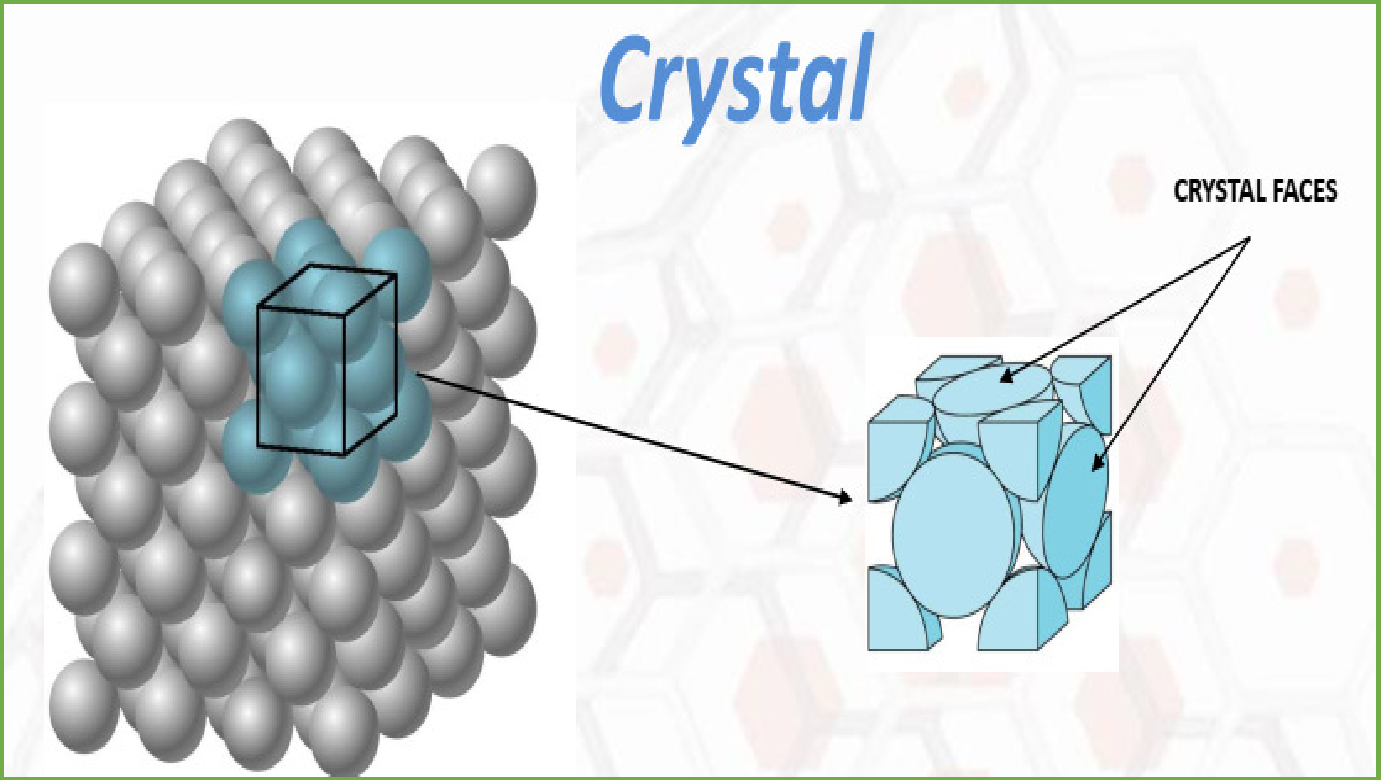
Crystallography

Crystallography is the experimental science of the arrangement of atoms in solids. The word "crystallography" derives from the Greek words *crystallon* = cold drop / frozen drop, with its meaning extending to all solids with some degree of transparency, and *grapho* = write.

OR

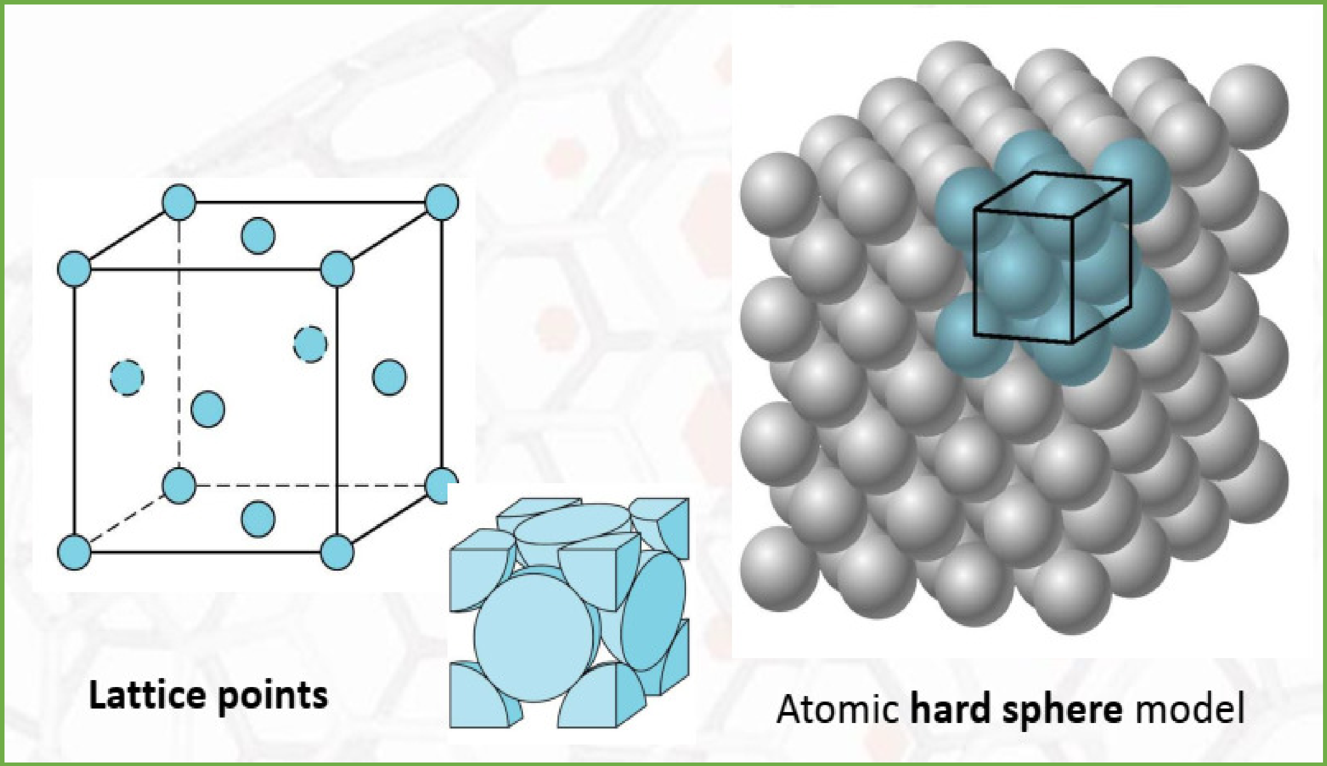
Crystallography is the study of crystal shapes based on symmetry.

Crystal: Crystal is any solid material in which the component atoms are arranged in a *definite pattern* and whose surface regularity reflects its *internal symmetry.*



Unit Cell

Unit cell is the smallest unit of volume that permits identical cells to be stacked together to fill all space. By repeating the pattern of the unit cell over and over in all directions, the entire crystal lattice can be constructed.



A **primitive unit cell** for a single lattice is a unit cell containing only one lattice point.

Lattice: This is an imaginary three-dimensional framework that can be referenced to a network of regularly spaced points, each of which represents the position of a motif.

Motif: This is the smallest representative unit of a structure. It is an atom or group of atoms that, when repeated by translation, give rise to an infinite number of identical regularly organized units.

Building a space lattice: from motifs to lattices:

Motif $\rightarrow$ Line lattice $\rightarrow$ Plane lattice $\rightarrow$ Space Lattice

Crystallization

Crystallization is defined as a process by which a chemical is converted from a liquid solution into a solid crystalline state.

The crystallization process consists of **two major** types:

1 Nucleation – Molecules gather together in clusters in a defined manner. Clusters need to be stable under current experimental conditions to reach the “critical cluster size” or they will re-dissolve. It is this point in the crystallization process that defines the crystal structure.

2 Crystal Growth – Nuclei that have successfully achieved the “critical cluster size” begin to increase in size. Crystal growth is a dynamic process, with atoms precipitating from solution and becoming redissolved. Supersaturation and supercooling are two of the most common driving forces behind crystal formation.

Note: Many compounds can exist in multiple crystal structures – a phenomenon known as "polymorphism" – and can have different physical properties (melting point, shape, dissolution rate, etc.).

