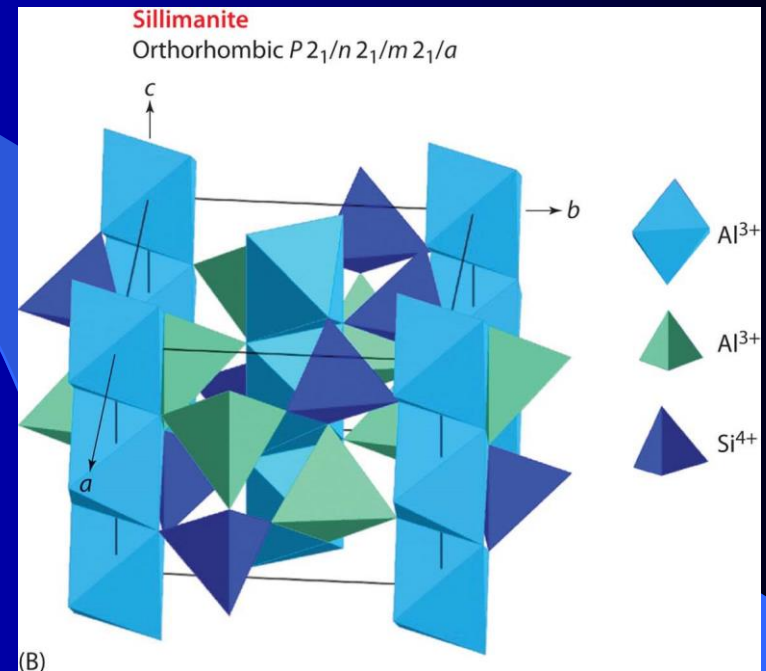
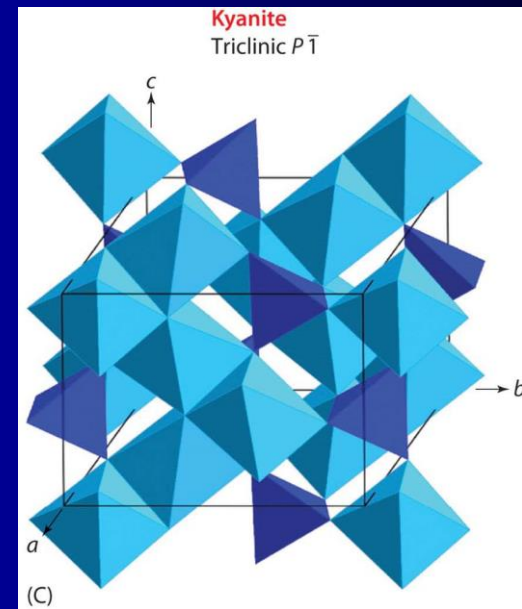
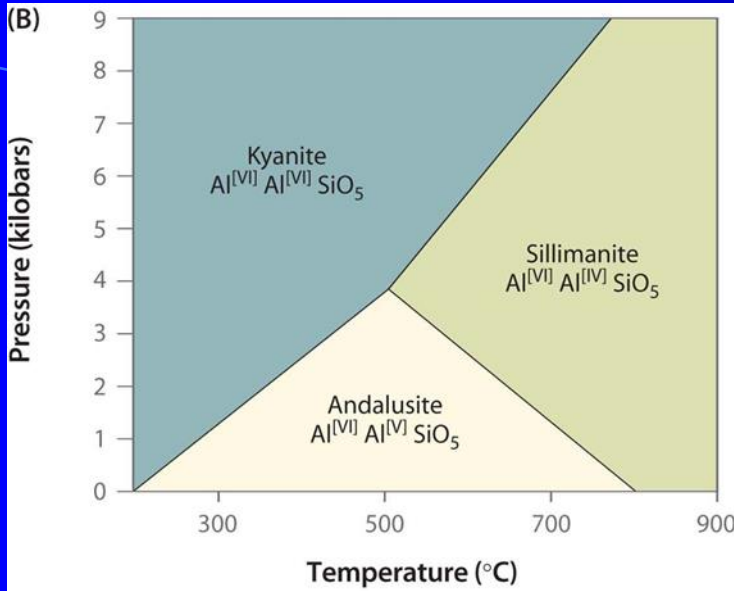


