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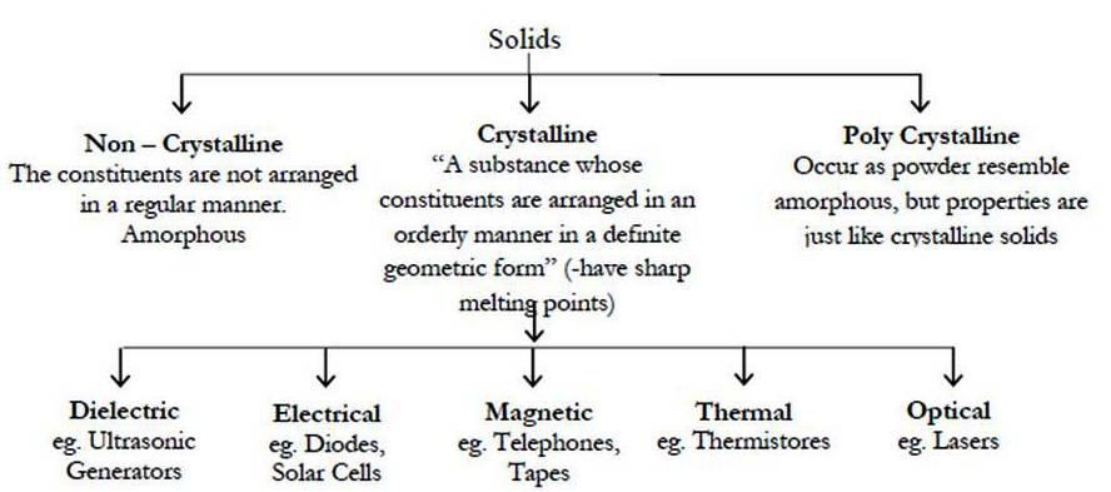
Unit 4: Solid State

[Syllabus: Types of crystal, space lattice, unit cell, seven crystal systems, fourteen Bravais lattices, law of constancy of interfacial angles, law of rational indices, Miller indices, and; X-ray diffraction, Bragg's law. Defects in crystals, Colour center, Energy band theory of Conductor, Semiconductors and insulators, Glasses, liquid crystal and their phases (Nematic, Smectic A and Smectic C)]

Solid state chemistry deals with the synthesis, structure, properties and applications of solid materials.

Properties of Solid

- They are incompressible, inflexible and Mechanical strength.
- They have specific mass, volume and shape.
- Intermolecular force is physically powerful.
- Intermolecular distance is minimum.



Crystalline Solids: The solids that have their atoms, ions, or molecules which are arranged in a definite three dimensional pattern are called as crystalline solids.

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They have the following characteristics

- Crystalline Solids have a characteristic geometrical shape.
- Crystalline solids have sharp melting points, indicating the presence of a long range order arrangement in them
- Crystalline solids are **anisotropic** by nature i.e., their mechanical, electrical and optical properties depend upon the direction along which they are measured.
- When cut or hammered gently they show a clean fracture along a smooth surface.

Types of Crystalline Solid

Crystalline solids may be classified into four types depending upon the nature of bonds present in them.

1. Ionic (Nature of force: Strong electrostatic forces of attraction) Eg: NaCl, LiF, MgO and etc.

2. Molecular: contain discrete molecular units held by relatively weak intermolecular forces (VanderWaal'sforces, Dipoleinteraction, Hydrogen bonding). Eg: Solid Ar, Kr and etc.

3. Covalent (Covalent bonds). Lattice points are atoms. Eg: Diamond, graphite, Si, Ge and etc.

4. Metallic (Metallic bonds). Eg: Al, Cu and etc

Crystals: A crystal is a homogenous solid, which is formed by a 3-D repeating unit (pattern of ions, atoms or molecules) with fixed distances.

Crystallography: Science that deals with the chemical and physical properties, structure, formation and applications of crystals.

Unit Cell: The smallest unit of a structure that can be indefinitely repeated to generate the whole structure. A unit cell is representative of the entire crystal in terms of properties and symmetry.

Crystallographic Laws

LAW OF CONSTANCY OF INTERFACIAL ANGLES

The law of the constancy of interfacial angles (also called the 'first law of crystallography') states that the angles between the crystal faces of a given species are constant, whatever the lateral extension of these faces and the origin of the crystal, and are characteristic of that species.

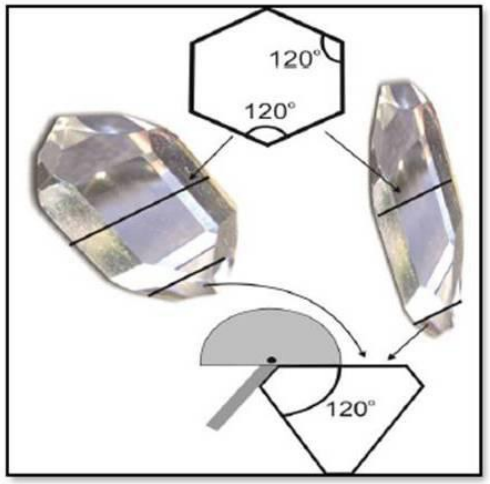


Fig. 1 Cross section along prism and rhombohedral faces indicating constancy of interfacial angles even if the quartz crystals is flattened along one axis

LAW OF RATIONAL INDICES

It states that the intercepts, OA, OB, OC, of the natural faces of a crystal form with the unit-cell axes a, b, c (Figure 2) are inversely proportional to prime integers, h, k, l. They are called the Miller indices of the face. In other words, Miller indices are a set of integers (h, k, l) which are used to describe a given plane in a crystal.