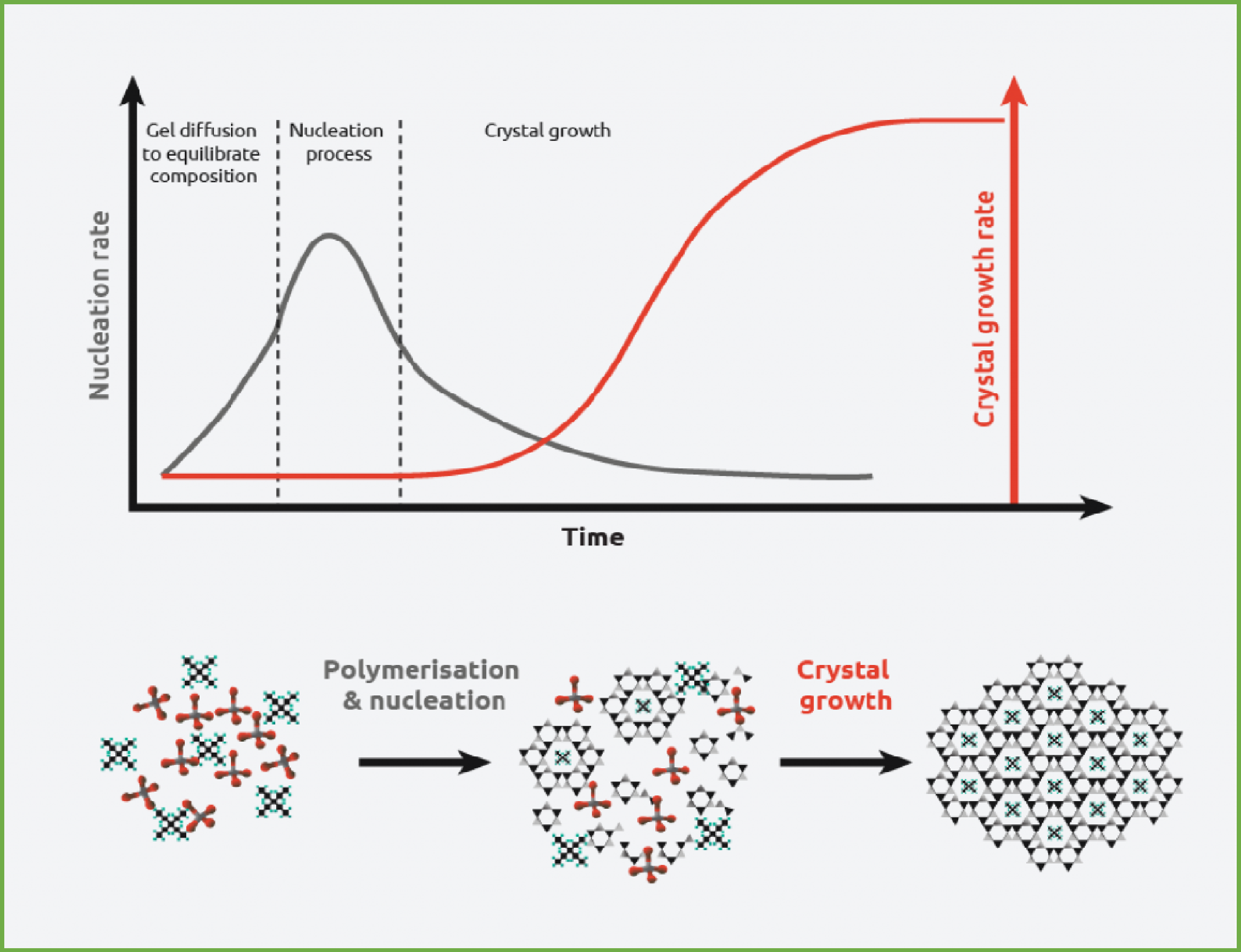


Figure 1: The crystallization process - crystal growth rate vs. nucleation rate

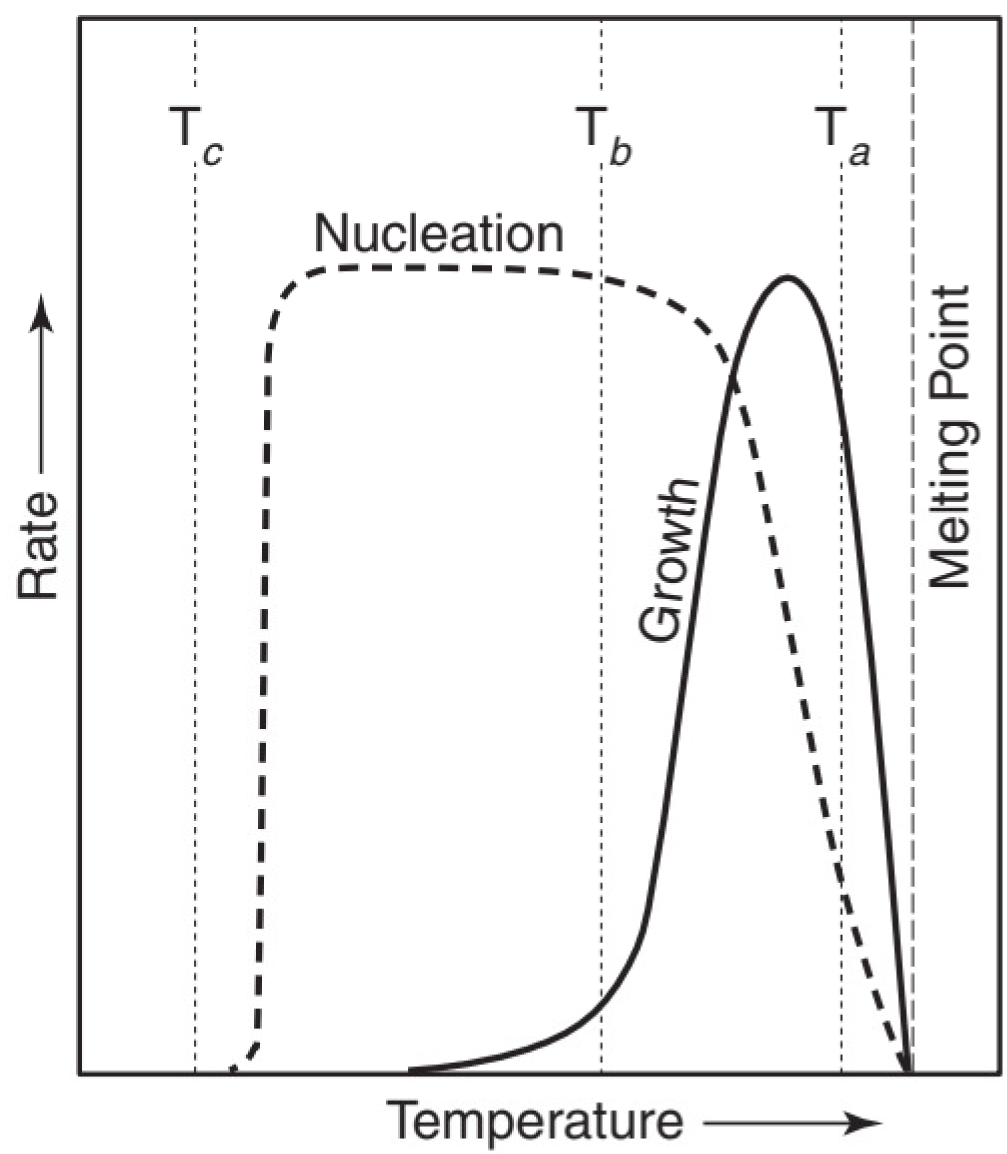


FIGURE 2 Idealized rates of crystal nucleation and growth as a function of temperature below the melting point.

Figure 2 to understand why the rate of cooling so profoundly affects the grain size of a rock. At temperature T_a, the nucleation rate is very low, and the growth rate is high. Fewer crystals thus form, and they grow larger, resulting in the coarse-grained texture common among slow cooled plutonic rocks. If rocks are undercooled to T_b the nucleation rate exceeds the growth rate, and many small crystals are formed, resulting in the very fine-grained texture of volcanic rocks. Very high degrees of undercooling T_c may result in negligible rates of nucleation and growth, such that the liquid solidifies to a glass with very few or no crystals.

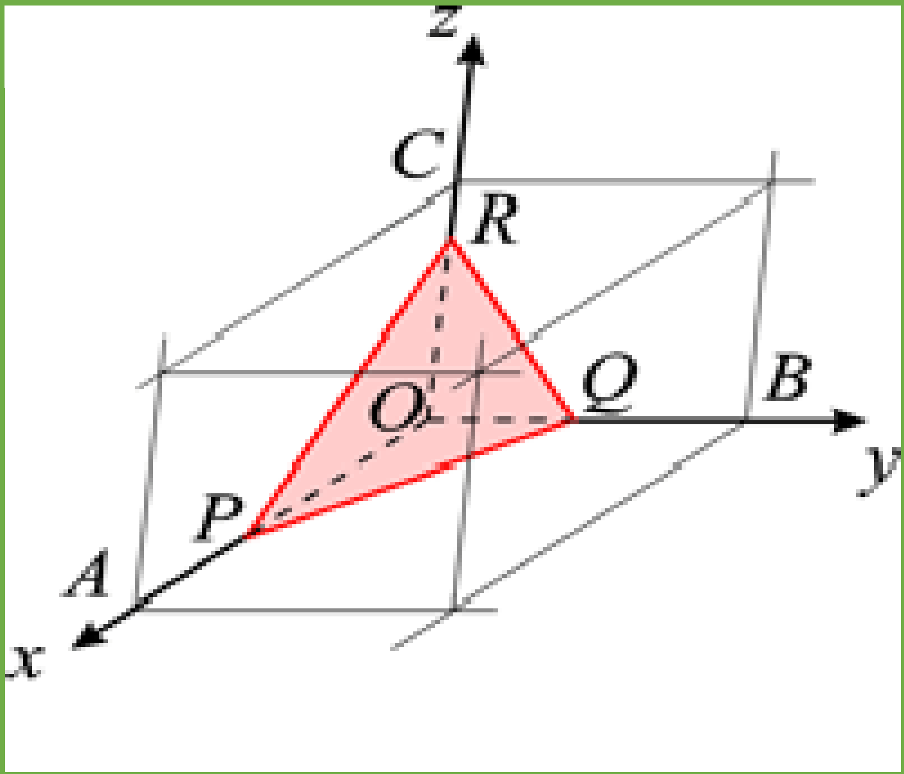
Laws of Crystallography:

Crystallography is based on three fundamental laws.

1 Steno's law OR Law of constancy of interfacial angles:

The relationship was discovered in 1669 by the Danish geologist Nicolaus Steno. This law states that angle between adjacent corresponding faces is inter facial angles of the crystal of a particular substance is always constant inspite of different shapes and sizes and mode of growth of crystal at constant temperature.

2 Law of rational indices: This law was given by A French crystallographer, René-Just Haüy, in 1784. This law states that the ratio of intercepts of different faces of a crystal with the three axes are constant and can be expressed by rational numbers that the intercepts of any face of a crystal along the crystallographic axes are either equal to unit intercepts (i.e., intercepts made by unit cell) p, q, r or some simple whole number multiples of them



3 Law of constancy of symmetry: According to this law, all crystals of a substance have the same elements of symmetry is plane of symmetry, axis of symmetry and Centre of symmetry.

Crystal: Crystals are solid geometrical figures which are bounded by well-defined more or less plane surfaces called 'faces'.

General characteristics of crystal:

- Crystals are polyhedral and homogeneous.
- It possesses a long range, three dimensional internal atomic structure and accordingly the faces of a crystal are arranged in a regular pattern.
- Regular geometry is developed only under suitable physico – chemical condition. Crystals are formed under slow cooling.

All solid matter is either **amorphous** (without definite shape) or **crystalline** (from the Greek word for clear **ice**). Crystals are defined by a regular, well-ordered molecular structure called a lattice, consisting of stacked planes of molecules. Because the molecules of the crystal fit together and contain strong electrical attractions between the atoms, a crystal is typically very strong.

There are many shapes in which crystals may be found, depending upon the type of atomic bond that is most dominant

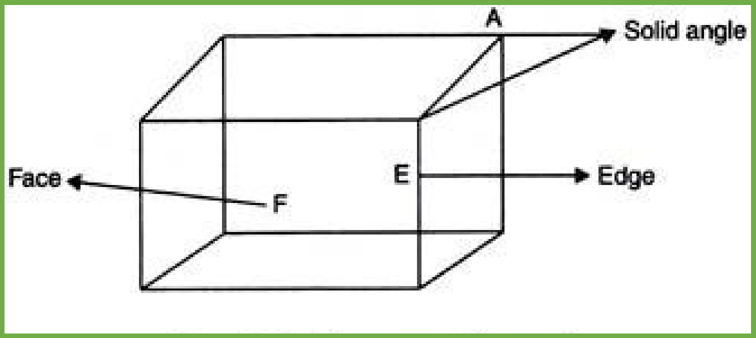
Crystal Morphology

Elements of Crystal Forms:

Face: Faces are the plain surfaces of the crystals.

Edge: The line of intersection of two adjacent faces is known as an edge.

Solid angle: It is a point where three or more faces meet.



The relationship of these faces, edges and solid angles are governed by a formula known as Euler's formula.

Euler's formula:

$$F + A = E + 2$$

Where, F = number of faces in a crystal, A = number of solid angles = number of edges in a crystal, 2 = constant.

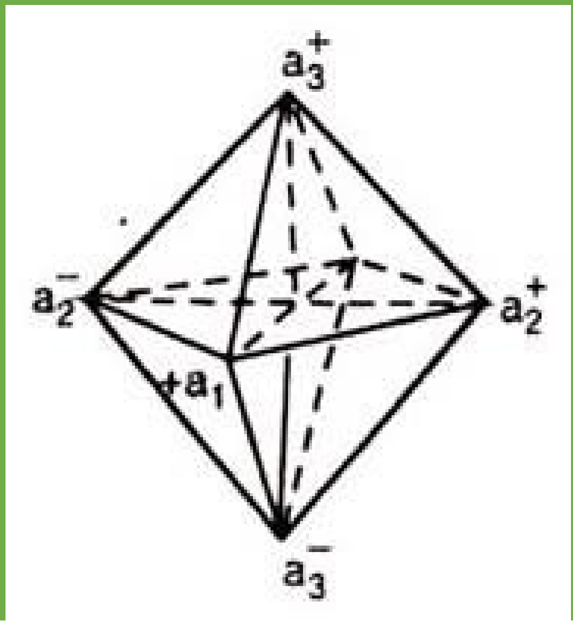
Example:

Serial No.	Model No.	No. of faces (F)	No. of solid angles (A)	No. of edges (E)	F + A	E + 2
1	111	8	6	12	14	14

- **Form:** It is a group of faces, which have a like position with respect to crystallographic axes of reference. A crystal form is a set of crystal faces that are related to each other by symmetry.
- *Forms may be classified in three ways:*
- **I** ***Simple Form*****:** When a crystal is made up of all like faces such as cube, octahedron, etc.
- ***Combination Form*****:** When a crystal is made up of two or more simple forms.
- ***II*** ***Closed form*** is a set of crystal faces that completely enclose space.
- ***Open form*** is one or more crystal faces that do not completely enclose space.
- ***II*** ***General Form*** is a form in a particular crystal class that contains faces that intersect all crystallographic axes at different lengths. It has the form symbol {hkl}.
- ***Special form*** here only one possible set of values exit for the indices.

Holohedral Form:

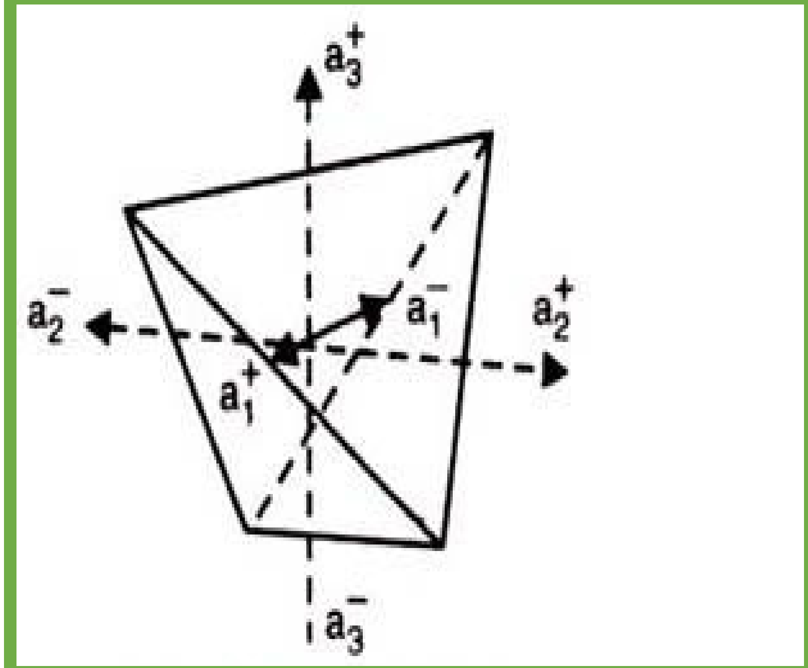
It is that form in a crystal system, which shows development of all the possible faces in its domain. Octahedron is a holohedral form because it shows all the eight faces developed on the crystal. *Generally, holohedral forms develop in the crystals of highest symmetry in a crystal system.* Such class of highest symmetry in a system is called its *normal class.*



Hemihedral Form:

It shows, as the name indicates, only half the number of possible faces of a corresponding holohedral form of the normal class of the same system. As such, all hemihedral forms may be assumed to have been derived from holohedral forms.