**Stishovite**  
Tetragonal  $P4_2/m2_1/n2/m$

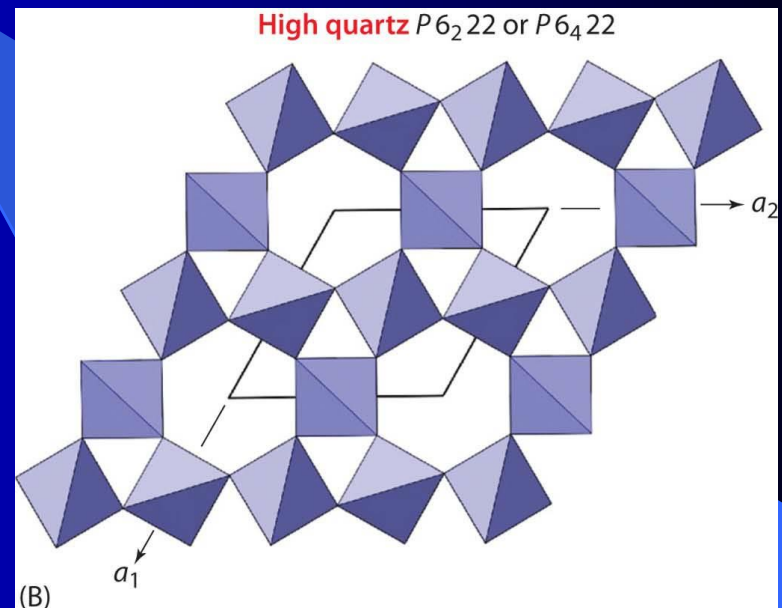
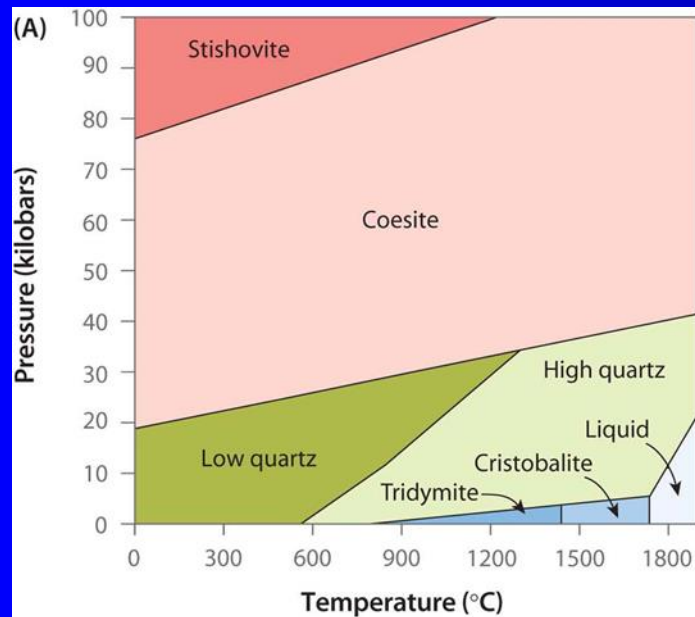
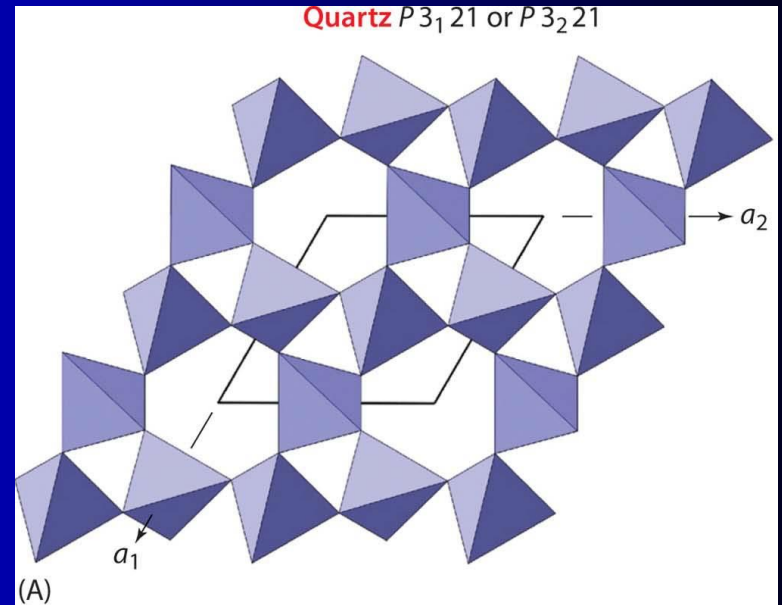




# Another example of reconstructive polymorphism – the $\text{Al}_2\text{SiO}_5$ polymorphs



Example of displacive polymorphism – low quartz vs high quartz. Note the very small change in the orientation of some of the silica tetrahedrons which leads to two different crystal structures. The differences are at the space group level.



Example of order-disorder polymorphism –  
the polymorphs of  $\text{KAlSi}_3\text{O}_8$ .

The distinction between the polymorphs is based on the ordering of Al in the tetrahedral sites.

- **Microcline** – low T polymorph – one in every four tetrahedral sites is filled with an Al. Total order
- **Orthoclase** – moderate T polymorph – Al is distributed over two equivalent tetrahedral sites. Partially ordered
- **Sanidine** – high T polymorph – equal probability of finding Al in any of the four tetrahedral sites. Completely disordered.