Weiss indices: The coefficients of a, b, c are known as Weiss indices.

Miller indices are : i) Used to characterise the crystal pattern, ii) Used to calculate the edge length of the unit cell.

i) Let OX, OY and OZ represent the 3 crystallographic axes.

ii) Let ABC a unit plane

iii) Let a, b, c be unit intercepts.

iv) Let KLM are the multiples of abc.

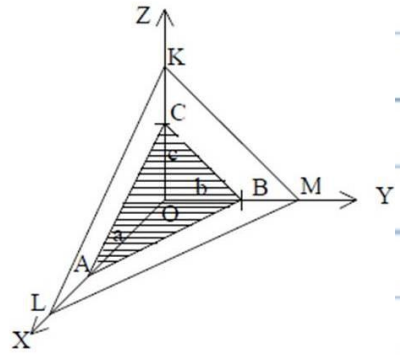


Fig. 2

The procedure for determining the Millar indices for a plane is as follows.

a) Prepare a three column table with the unit cell axes at the top of the column.

b) Enter in each column the intercepts (expressed as a multiples of a, b or c)

c) Invert all the numbers.

d) Clear the fraction to obtain the whole number h, k and l.

(Note: The negative sign in the Miller indices are indicated by placing a bar on the integer. The Miller indices are enclosed within parentheses).

Problems:

1. Calculate the Miller indices of Crystal planes which cut through the crystal axes at (2a,3b,c).

Solution:

Unit cell axes	a	b	c
intercepts	2	3	1
reciprocals	1/2	1/3	1
Clear fractions	3	2	6

Hence, the Miller indices are (326).

2. Calculate the Miller indices of Crystal planes which cut through the crystal axes at (2a,-3b,-3c).

Refer to class notes

Types of unit cell

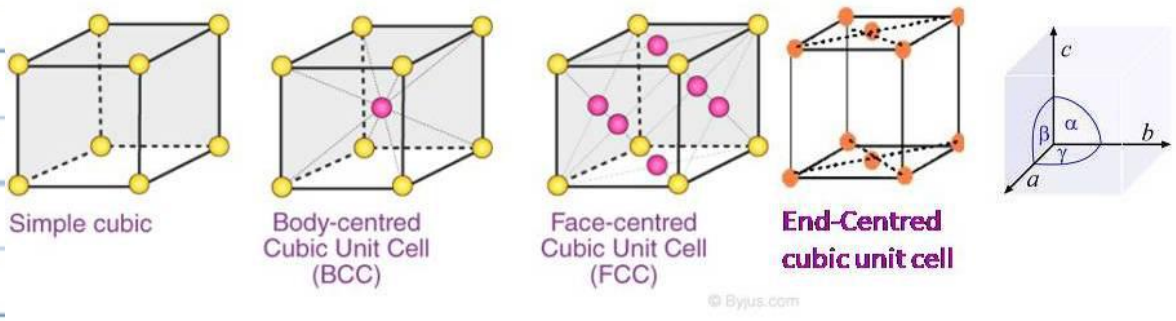
There are four different types of unit cells

Simple cubic or primitive or basic unit cell: In case of simple cube, the lattice points are situated only at the corners of the cube.

Body centered cubic (BCC) unit cell : In BCC, an additional one lattice point is placed at the center of the body of the simple cube.

Face centred cubic (FCC)unit cell: In FCC, the additional one lattice point is placed on each face of the simple cube (on six faces).

End face centered unit cell or Base centred unit cell: The unit cell having lattice points at the two opposite faces in addition to the lattice points at the corners.



3D Bravais Lattice

Bravais found that in three dimension, from seven crystal system, we can get fourteen type of lattice and these fourteen type of lattice is basically called the Bravais lattice after his name. So, the Bravais lattice are of fourteen types and shown in the table :

3 D Bravais Lattice

S. No.	Crystal System	Lattice Parameters	Bravais Lattice	Common abberevation
1.	Cubic	$a = b = c$ and $\alpha = \beta = \gamma = 90°$.	Simple	SC
			Body centred	BCC
			Face-centred	FCC
2.	Tetragonal	$a = b \neq c$ and $\alpha = \beta = \gamma = 90°$.	Simple	ST
			Body centred	BCT
3.	Orthorhombic	$a \neq b \neq c$ and $\alpha = \beta = \gamma = 90°$.	Simple	SO
			Body centred	BCO
			Face-centred	FCO
			End centred	ECO
4.	Rhombohedral or Trigonal	$a = b = c$ and $\alpha = \beta = \gamma \neq 90°$.	Simple	
5.	Hexagonal	$a = b \neq c$ and $\alpha = \beta = 90°, \gamma = 120°$.	Simple	
6.	Monoclinic	$a \neq b \neq c$ and $\alpha = \gamma = 90° \neq \beta$.	Simple	
			End-centred	
7.	Triclinic	$a \neq b \neq c$ and $\alpha \neq \beta \neq \gamma \neq 90°$.	Simple	