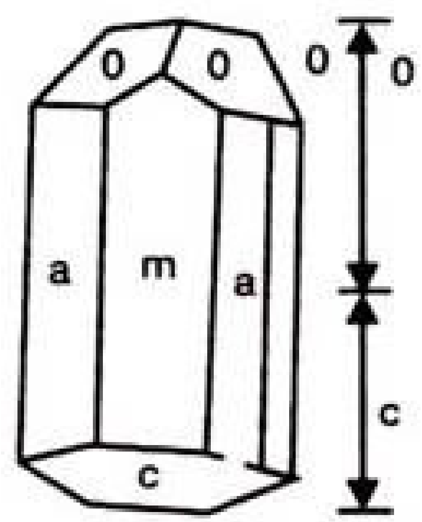
A hemihedral form develops due to decrease in the symmetry of a crystal.



Example: Octahedron is the holohedral form and Tetrahedron (only four faces) is a hemihedral form developed from it. It has only four faces and occurs in crystals of Tetrahedrite class of isometric system, which has a lower symmetry than normal class.

Hemimorphic Form:

It is also derived from a holohedral form and has only half the number of faces as in hemihedral form. In this case, however, all the faces of the form are developed only on one extremity of the crystal, being absent from the other extremity. In other words, such a crystal will not be symmetrical with reference to a center of symmetry.



Hemimorphic Form
See Top and Bottom Faces

Enantiomorphous Form:

An enantiomorphous form is composed of faces placed on two crystals of the same mineral in such a way that faces on one crystal become the mirror image of the form of faces on the other crystal. As right hand and left hand having similar relation to the body axis are not interchangeable, so is the case with enantiomorphous forms.

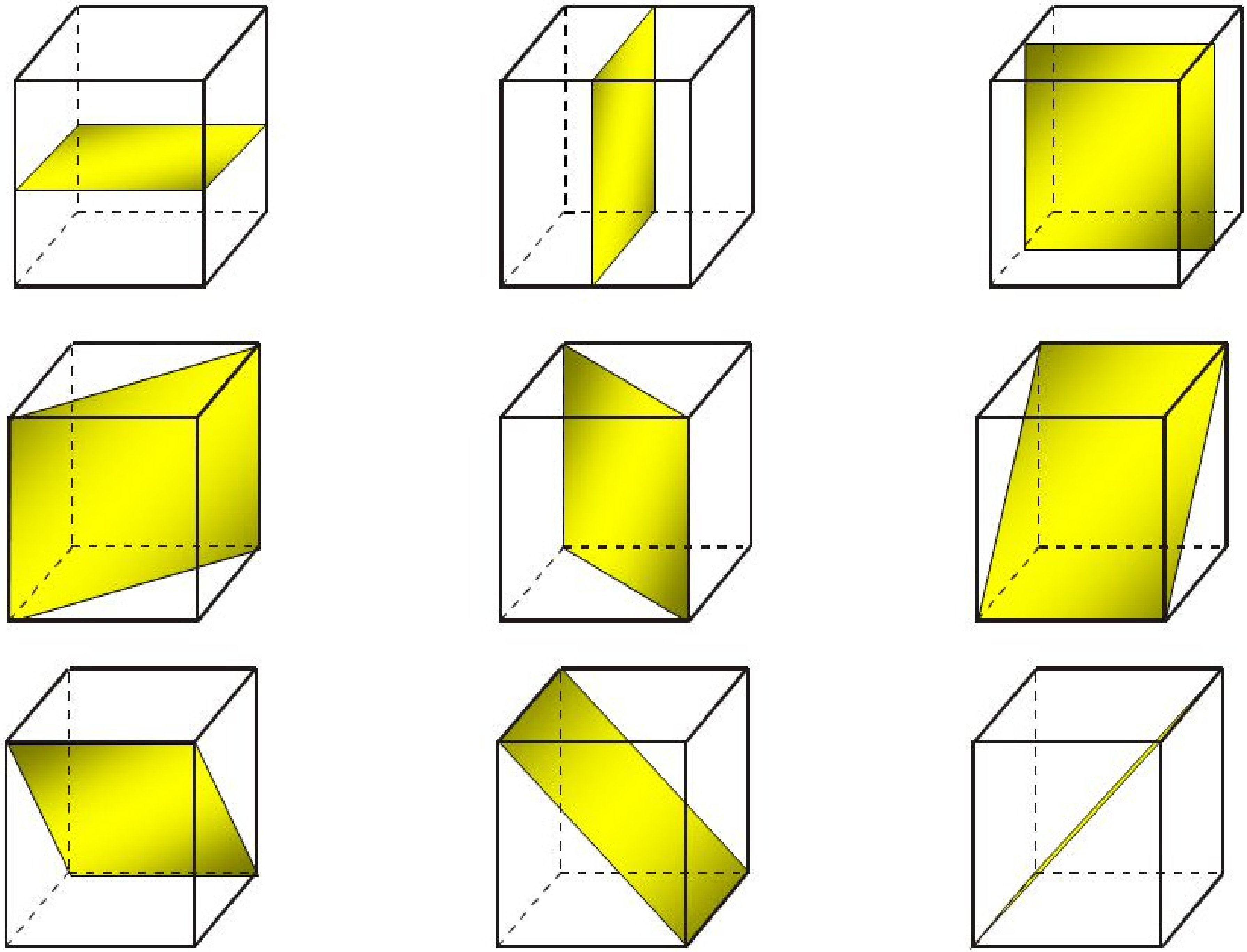
Crystals of quartz show best-developed enantiomorphous forms.

SYMMETRY FUNCTIONS

Plane of Symmetry:

Any imaginary plane passing through the centre of a crystal in such a way that it divides the crystal in two exactly similar halves is called a plane of symmetry. In other words, a plane of symmetry is said to exist in a crystal when for each face, edge or solid angle there is another similar face, edge or solid angle occupying identical position on the opposite side of this plane.

A crystal may possess one, two or more planes of symmetry, the highest number being 9 (nine) occurring in the normal class of isometric system. Plane of symmetry may be described as axial, horizontal, vertical or diagonal depending upon its position with reference to the outline of the crystal.



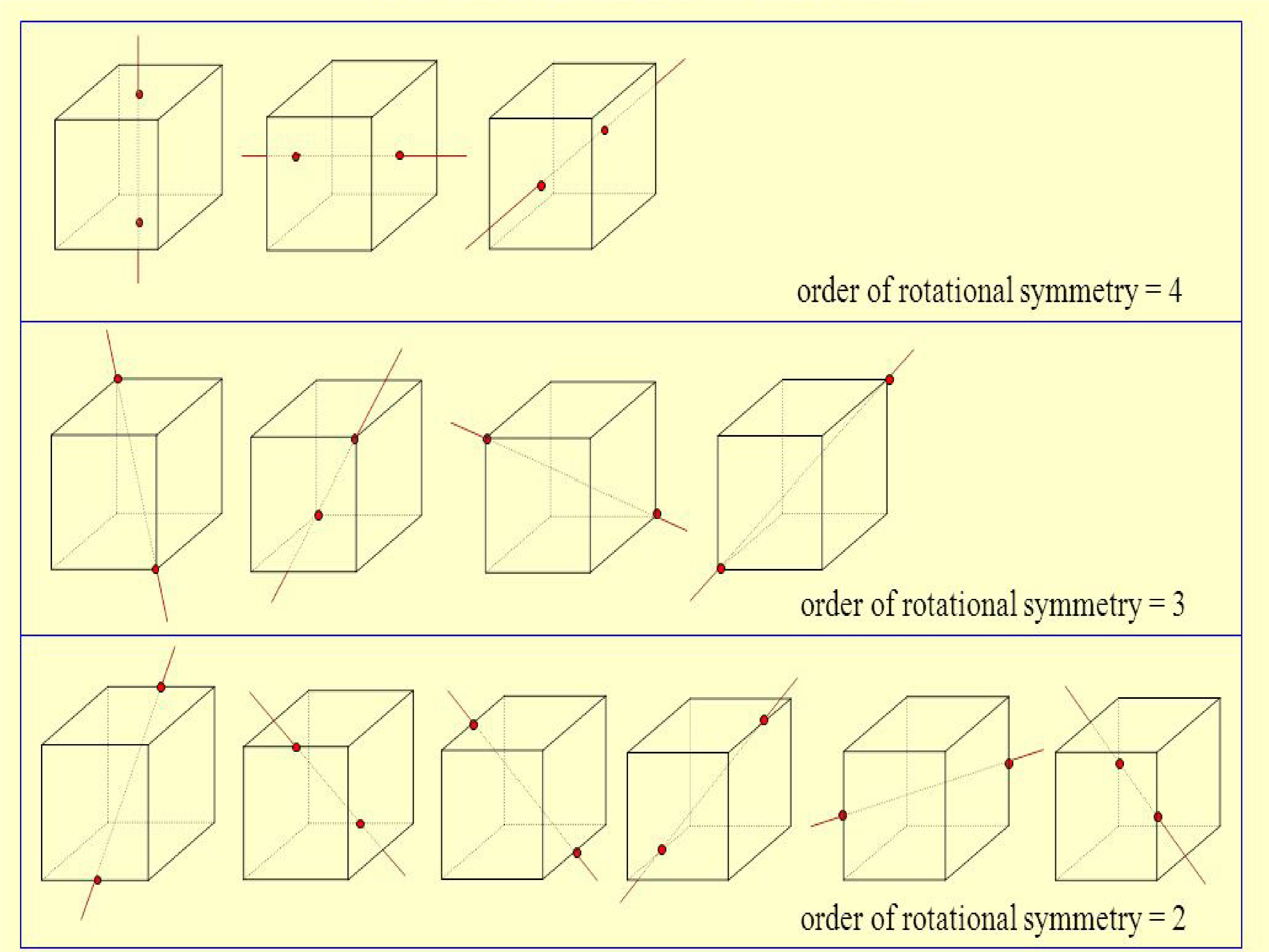
Axis of Symmetry:

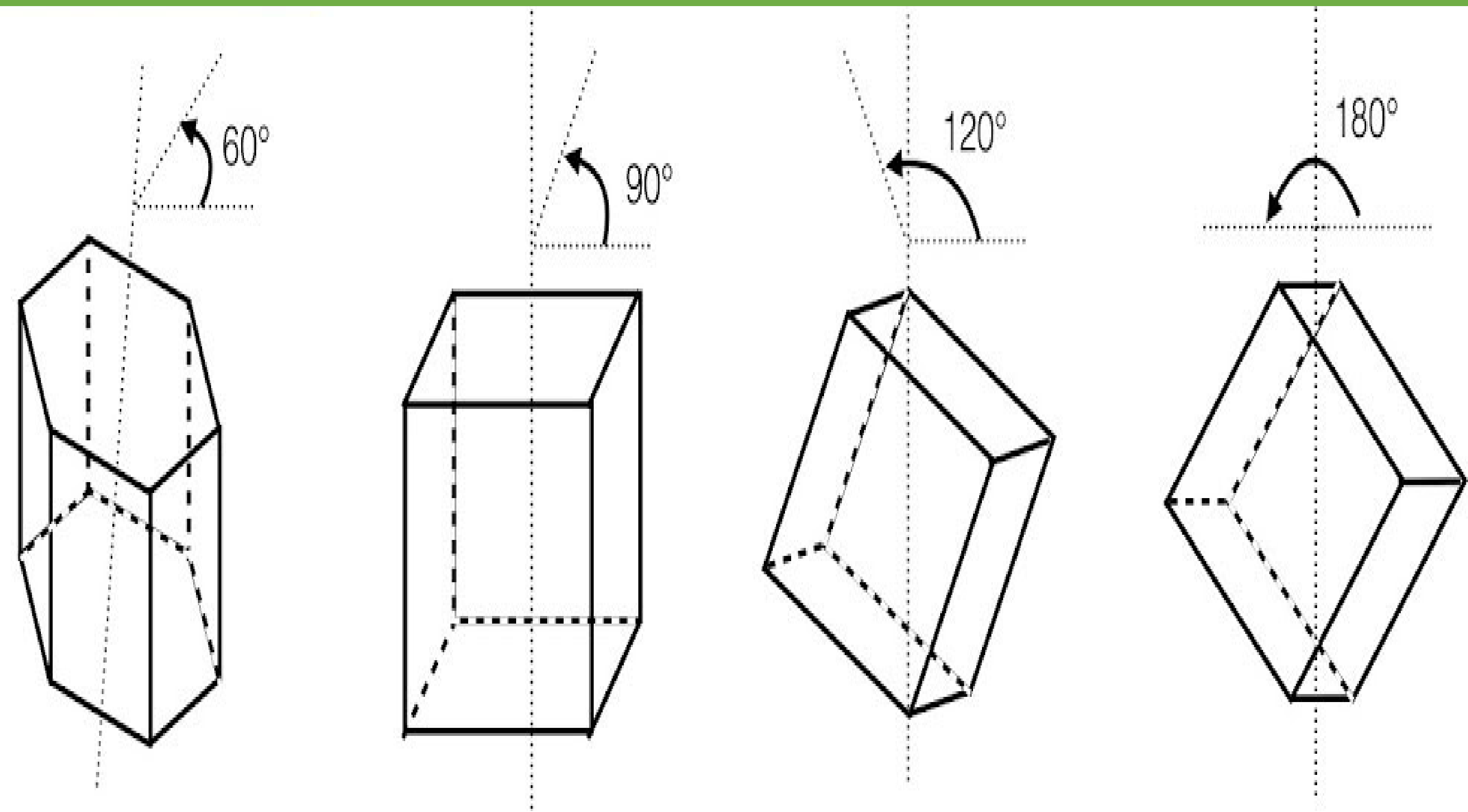
It is defined as an imaginary line in a crystal passing through its centre in such a way that when a crystal is given a complete rotation along this line a certain crystal face comes to occupy the same position at least twice.

Rotation of a crystal through 360 degrees on an axis may reveal 2, 3, 4, or 6 reproductions of original face or faces--these kinds of fold axes are:

- A_2= 2-fold--a reproduction of face(s) twice
- A_3= 3-fold--the same 3 times
- A_4= 4-fold--the same 4 times
- A_6= 6-fold--the same 6 times

The highest number of axes of symmetry is thirteen (13), observed in normal class of isometric system.


order of rotational symmetry = 4
order of rotational symmetry = 3
order of rotational symmetry = 2



60° rotation

90° rotation

120° rotation

180° rotation

$$\frac{360}{60} = 6 \text{ fold axis}$$

$$\frac{360}{90} = 4 \text{ fold axis}$$

$$\frac{360}{120} = 3 \text{ fold axis}$$

$$\frac{360}{180} = 2 \text{ fold axis}$$

Centre of Symmetry:

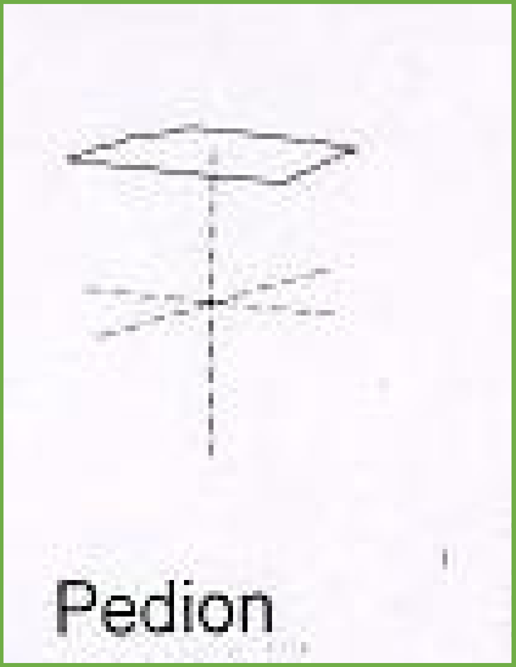
A crystal is said to possess a centre of symmetry if on passing an imaginary line from some definite face, edge or corner on one side of the crystal through its centre, another exactly similar face or edge or corner is found on the other side at an equal distance from the centre. *Many crystals have no planes or axes of symmetry but do possess a centre of symmetry.* The centre of symmetry may not be there whereas the crystal may be symmetrical to a plane of symmetry.

Common Forms in Crystallography:

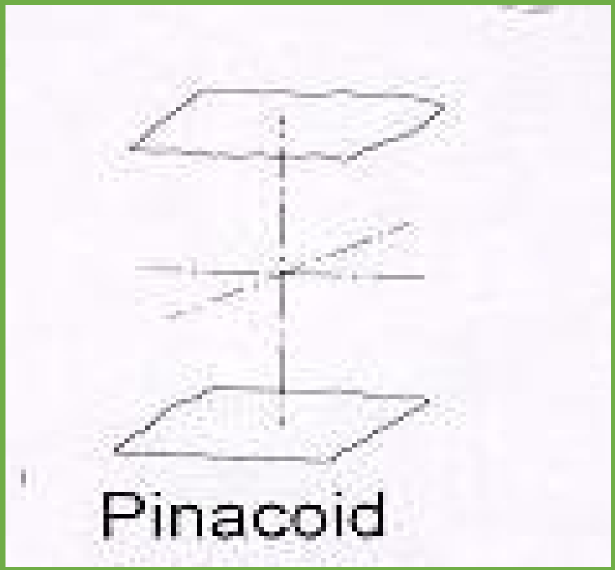
There are 48 possible forms that can be developed as the result of the 32 combinations of symmetry.

Non – Isometric Forms

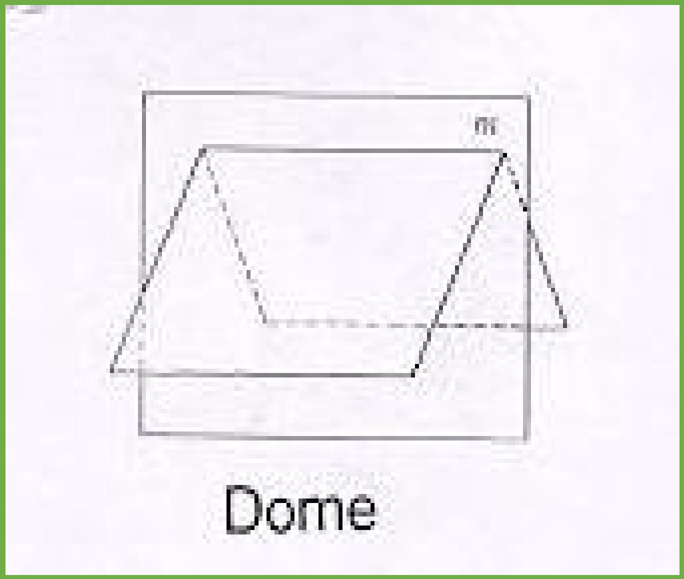
Pedion: A pedion is an open, one face formed.



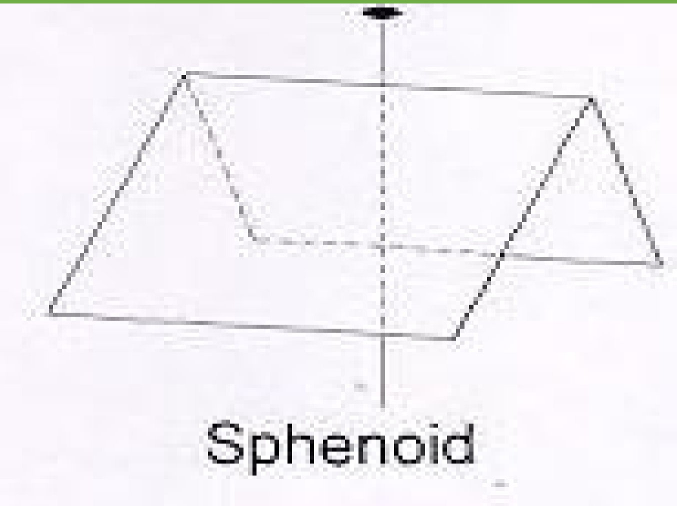
Pinacoid: A Pinacoid is an open 2-faced form made up of two parallel faces.



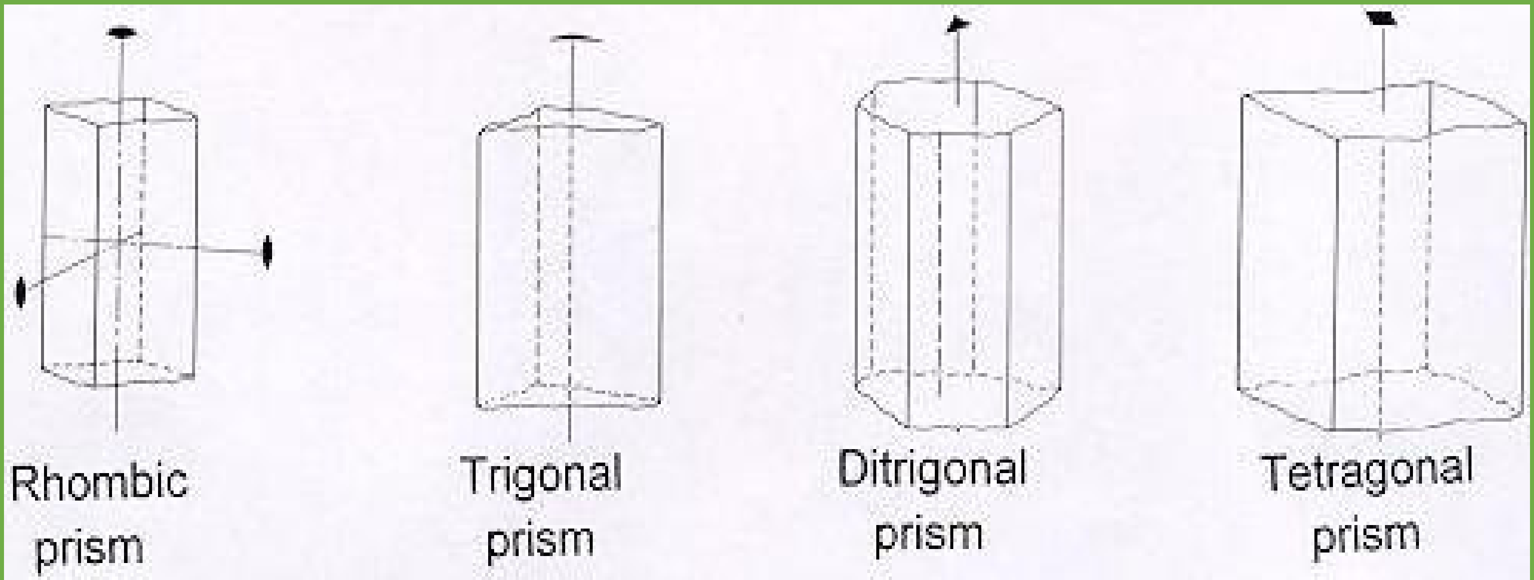
Domes: Domes are 2- faced open forms where the 2 faces are related to one another by a mirror plane.

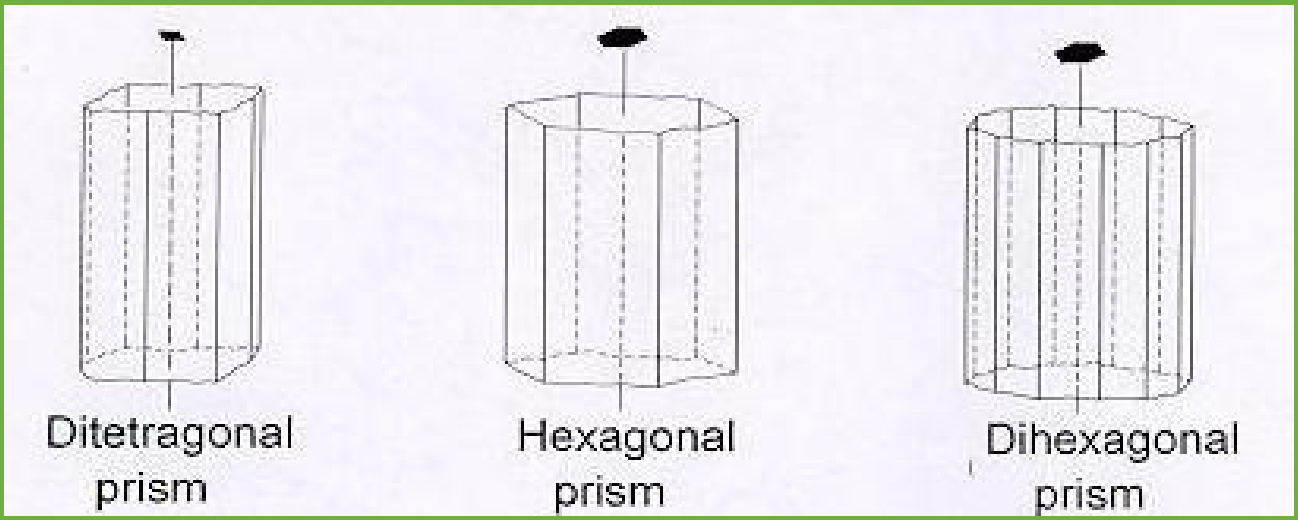


Sphenoids: Sphenoids are2 - faced open forms where the faces are related to each other by a 2-fold rotation axis and are not parallel to each other.

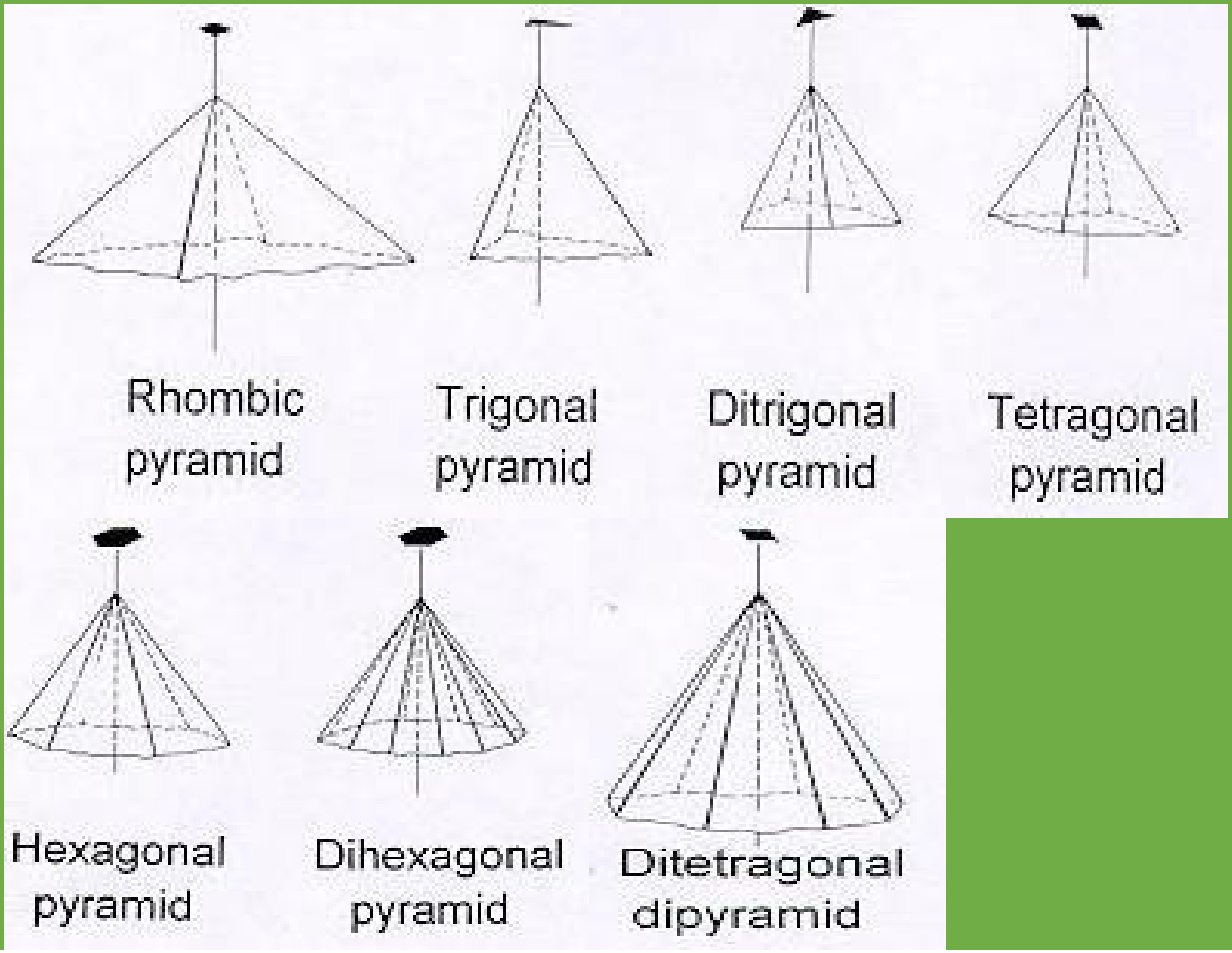


Prism: an open form of 3 (trigonal), 4 (tetragonal or Rhombic prism), 6 (hexagonal or ditrigonal), 8 (ditetragonal), or 12 (dihexagonal) faces all parallel to same axis.



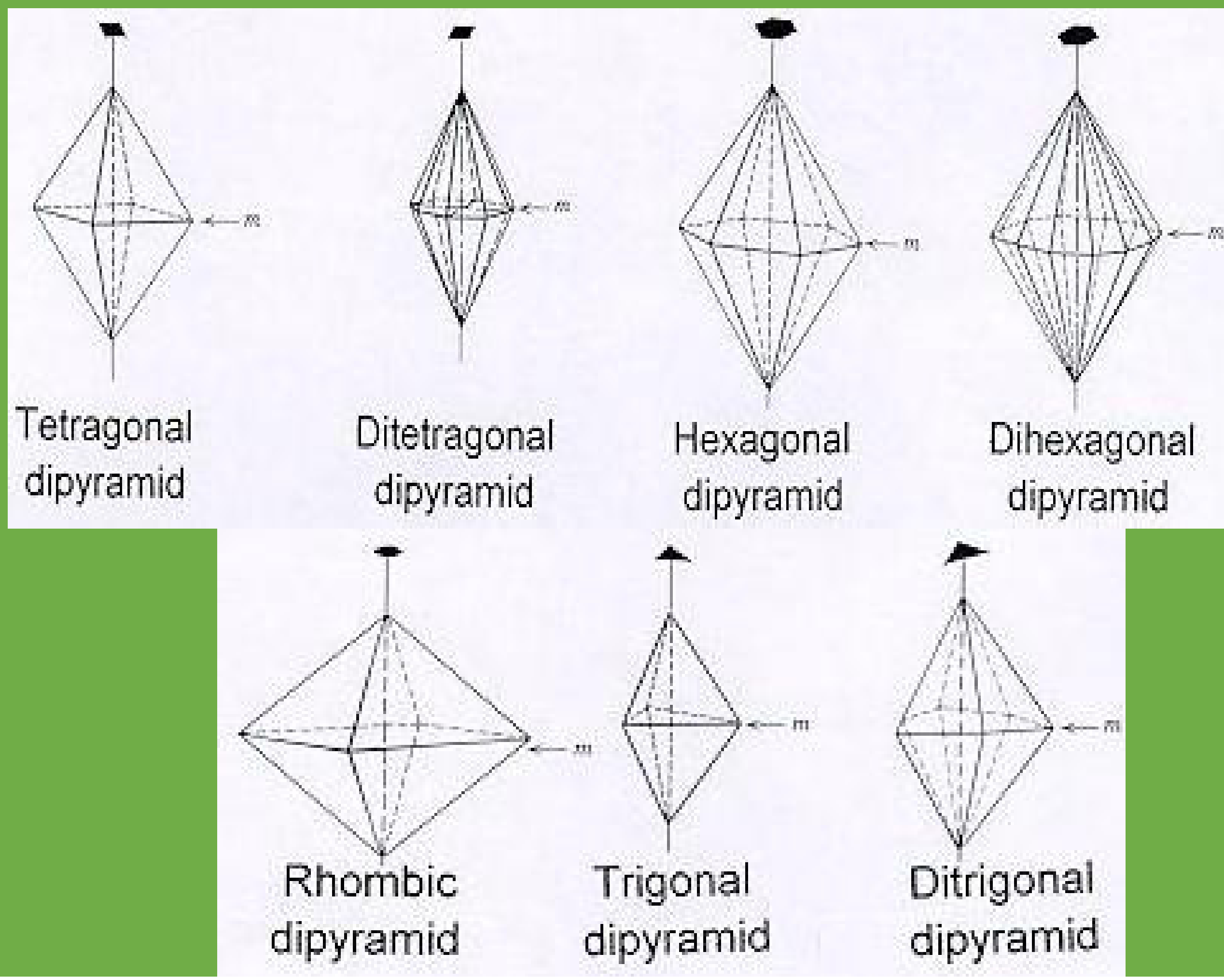

Ditetragonal prism
Hexagonal prism
Dihexagonal prism

Pyramids: A pyramid is a 3(trigonal), 4(tetragonal or rhombic), 6(hexagonal or ditrigonal), 8(ditetragonal) or 12(dihexagonal) faced open form where all faces in the form meet, or could meet if extended, at a point.



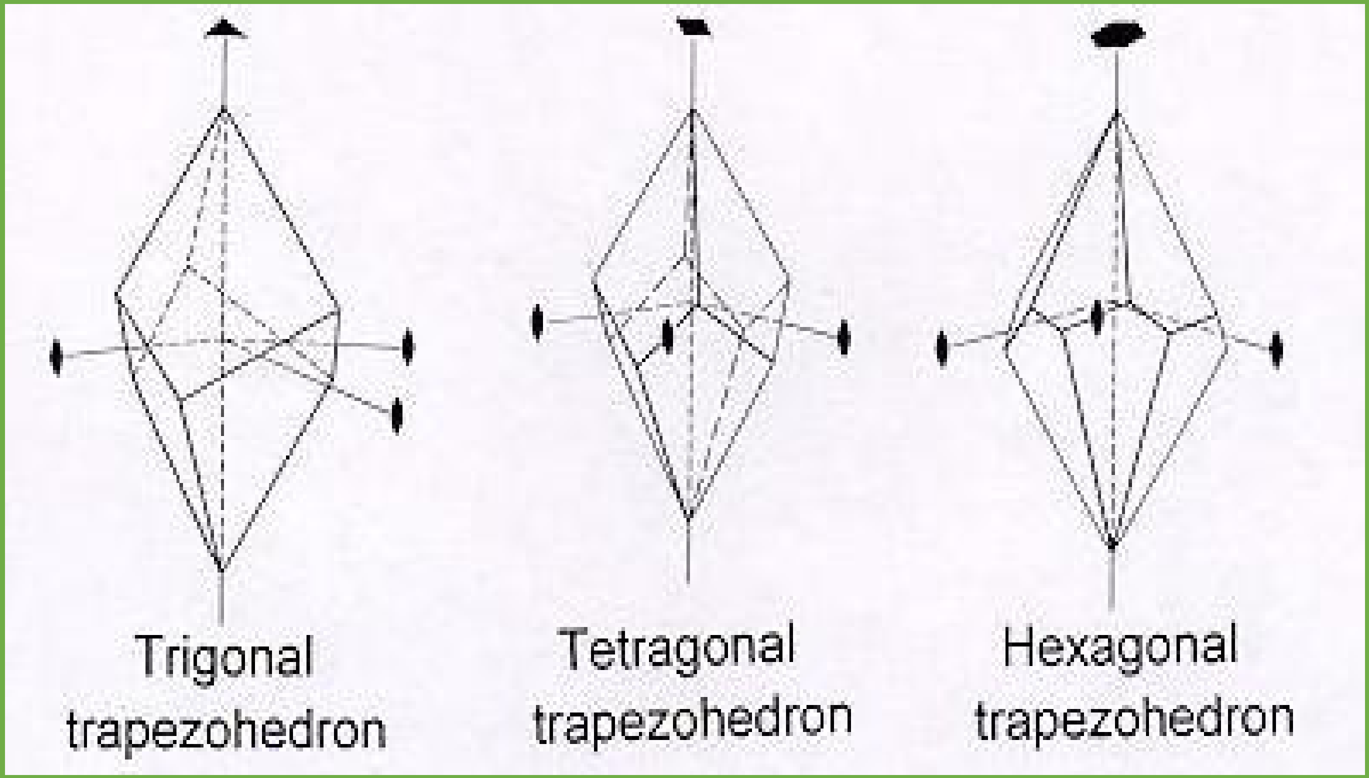
Dipyramids:

Dipyramids are closed forms consisting of 6, 8, 12, 16, or 24 faces. Dipyramids are pyramids that are reflected across a mirror plane. Thus, they occur in crystal classes that have a mirror plane perpendicular to a rotation or rotoinversion axis.



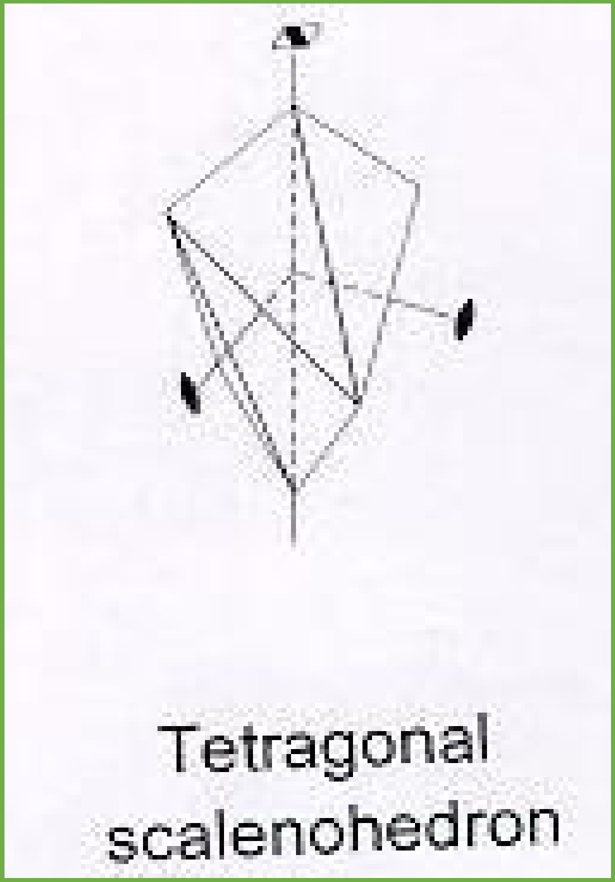
Trapezohedrons:

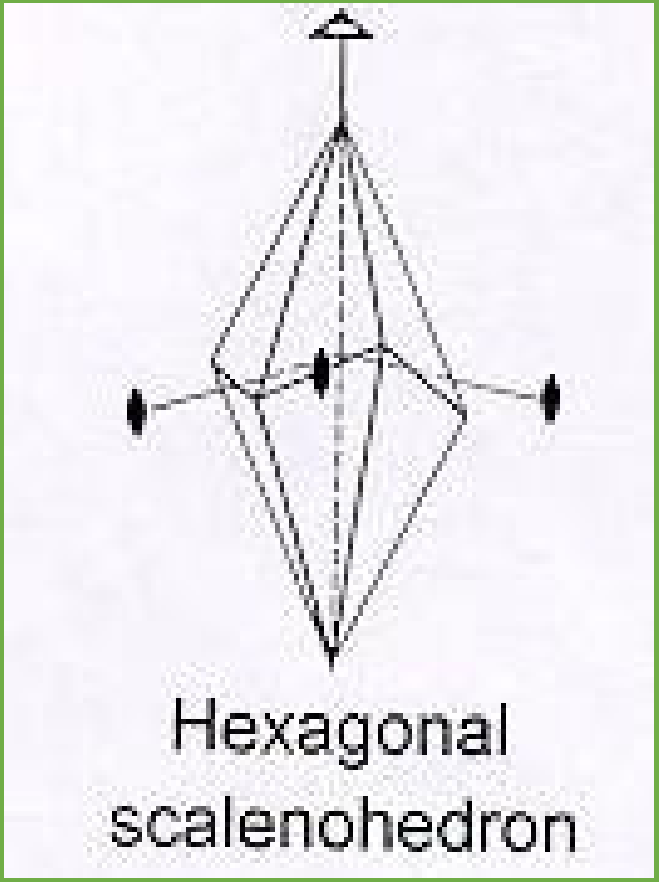
Trapezohedrons are closed 6, 8, or 12 faced forms, with 3 (trigonal), 4(tetragonal), or 6(hexagonal) upper faces offset from 3, 4, or 6 lower faces.



Scalenohedrons:

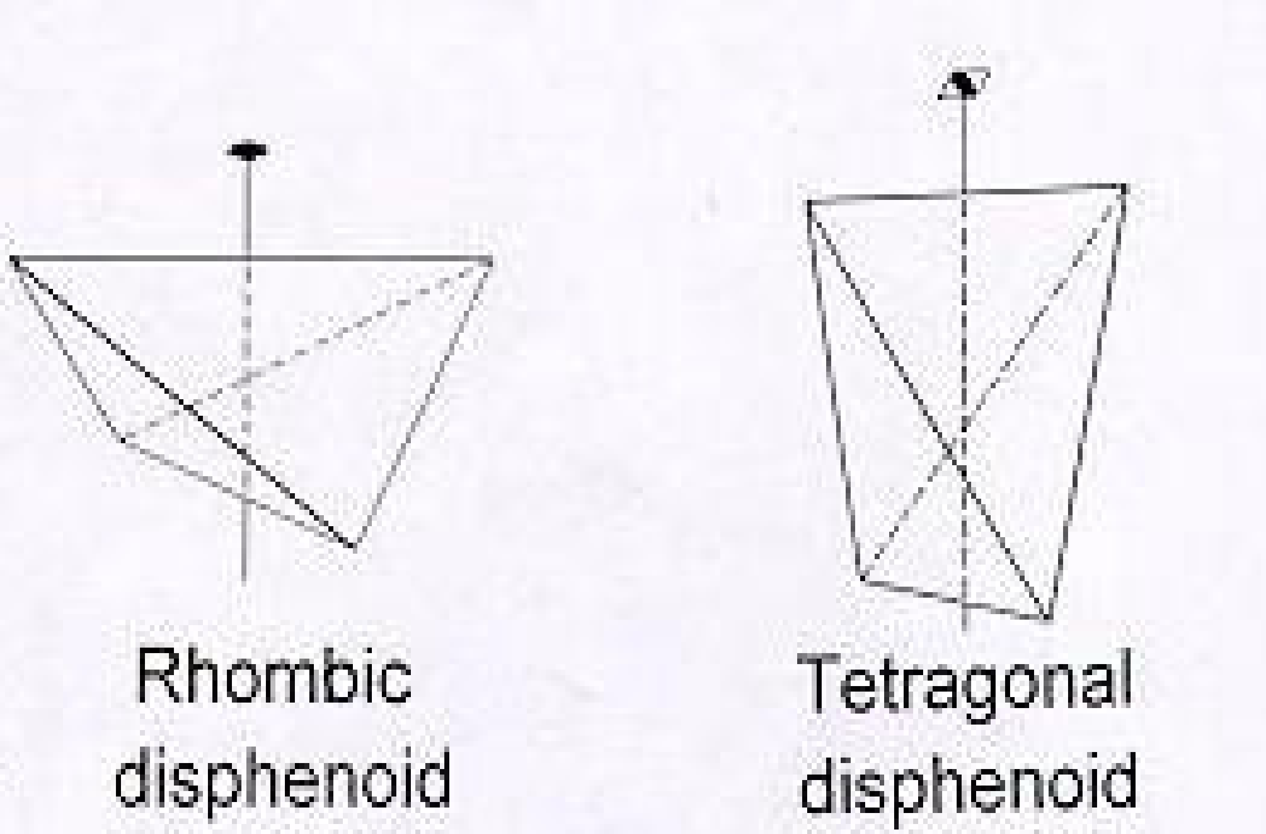
A scalenohedron is a closed form with 8 (tetragonal) or 12 (hexagonal) faces. In ideally developed faces each of the faces is a scalene triangle.





Disphenoids

A disphenoid is a closed form consisting of 4 faces. With 2 upper faces alternating with 2 lower faces offset by 90 degrees.

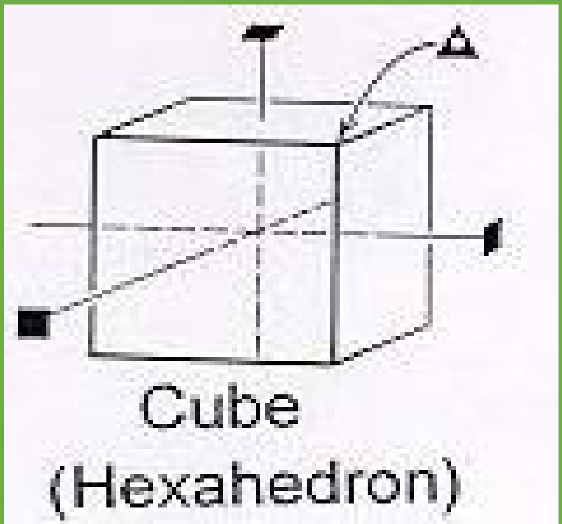


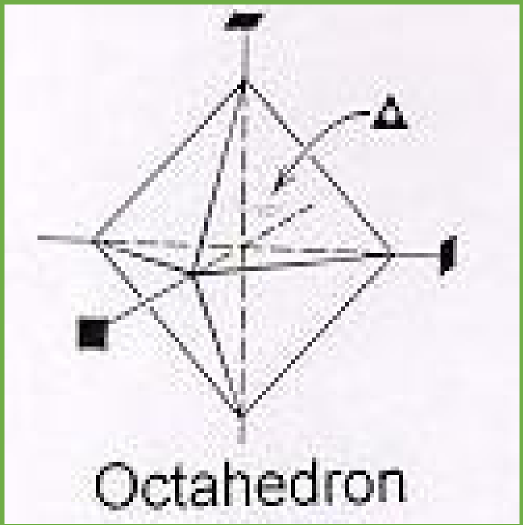
Isometric Forms

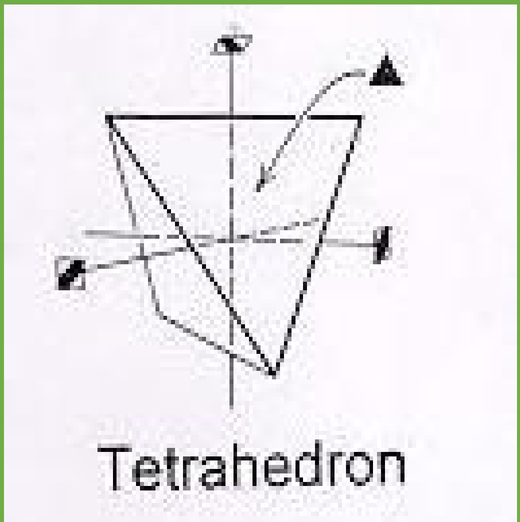
Cube (hexahedron)--6 equal faces intersecting at 90 degrees.

Octahedron--8 equilateral triangular faces.

Tetrahedron--4 equilateral triangular faces.





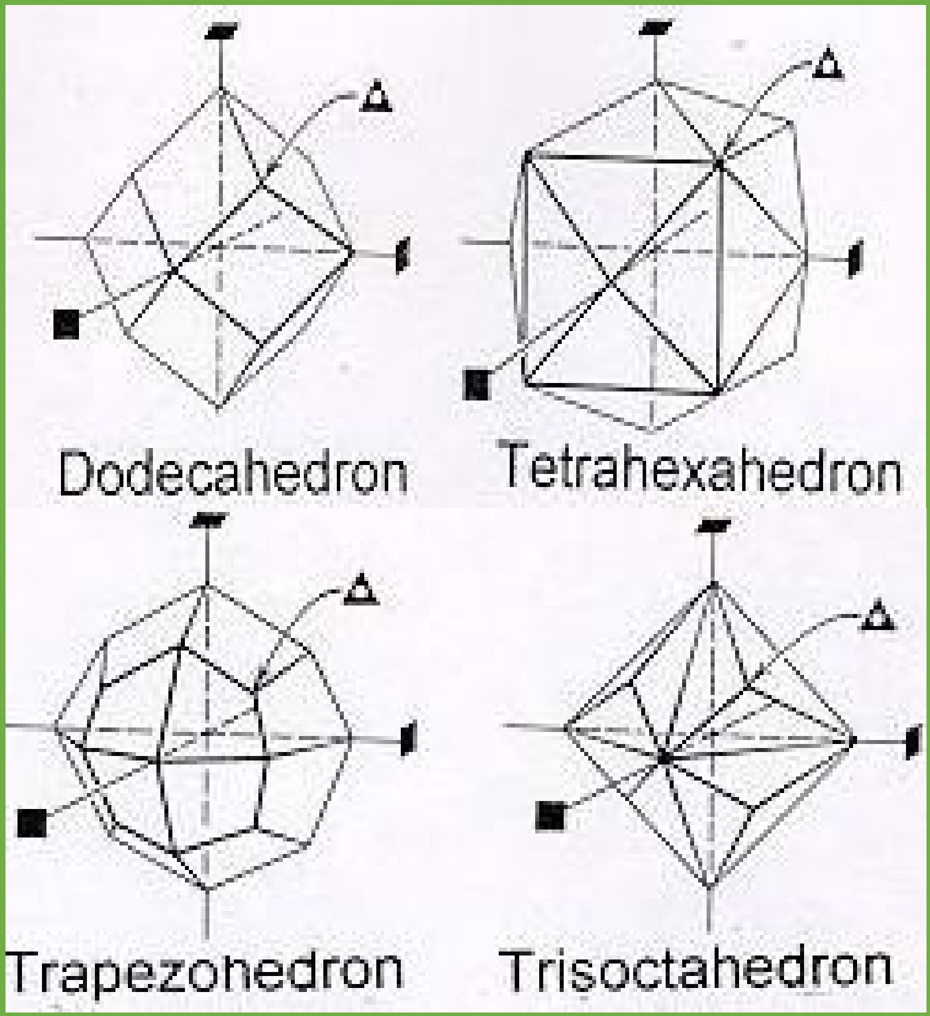


Dodecahedron--12 rhombed faces.

Tetrahexahedron--24 isosceles triangular faces--4 faces on each basic hexahedron face.

Trapezohedrons--24 trapezium shaped faces.

Trisoctahedron--24 isosceles triangular faces--3 faces on each octahedron face.

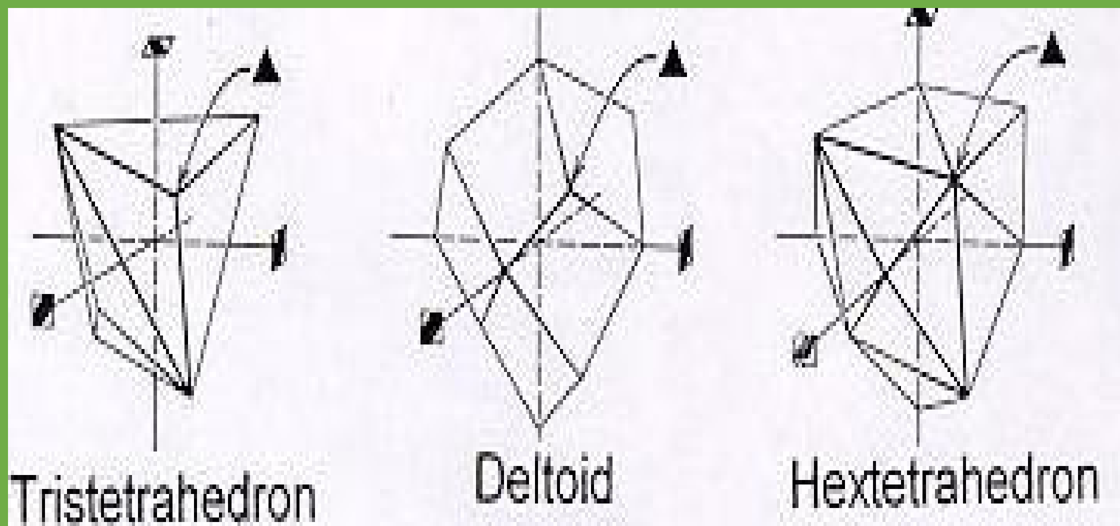


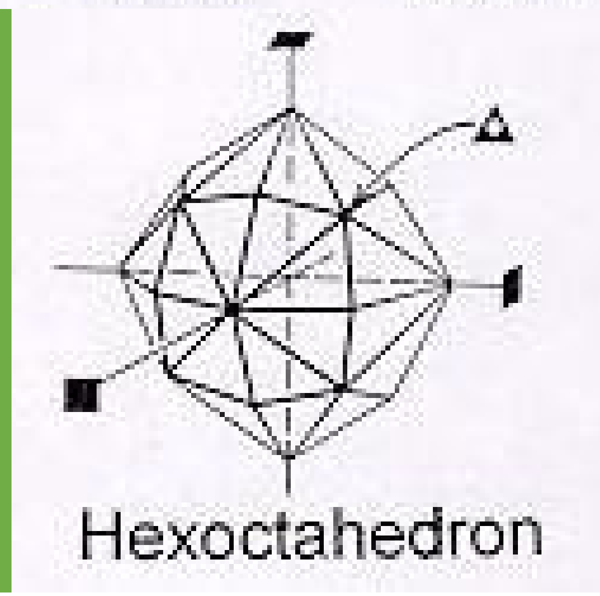
Hexoctahedron--48 triangular faces--6 faces on each basic octahedron face.

Tristetrahedron--12 triangular faces--3 faces on each basic tetrahedron face.

Deltoid dodecahedron--12 faces corresponding to 1/2 of trisoctahedron faces.

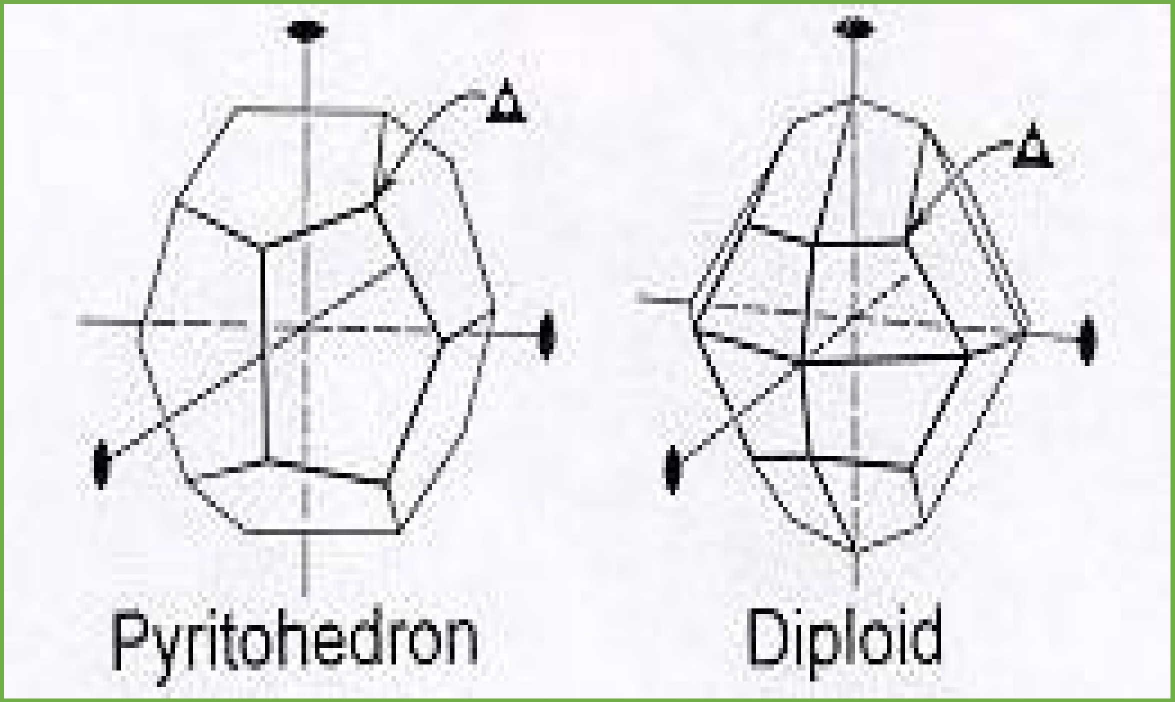
Hextetrahedron--24 faces--6 faces on each basic tetrahedron faces.





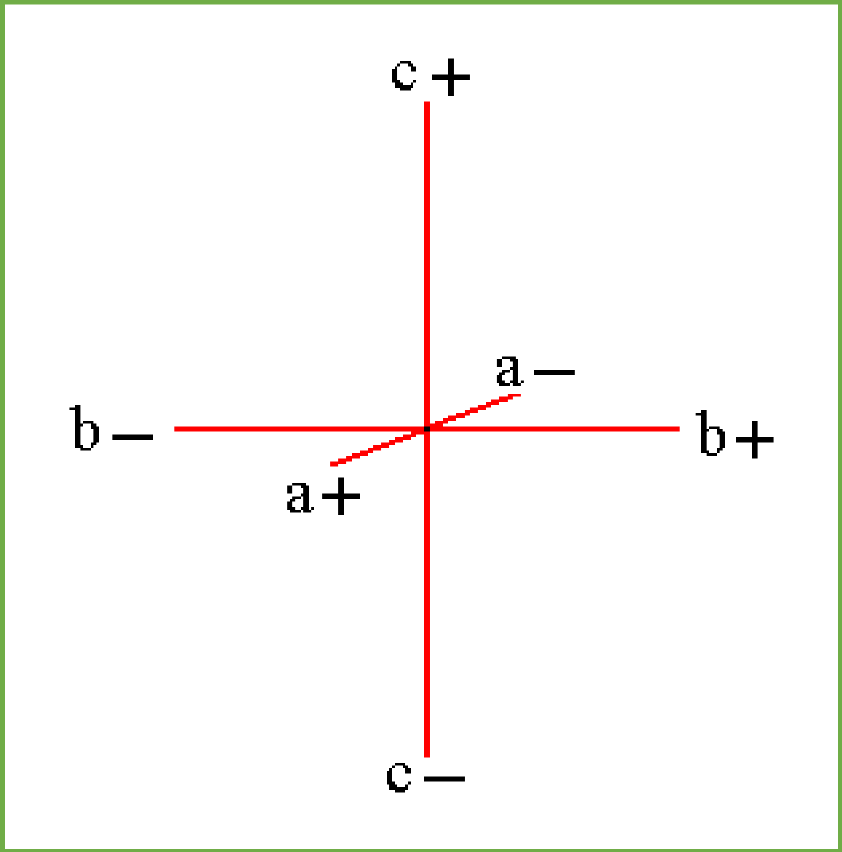
Diploid--24 faces

Pyritohedron--12 pentagonal faces



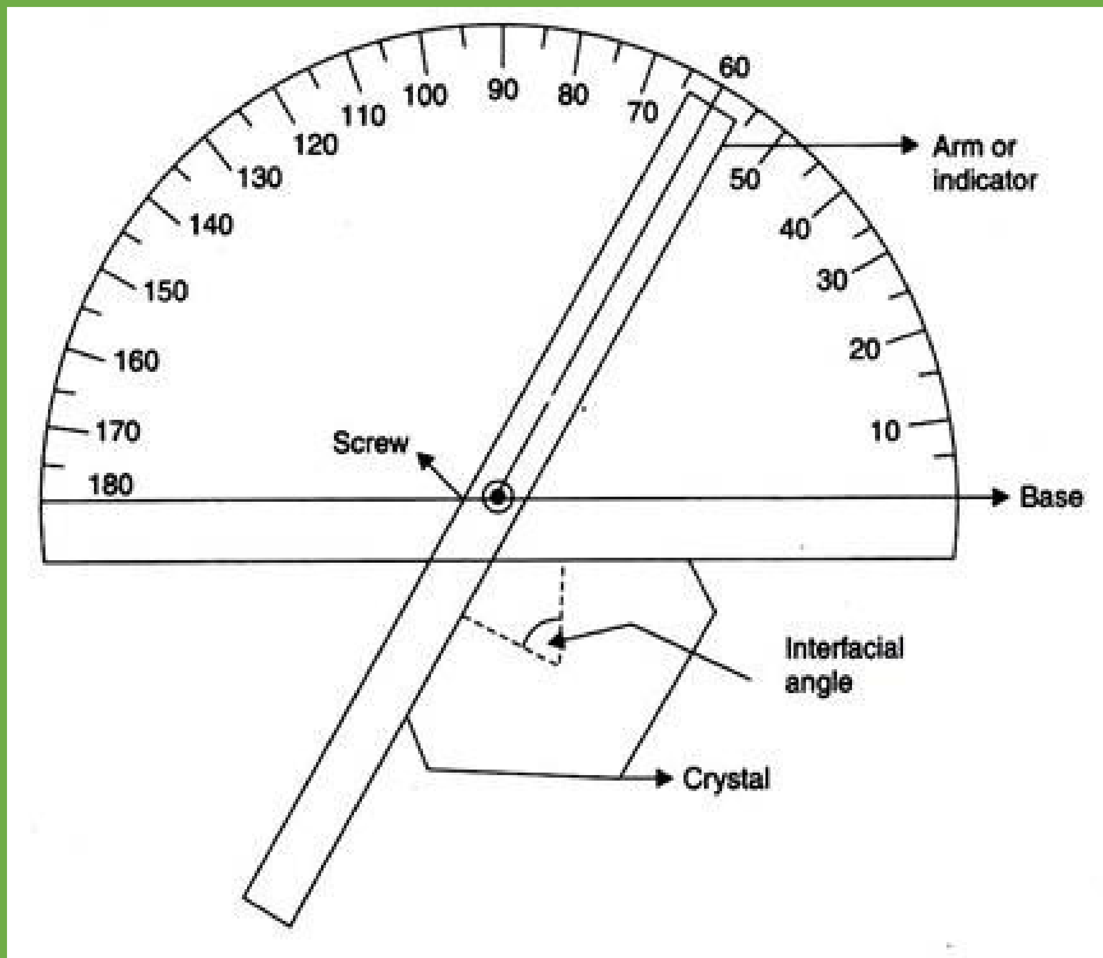
Crystallographic Axes:

Crystallographic Axes are the imaginary lines passing through the centre of the crystal, but not lying in the same plane, and used as axes of reference for denoting the position of faces.



Interfacial Angle (IFA):

Interfacial angle is angle between any two adjacent faces of a crystal. The instrument used to measure interfacial angle is called Contact Goniometer.



Law of constancy of interfacial angle:

Law of constancy of interfacial angle states that measured at the same temperature, similar angle on crystal of the same substances remain constant, regardless the size and shape of the crystal.

Based on the crystallographic axis all the crystals are classified into six different crystal systems such as:

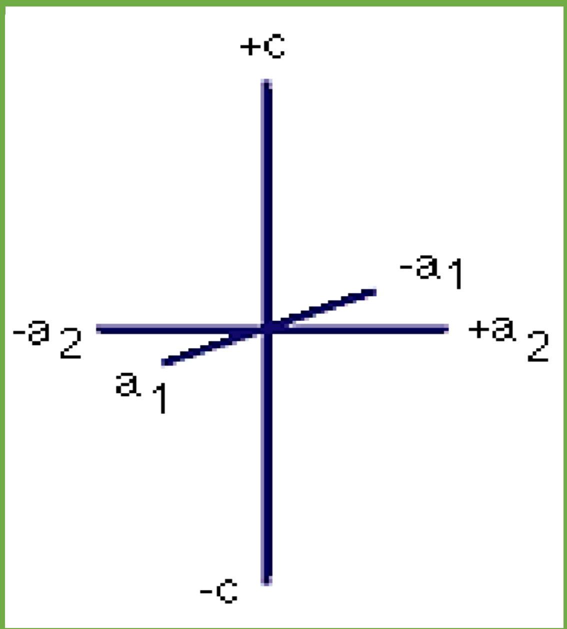
1. Isometric System.
2. Tetragonal System.
3. Hexagonal System.
4. Orthorhombic System.
5. Monoclinic System.
6. Triclinic System.

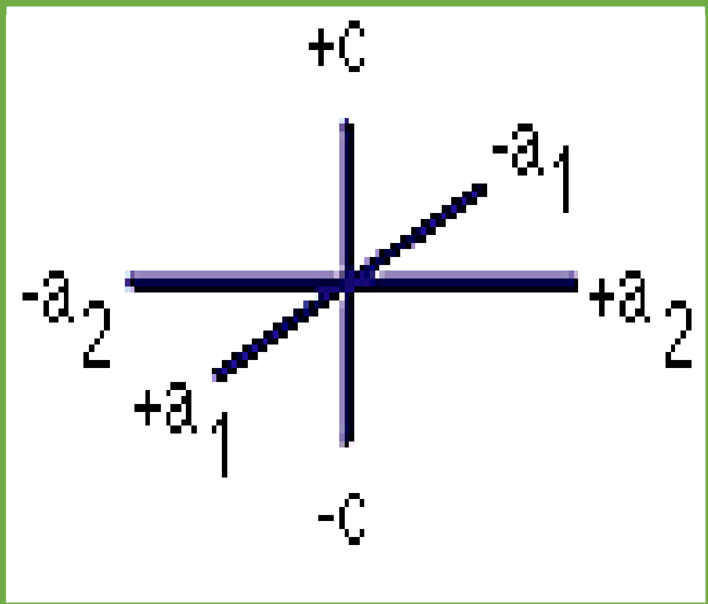
Isometric System:

In this system there are three crystallographic axes. All the three crystallographic axes which are equal and interchangeable cut at 90°, therefore, the symbol is ***a*= *b*= *c*** and the axial angle is $\alpha = \beta = \gamma = 90°$.

Tetragonal System:

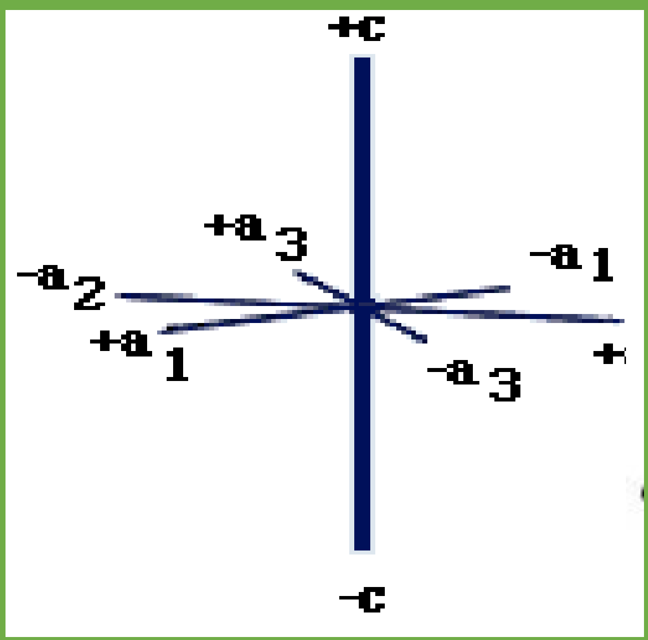
In this system there are three crystallographic axes, among these two crystallographic axes (Front to Back and Side to Side) which are equal and interchangeable. The third crystallographic axes (vertical crystallographic axis) which is unequal (it may be bigger or smaller) therefore the symbol is ***a*= *b* ≠ *c*** and the axial angle is α =β =γ = 90°. *Zircon*.

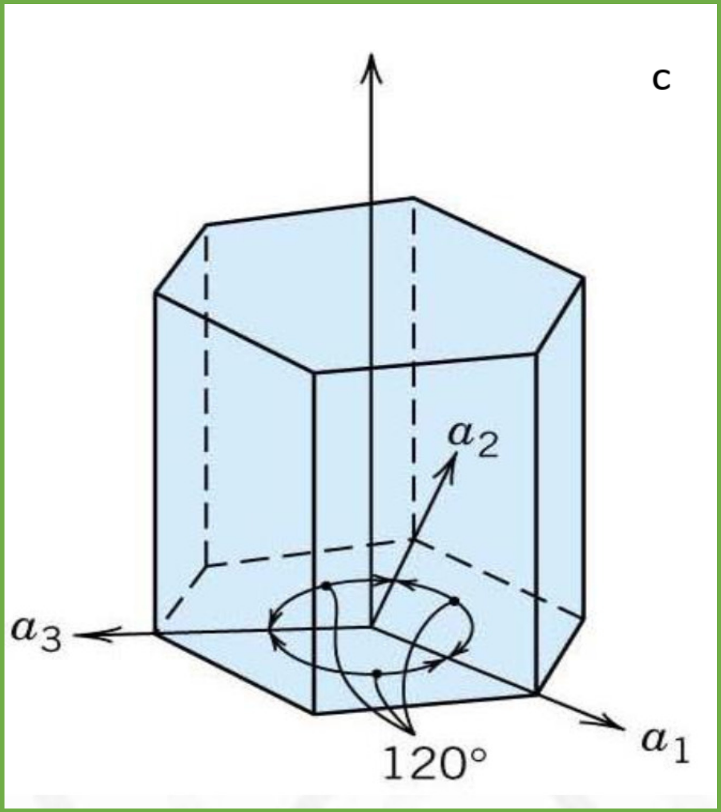




Hexagonal System:

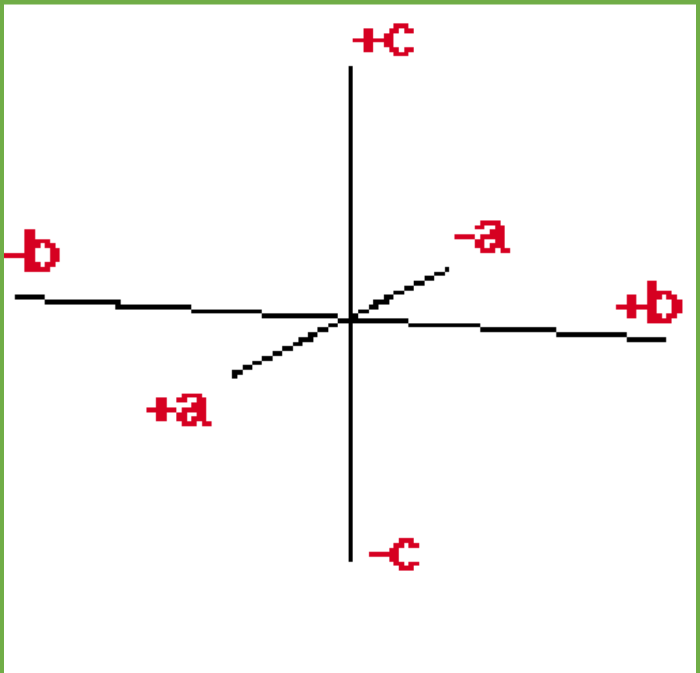
In this system there are four crystallographic axes. Three crystallographic axes which are equal and interchangeable cut at 60° or 120°. The fourth one that is vertical crystallographic axis which is unequal (it may be bigger or smaller), therefore, the symbol is a_1=$a_{2,}$ a_3 and the axial angle is ∠a ∠a = 60° or 120°, ∠a ∠c = 90°.Quartz.





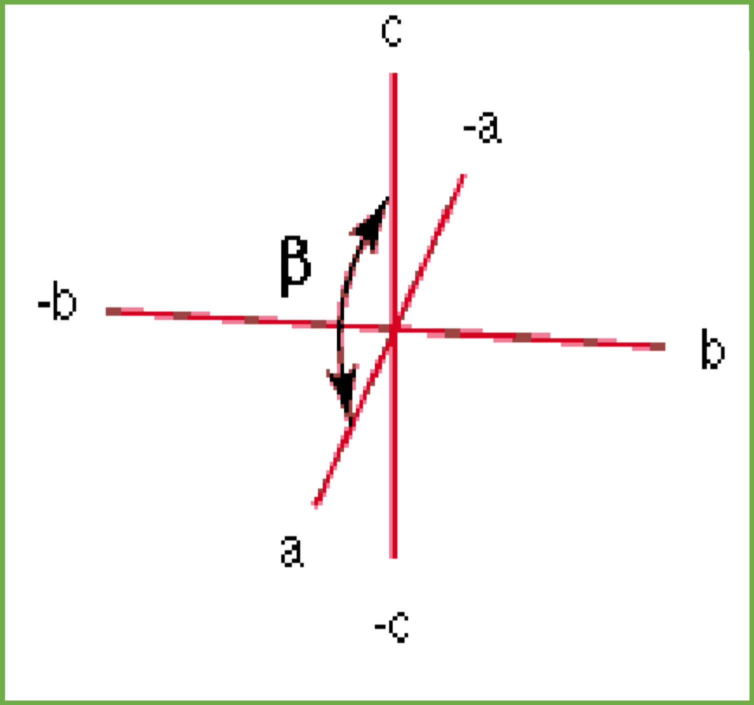
Orthorhombic System:

In this system there are three crystallographic axes. All the three crystallographic axes, which are unequal in length and cut at 90°, therefore, the symbol is a : b : c and the axial angle is ∠a ∠b ∠c = 90°. Staurolite.



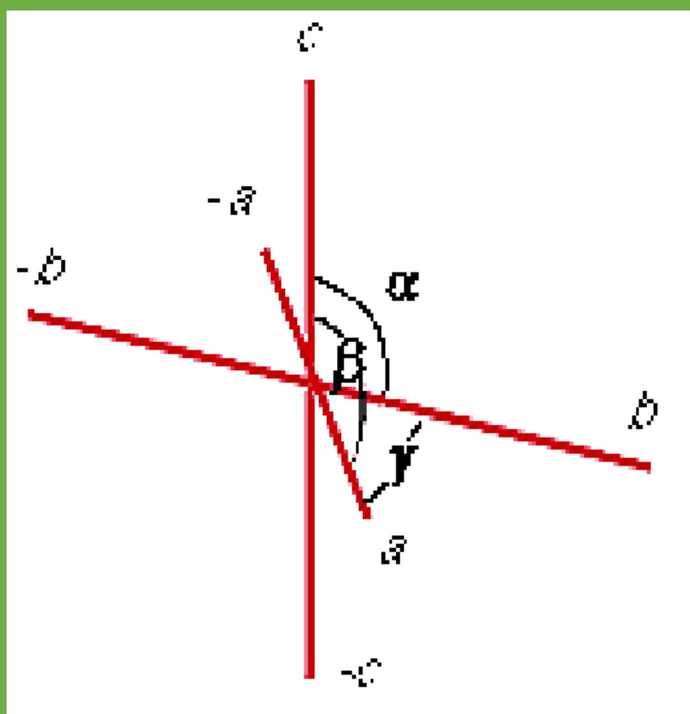
Monoclinic System:

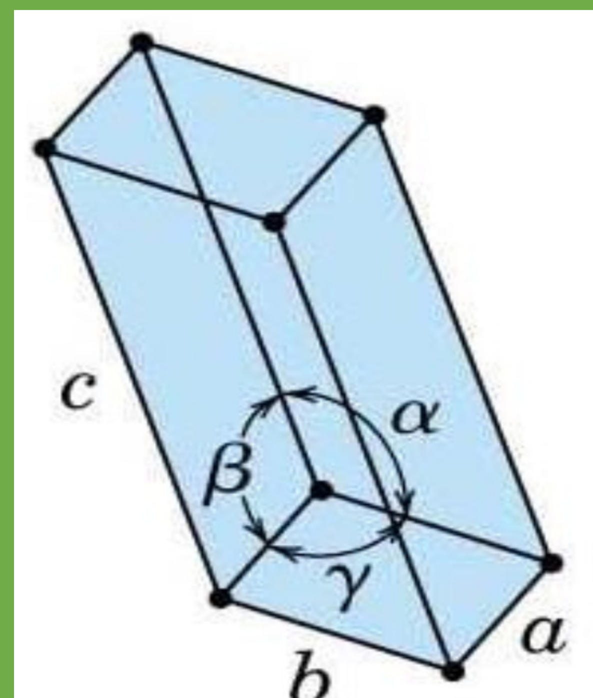
In this system there are three crystallographic axes. All the three crystallographic axes, which are unequal in length. Therefore, the symbol is a: b: c and the axial angle is ∠a ∠c = 90°, ∠b ∠c = 90°, ∠a ∠c not equal to 90°. Orthoclase.



Triclinic System:

In this system there are three crystallographic axes. All the three crystallographic axes, which are unequal in length and not cut at 90°, therefore, the symbol is a :b : c and the axial angle is ∠a ∠a ∠c not equal to 90°. example Albite.





Note: *The lengths of the crystallographic axes are controlled by the dimensions of the unit cell upon which the crystal is based. The angles between the crystallographic axes are controlled by the shape of the unit cell.*

Axial Ratios

Axial ratios are defined as the relative lengths of the crystallographic axes. They are normally taken as relative to the length of the b crystallographic axis. Thus, an axial ratio is defined as follows:

Axial Ratio = a/b: b/b: c/b

Where a is the actual length of the crystallographic axis, b, is the actual length of the b crystallographic axis, and c is the actual length of the c crystallographic axis.

- For Triclinic, Monoclinic, and Orthorhombic crystals, where the lengths of the three axes are different, this reduces to

a/b : 1 : c/b (this is usually shortened to a : 1 : c)

- For Tetragonal crystals where the length of the a and b axes are equal, this reduces to

1 : 1 : c/b (this is usually shorted to 1 : c)

- For Isometric crystals where the length of the a, b, and c axes are equal this becomes

1 : 1 : 1 (this is usually shorted to 1)

- For Hexagonal crystals where there are three equal length axes (a_1, a_2, and a_3) perpendicular to the c axis this becomes:

1 : 1 : 1: c/a (usually shortened to 1 : c)

Intercepts of Crystal Faces (Weiss Parameters):

Crystal faces can be defined by their intercepts on the crystallographic axes.

Miller Indices:

The Miller Index for a crystal face is found by

- First determining the parameters.
- second inverting the parameters, and
- Third clearing the fractions.

For example, if the face has the parameters 1 a, 1 b, ∞ c

Inverting the parameters would be 1/1, 1/1, 1/ ∞

This would become 1, 1, 0

The Miller Index is written inside parentheses with no commas - thus (110)

Examples: