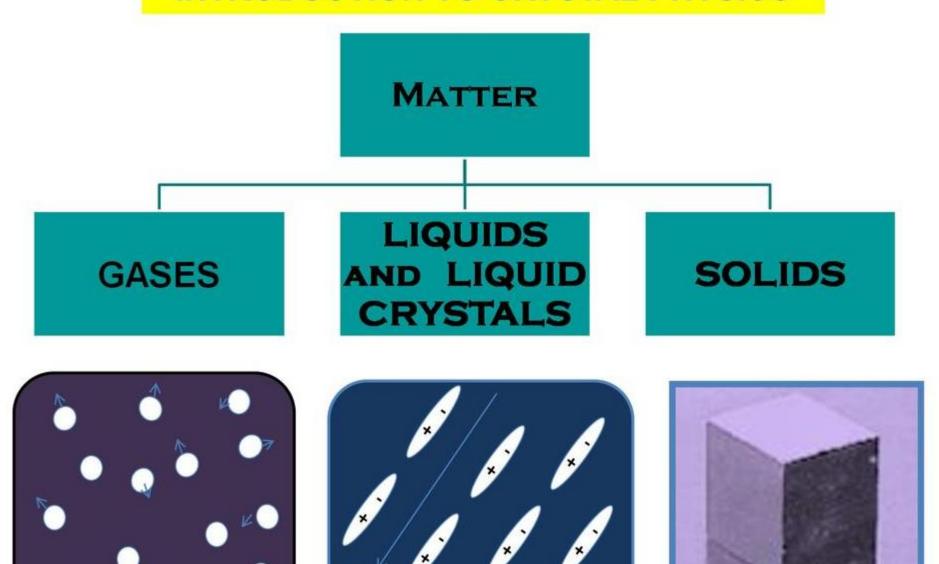
# UNIT-4 CRYSTALLOGRAPHY & NANO MATERILAS

- **INTRODUCTION TO CRYSTAL PHYSICS**
- **CRYSTALLINE AND NON-CRYSTALLINE SOLIDS**
- **SPACE LATTICE**
- **♣ CRYSTAL STRUCTURE**
- **LATTICE PARAMETERS**
- CRYSTAL SYSTEMS
- **BRAVAIS LATTICES**

# INTRODUCTION TO CRYSTAL PHYSICS



# What is Crystal Physics

- physical properties of crystalline solids
- determination of their actual structure by using

X-rays, neutron beams and electron beams.-

# **CLASSIFICATION OF SOLIDS**

# SOLID MATERIALS

CRYSTALLINE

**POLYCRYSTALLINE** 

AMORPHOUS (Non-crystalline)

**Single Crystal** 

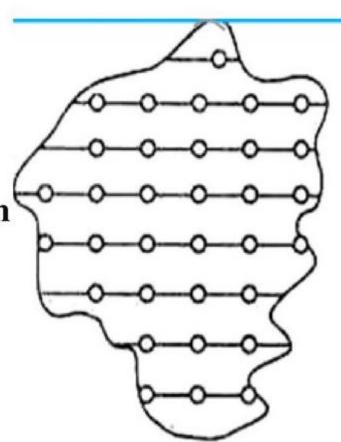






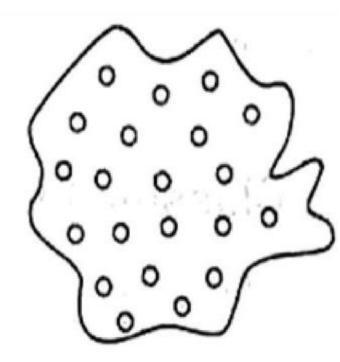
# **CRYSTALLINE SOLIDS**

- arrangement of units of matter is regular and periodic.
- anisotropic substance.
- sharp melting point.
- possesses a regular shape
- · Ex: Iron, Copper, Carbon, Germanium



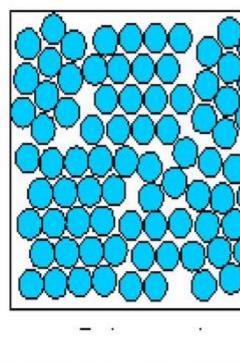
# NON CRYSTALLINE SOLIDS

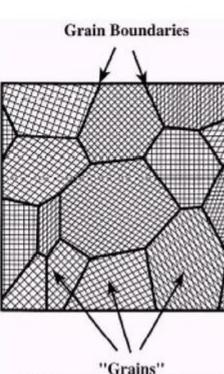
- amorphous solids
- particles are randomly distributed.
- `isotropic' substances.
- have wide range of melting point
- Examples: Glass, Plastics, Rubber etc.,



# POLYCRYSTALLINE SOLIDS

- aggregate of many small single crystals
- high degree of order over many atomic or molecular dimensions.
- grain boundaries.
- grains are usually 100 nm 100 microns in diameter.
- Polycrystals with grains < 10 nm in diameter are nanocrystalline</li>
- Examples: Inorganic solids, Most of the metals and Ceramics





CRYSTALLINE SOLIDS	AMORPHOUS SOLIDS (NON-CRYSTALLINE SOLIDS)
In crystalline solids, the atoms or molecules are arranged in a regular and periodic manner.	In amorphous solids the atoms or molecules are arranged in an irregular manner.
If a crystal breaks, the broken pieces also have regular in shape.	If an amorphous solid breaks, the broken pieces have irregular in shape
These solids have directional properties and are therefore called anisotropic substances.	These solids have no directional properties and are therefore called <b>isotropic</b> substances.
The crystalline solids have sharp melting point.	The amorphous solids have wide range melting point.
Examples Metallic solids - Cu, Ag, Au, Al Non - Metallic solids - NaCl, MgO, CaO, Diamond, Si, Ge.	Examples Glass, plastic, wood

# **CRYSTALLOGRAPHIC TERMS**

- **SPACE LATTICE**
- **\*** LATTICE POINTS
- **\*** LATTICE LINES
- **\*** LATTICE PLANES
- BASIS or MOTIF
- **❖ CRYSTAL STRUCTURE**
- **\* UNIT CELL**
- **\*** LATTICE PARAMETERS

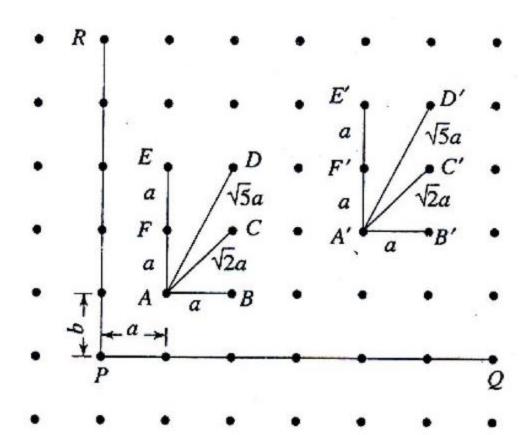






# SPACE LATTICE

- **regular and periodic** arrangement of points in three dimension.
- **dentical surroundings** to that of every other point in the array.

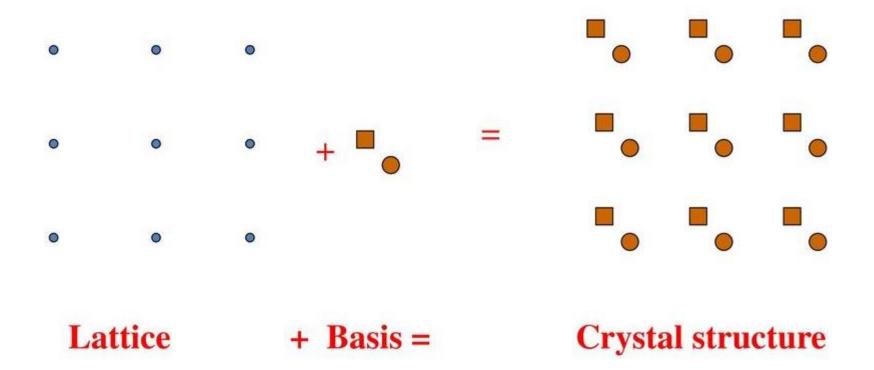


# BASIS

- a unit assembly of atoms or molecules identical in composition arrangement and orientation.
- repeatation of basis correct periodicity in all directions
- ♣ The crystal structure is real, while the lattice is imaginary.

Examples	No. of atoms in Basis
Aluminim	01
Barium	01
NaCl	02
KCI	02
CaF <sub>2</sub>	03

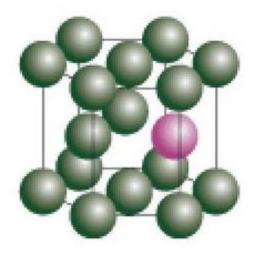
# **CRYSTAL STRUCTURE**

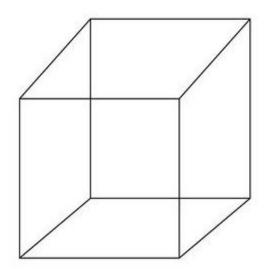


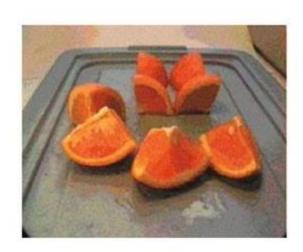
# **UNIT CELL**

a fundamental building block

 repeating its own dimensions in various directions gives crystal structure







# **Lattice parameters**

x, y and z are crystallographic axes

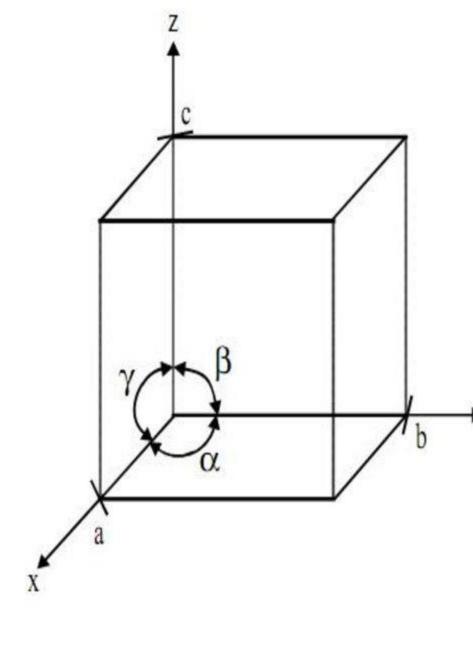
Length of the unit cell along the x, y, and z direction are a, b, and c

# **Interaxial angles:**

 $\alpha$  = the angle between a and b

 $\beta$  = the angle between b and c

 $\gamma$  = the angle between c and a



a, b, c,  $\alpha$ ,  $\beta$ ,  $\gamma$  are collectively known as the lattice parameters

#### **PRIMITIVE CELL**

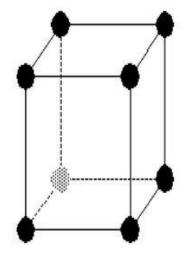
♣ A unit cell consists of only one full atom

♣ A primitive cell got the points or atoms only at the corners

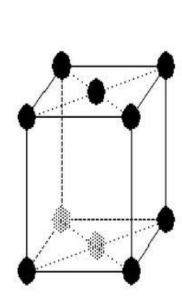
♣ If a unit cell consists more than one atom, then it is not a primitive cell.

- Example for primitive cell :
  Simple Cubic(SC)
- Examples for non-primitive cell:

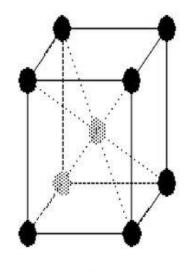
BCC and FCC unit cell.



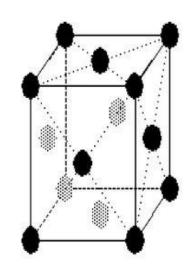
Primitive



Side-Centered



Body-Centered (bcc)



Face-Centered (fcc)

Seven crystal systems and its lattice Parameters Axial

Sr. No.	Crystal System	length of	Inter axial angles	Lattice in the
		Unit Cell		system
1	Cubic	a=b=c	$\alpha = \beta = \gamma = 90^{\circ}$	3
2	Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^{\circ}$	2
3	Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^{\circ}$	4

Number of

3 Orthorhombic 
$$\alpha \neq b \neq c$$
  $\alpha = \beta = \gamma = 90^{\circ}$  4

4 Monodinic  $\alpha \neq b \neq c$   $\alpha = \beta = 90^{\circ} \neq \gamma$  2

3 Orthorhombic 
$$\alpha \neq b \neq c$$
  $\alpha = \beta = \gamma = 90^{\circ}$  4

4 Monodinic  $\alpha \neq b \neq c$   $\alpha = \beta = 90^{\circ} \neq \gamma$  2

 $a \neq b \neq c$ 

a = b = c

 $a = b \neq c$ 

 $\alpha \neq \beta \neq \gamma \neq 90^{\circ}$ 

 $\alpha = \beta = \gamma < 120^{\circ}, \neq 90^{\circ}$ 

 $\alpha = \beta = 90^{\circ}$ , and  $y = 120^{\circ}$ 

5

6

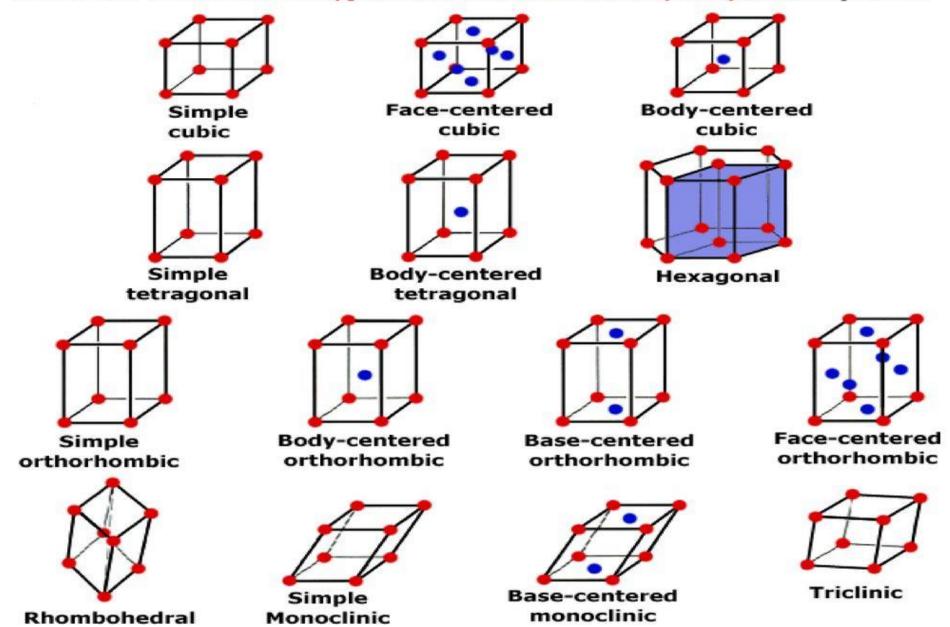
Triclinic

Trigonal

Hexagonal

#### **BRAVAIS LATTICE**

Bravais in 1948 showed that 14 types of unit cells under seven crystal systems are possible.



# 14 Bravais Lattices divided into 7 Crystal Systems

	Crystal System	Shape of UC	В	ravais	Lattic	es
			P	I	F	С
1	Cubic	Cube	1	<b>✓</b>	✓	
2	Tetragonal	Square Prism (general height)	<b>✓</b>	<b>✓</b>		
3	Orthorhombic	Rectangular Prism (general height)	<b>✓</b>	<b>✓</b>	✓	1
4	Hexagonal	120° Rhombic Prism	<b>✓</b>			
5	Trigonal	Parallopiped (Equilateral, Equiangular)	<b>✓</b>			
6	Monoclinic	Parallogramic Prism	<b>✓</b>			<b>✓</b>
7	Triclinic	Parallopiped (general)	✓			

P	Primitive	
Ι	Body Centred	
F	Face Centred	
C	Base- Centred	

### Characteristics of unit cell

## Number of atoms / unit cell

#### Coordination number

No. of equidistant nearest neighbouring atoms to a particular atom

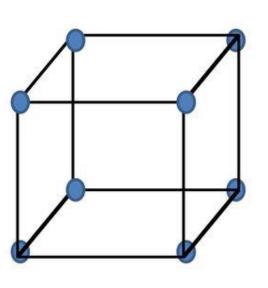
## Atomic Radius (r)

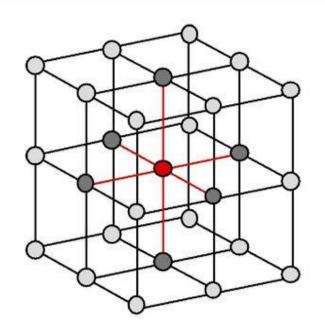
half the distance between the nearest neighbouring atoms

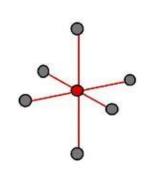
## Atomic Packing factor or Packing Density

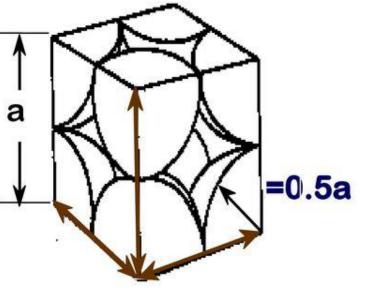
ratio of the volume occupied by the atoms in an unit cell (v) to the volume of the unit cell (V)

# Simple Cubic Structure (SC)



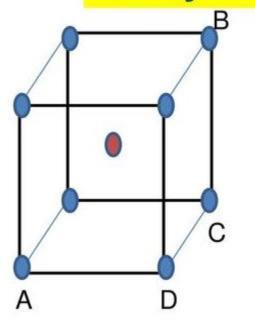


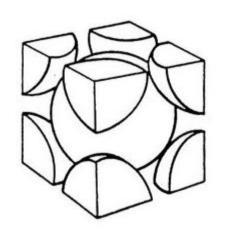


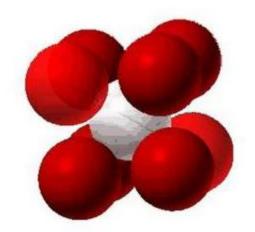


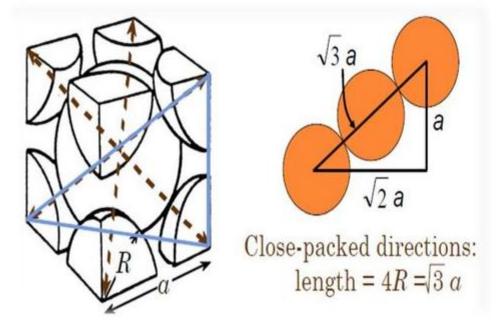
No. of atoms/unit cell	1
Atomic Radius	a/2
Coordination No.	6
APF	<b>0.52</b> <sub>21</sub>

# **Body Centered Cubic Structure (BCC)**



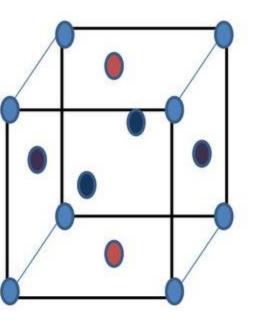


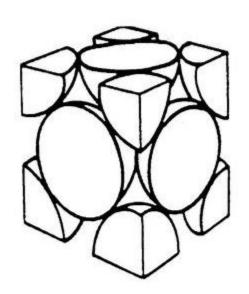


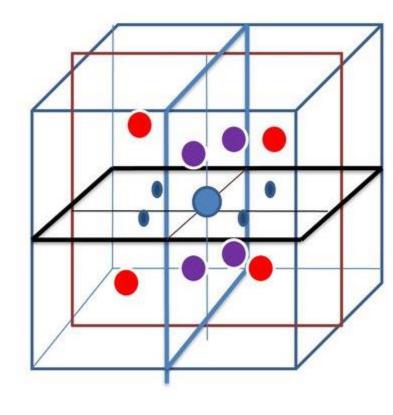


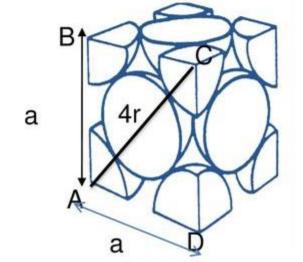
No. of atoms/unit cell	2
Atomic Radius	√3 a/4
Coordination No.	8
ADE	√3π/8 or
APF	0.68

# **Face Centered Cubic Structure (FCC)**



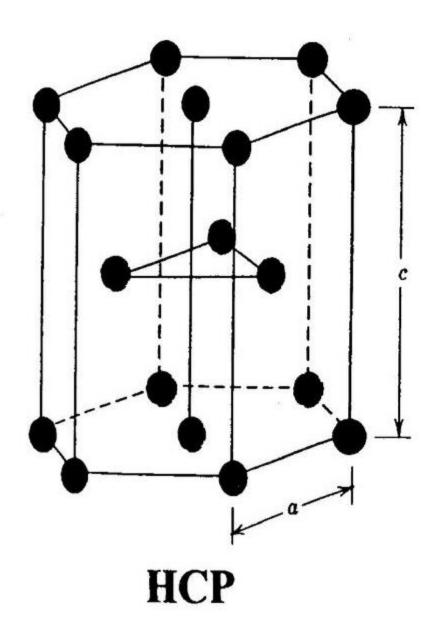


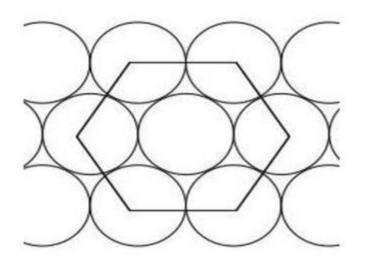


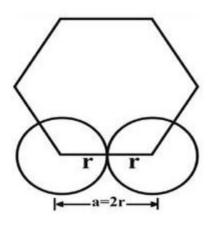


No. of atoms/unit cell	4
Atomic Radius	√2a/4
Coordination No.	12
APF	$\pi/(3\sqrt{2})$ or 0.74

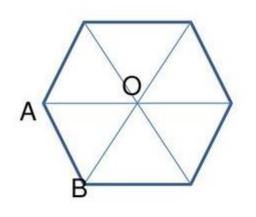
# HEXAGONAL CLOSED PACKED STRUCTURE

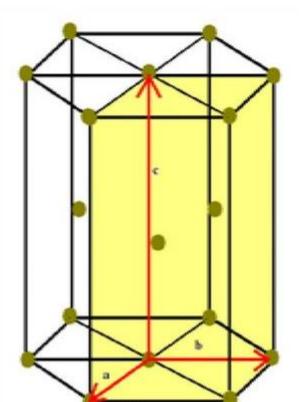






#### ATOMIC PACKING FACTOR (APF) of HCP





Area of 1 triangle = 
$$\frac{\sqrt{3}a^2}{4}$$

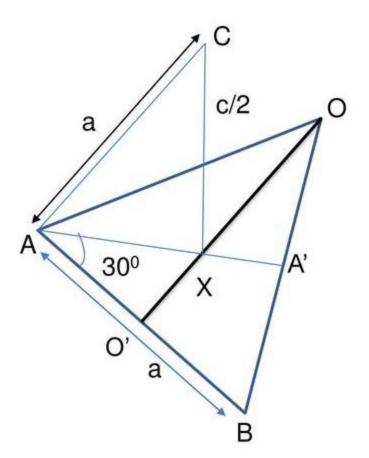
Volume of HCP unit cell

$$= 6 \times \text{Area of } 1 \triangle^{\text{le}} \times \text{Height}$$

$$=\frac{3\sqrt{3}a^2C}{2}$$

No. of atoms/unit cell	6
Atomic Radius	a/2
<b>Coordination No.</b>	12
APF	$\pi / (3\sqrt{2}) \text{ or } 0.74$

## C/a Ratio



In the triangle AXC,

$$AC^2 = AX^2 + CX^2$$

$$a^2 = \left(\frac{a}{\sqrt{3}}\right)^2 + \left(\frac{C}{2}\right)^2$$

$$\frac{c}{a} = \sqrt{\frac{8}{3}}$$

# MILLER INDICES

- > set of three possible integers represented as (h k l)
- reciprocals of the intercepts made by the plane on the three crystallographic axes
- designate plane in the crystal.
- Step 1 : Determine the intercepts of the plane along the axes
- Step 2: Determine the reciprocals of these numbers.
- Step 3: Find the *LCD* and multiply each by this *LCD*
- Step 4: Write it in paranthesis in the form (h k l).

# **ILLUSTRATION**

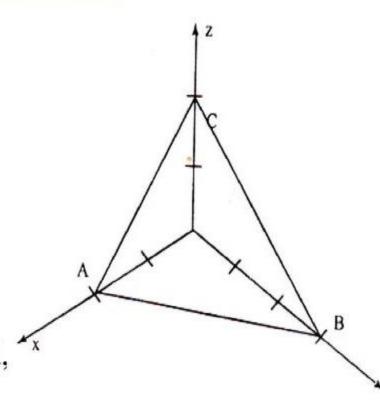
Step 1: intercepts - 2a,3b and 2c

Step 2: reciprocals - 1/2, 1/3 and 1/2.

Step 3: LCD is '6'.

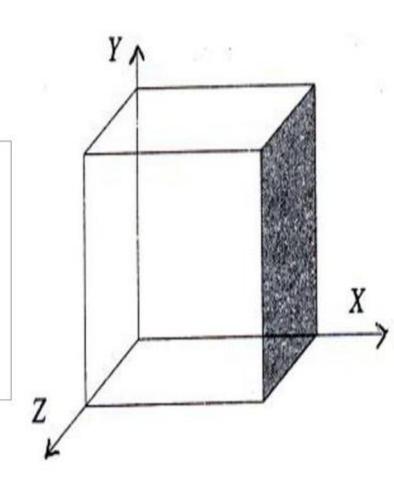
Multiply each reciprocal by lcd, we get, 3,2 and 3.

Step 4: Miller indices for the plane ABC is (3 2 3)

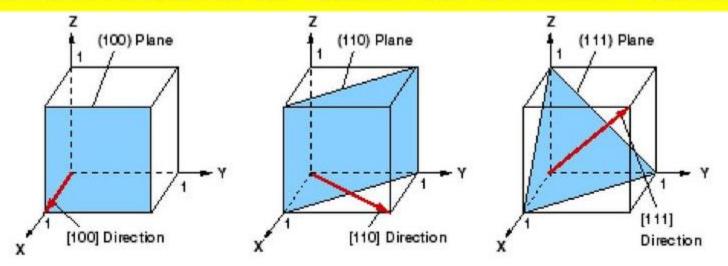


## **EXAMPLE**

- intercepts are  $1, \infty$  and  $\infty$ .
- reciprocals of the intercepts are 1/1,  $1/\infty$  and  $1/\infty$ .
- Miller indices for the plane is (1 0 0).



# MILLER INDICES OF SOME IMPORTANT PLANES



#### IMPORTANT FEATURES OF MILLER INDICES

■ a plane parallel to the axes has an intercept of infinity  $(\infty)$ .

 a plane cuts an axis on the negative side of the origin, is represented by a bar, as (T00).

a plane passing through the origin have non zero intercepts

All equally spaced parallel planes have same Miller indices

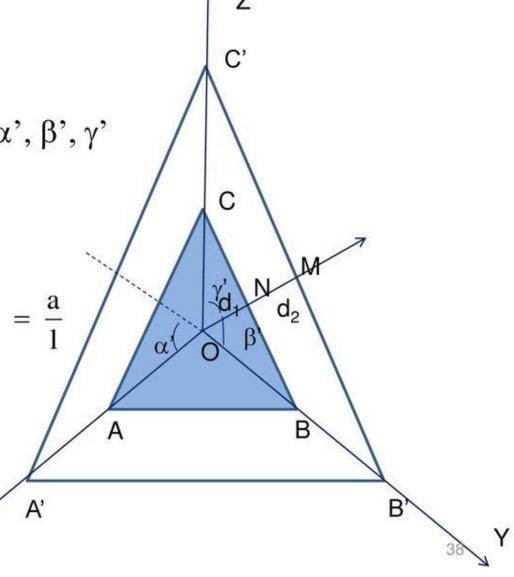
# **INTERPLANAR DISTANCE** or d-Spacing

Two planes ABC and A'B'C'

• Interfacial angles  $\alpha$ ,  $\beta$ , $\gamma$  and  $\alpha$ ',  $\beta$ ',  $\gamma$ '

Intercepts of the plane ABC

$$OA = \frac{a}{h}$$
,  $OB = \frac{a}{k}$  and  $OC = \frac{a}{1}$ 



From the property of direction of cosines,  $\cos^2 \alpha + \cos^2 \beta + \cos^2 \gamma = 1$ 

$$d_1 = ON = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

Similarly, for the plane A'B'C'

$$d_2 = OM = \frac{2a}{\sqrt{h^2 + k^2 + 1^2}}$$

Interplanar spacing

$$d = (d_2 - d_1) = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

# **RELATION BETWEEN LATTICE CONSTANT (a) AND DENSITY (ρ)**

Consider a cubic crystal of lattice constant'a'

Density of the crystal =  $\rho$ 

Volume of the unit cell =  $a^3$ 

 $\therefore$  Mass of the unit cell =  $\rho$  a<sup>3</sup>

 $\left(\because density = \frac{mass}{volume}\right)$ 

Number of atoms per unit cell = n

Atomic weight of the material = M

Avogadro's number = N

Mass of each atom = 
$$\frac{M}{N}$$

Mass of the unit cell = mass of the each atom in unit cell  $\times$  number of atoms per unit cell

$$=\frac{M}{N}\times n$$
 (for n atoms per unit cell)

$$\rho a^3 = \frac{M}{N} \times n$$

$$\rho = \frac{nM}{Na^3}.$$

# X- Ray Diffraction:

- There are three main diffraction methods by which the crystal structures can be analyzed.
- a. Laue method: applicable to single crystals
- b. Powder method : applicable to finely divided crystalline (or) Polycrystalline specimen powder
- c. Rotating crystal method: applicable to single crystals.

# Bragg's law

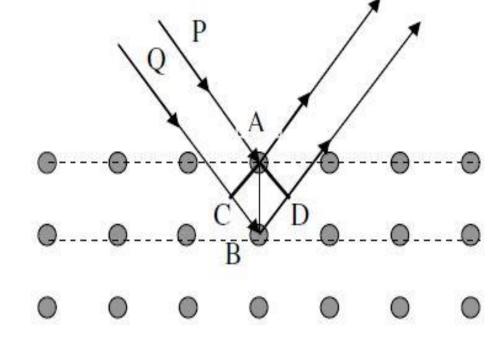
Bragg's law states that the path difference between the two reflected X-rays by the crystal planes should be an integral multiple of wave length of incident X-rays for producing maximum or constructive interference. Let us consider a set of parallel lattice planes of a crystal separated by a distance d apart. Suppose a narrow beam of X-rays of wave length  $\lambda$  be incident upon these planes at an angle  $\Theta$  as shown in the figure.

Consider a ray PA reflected at the atom A in the direction AR from plane 1 and another ray QB reflected at another atom B in the direction of BS. The path difference between the two rays is (CB+BD). When the path difference between the two rays is an integral multiple of X-rays wavelength, the constructive interference phenomenon will occur. Thus the condition for constructive interference is

### Thus the condition for constructive interference is

om 
$$\Delta ABC$$
  $\sin \theta = \frac{CB}{AB} = \frac{CB}{d}$   $CB = d \sin \theta$ 

From 
$$\triangle ABD$$
  $\sin \theta = \frac{BD}{AB} = \frac{BD}{d}$   
 $BD = d \sin \theta$ 



$$2d\sin\theta = n\lambda$$

 $(CB + BD) = 2d \sin \theta$ 

For third maxima

Where 
$$n = 1, 2, 3, \dots$$
 etc for first order, second order, third order ...... etc maxima respectively.

For first maxima 
$$\sin \theta_1 = \frac{\lambda}{2d}$$
  
For second maxima  $\sin \theta_2 = \frac{2\lambda}{2d}$ 

$$\sin \theta_3 = \frac{3\lambda}{2d}$$

#### **Powder method**

The powder method was developed by Debye and Sherrer in Germany and by hill in America simultaneously. This method is used to study the structure of crystals which cannot be obtained in the form of perfect crystals of appreciable size. This method can be used for pure metals, compounds and alloys.

# **Basic Principle**

The basic principle underlying this powder technique is that, the specimen contains a large number of micro crystals ( $^{\sim}10^{12}$  in  $1mm^3$  of powder sample) with random orientations, almost all the possible  $\Theta$  and d values are available. The diffraction takes place for these values of  $\Theta$  and d which satisfy Bragg's condition, i.e.,  $2d \sin\Theta = n\lambda$ .

## **Experimental arrangement:-**

The experimental arrangement is shown in figure. The finely powdered sample is filled in a thin capillary tube and mounted at the center of the drum shaped cassette with photographic film at the inner circumference.

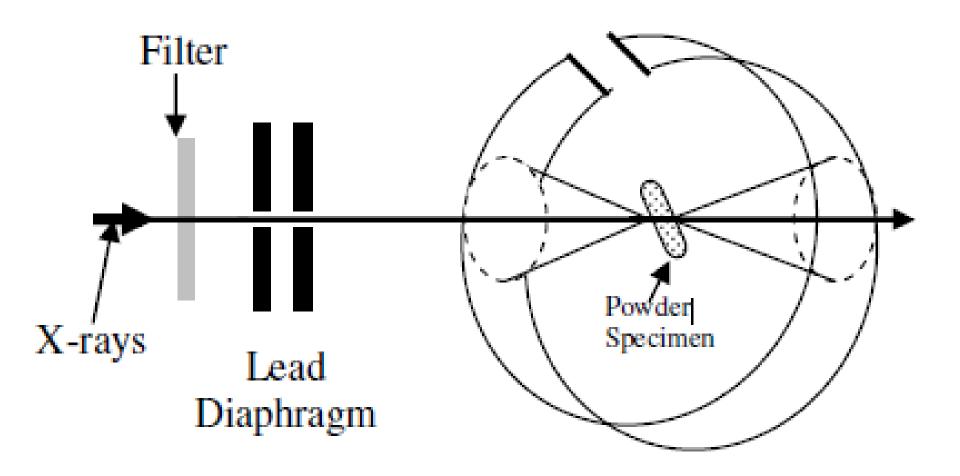
Collect the X-rays (non monochromatic or heterogeneous or continuous) from the X-ray tube. Heterogeneous can be converted into monochromatic X-Rays by passing through the filter.

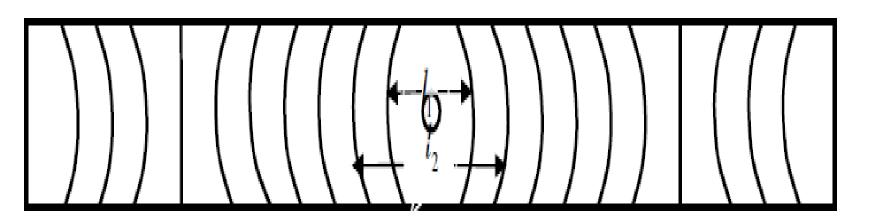
This monochromatic (or homogenous) x-rays can be converted into fine pencil beam by passing through the lead sheet. The pencil beam of X-rays is allowed to fall on the powder specimen (sample).

#### Theory

The basic principle underlying this powder technique is that, the specimen contains a large number of micro crystals ( $^{\sim}$  10  $^{12}$  in 1 $mm^3$  of powder sample) with random orientations, almost all the possible  $\Theta$  and d values are available. The diffraction takes place for these values of  $\Theta$  and d which satisfy Bragg's condition, i.e.,  $2d \sin \Theta = n\lambda$ .

Reflection takes place at the lattice planes, which satisfy the Bragg's condition. For the value of  $\Theta$ , the beam appears at the corresponding  $2\Theta$  deviation. The pattern recorded on the photographic film is shown in the figure when the film is laid flat. Due to the narrow width of the film, only parts of circular rings are register on it. The curvature of arcs reverses when the angle of diffraction exceeds  $90^{\circ}$ .

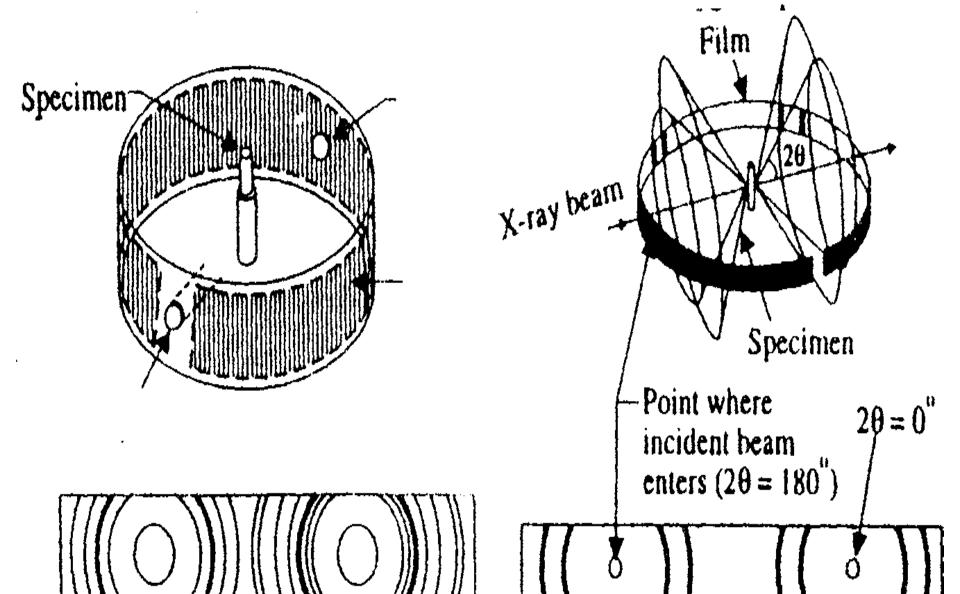




Knowing the distances between the pair of arcs, various diffraction angles  $\theta'^s$  can be calculated by using the formula.

$$\theta = \frac{90^{\circ}}{\pi D}$$

Where D, is the diameter of the cylindrical film.



$$2\theta = \frac{180^{0} x_{1}}{\pi r}$$
 where r is radius of drum 
$$\theta = \frac{90^{0} x_{1}}{\pi r}$$

Let  $x_1, x_2, x_3$  be the distance between symmetrical arcs on the stretched photographic film then -

$$2\theta_1 = \frac{180^0 x_1}{\pi r} \quad \text{i.e. } \theta_1 = \frac{90^0 x_1}{\pi r} \quad ,$$

Similarly 
$$\theta_2 = \frac{90^0 x_2}{\pi r}$$
 and  $\theta_3 = \frac{90^0 x_3}{\pi r}$ 

Using the value of  $\theta$  in to the Bragg's equation, the interplaner distance (spacing) d can be calculated.

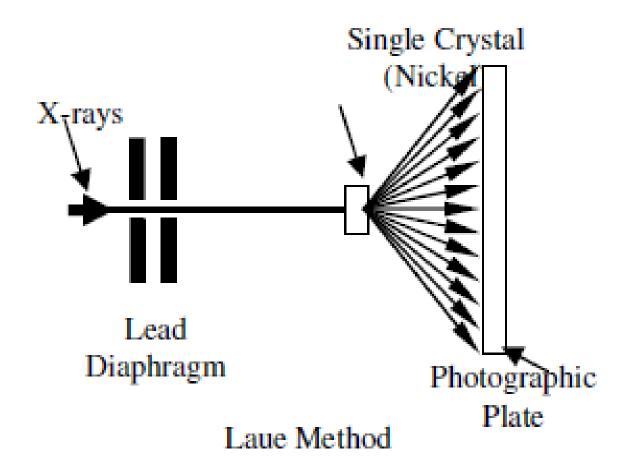
Such a diffraction pattern helps us to distinguish amorphous materials from crystalline materials. Amorphous material does not have reflecting planes. Therefore diffraction rings are not produced on the film. However, they may produce smeared ring as there is some kind of short range order in the arrangement of its molecules.

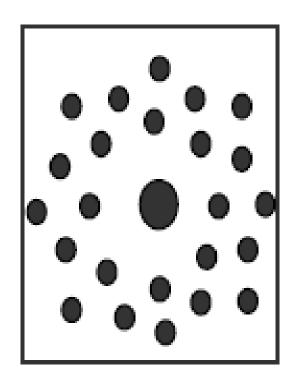
# Laue method Basic principle

The basic Principe underlying this Laue technique is that, each reflecting plane selects a wave length according with the Bragg's relation, i.e.,  $2d \sin\theta = n\lambda$ . The resulting diffraction is recorded on the photographic plate.

## **Experimental arrangement**

The experimental arrangement of the Laue technique is shown in the figure. Collect the X-rays of wavelength 0.2 A<sup>0</sup> to 2.0 A<sup>0</sup> from X-ray tube. Collected X-rays are converting in to fine pencil beam by passing through the pin-hole arrangements in lead diaphragms. The size of pin hole should be kept very small to get sharp interference pattern. The smaller is the pinhole diameter, sharper is the interference pattern.





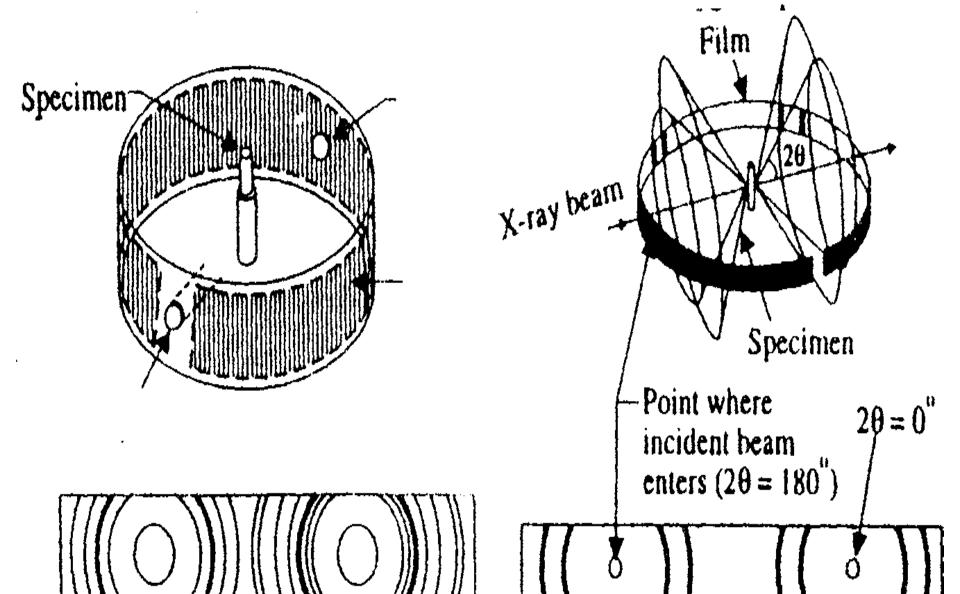
# **Theory**

The fine pencil beam of X-rays is allowed to fall on the single crystal; the X-rays are diffracted and recorded on the photographic plate. The diffraction pattern consists of a bright central spot and a set of spots arranged in a definite pattern about the central spot. The symmetrical pattern caused by X-rays by crystal planes is called the Laue pattern. Each spot in the Laue pattern corresponding to an interference maximum for a set of planes satisfying the Bragg's relation  $2d \sin\Theta = n\lambda$ .

#### **CRYSTALLOGR APHY BY POWDER METHOD:**

Investigation of crystal structure using Laue method is possible only when the material is available in the form of single crystals of reasonable size. There are many materials for which it is impossible to obtain single crystals of required size. For such materials powder photography is highly suitable. One form of powder photography is known as Debye-Scherrer method invented by P. Debye and Scherrer.

In this method the material under investigation is crushed into a fine grain powder and compressed into a thin rod or packed into capillary tube.



shows the principle of Debye-Scherrer powder method. A strip of photography film wrapped in opaque is mounted round the inside of a cylindrical drum. The specimen is positioned vertically at the center of the drum. A narrow beam of monochromatic x-rays enter and leave the drum through the aperture on opposite of the drum.

The principle of the technique is that the powder consists of millions of tiny crystals oriented at random in all possible direction. Each crystallite has the some system of atomic planes. Some of the crystallites are bound to lie with their planes at glancing angle 8 to the incident ray such that Bragg's equation is satisfied. Each such crystal will produce a spot on photographic plate. Reflections will be produced by all such crystallites whose normal to the planes from a cone, as illustrated in fig.

$$2\theta = \frac{180^{0} x_{1}}{\pi r}$$
 where r is radius of drum 
$$\theta = \frac{90^{0} x_{1}}{\pi r}$$

Let  $x_1, x_2, x_3$  be the distance between symmetrical arcs on the stretched photographic film then -

$$2\theta_1 = \frac{180^0 x_1}{\pi r} \quad \text{i.e. } \theta_1 = \frac{90^0 x_1}{\pi r} \quad ,$$

Similarly 
$$\theta_2 = \frac{90^0 x_2}{\pi r}$$
 and  $\theta_3 = \frac{90^0 x_3}{\pi r}$ 

Using the value of  $\theta$  in to the Bragg's equation, the interplaner distance (spacing) d can be calculated.

Such a diffraction pattern helps us to distinguish amorphous materials from crystalline materials. Amorphous material does not have reflecting planes. Therefore diffraction rings are not produced on the film. However, they may produce smeared ring as there is some kind of short range order in the arrangement of its molecules.

#### 1. Introduction

- ➤ In recent years nanotechnology has become one of the most important and exiting forefront fields in physics, chemistry, biology and engineering and technology. Nano means 10<sup>-9</sup>m.
- A nanometer (nm) is one thousand millionth of a meter. Atoms are extremely small and the diameter of a single atom varies from 0.1 to 0.5 nm depending on the type of the element.
- For example, one carbon atom is approximately 0.15nm in diameter and a water molecule is almost 0.3nm across. A red blood cell is approximately 7,000 nm wide and human hair is 80,000 nm wide.

#### **Basic principles of nano materials**

When the material size of the object is reduced to nanoscale, then it exhibits different properties than the same material in bulk form. The factors that differentiates the nanomaterials form bulk material is

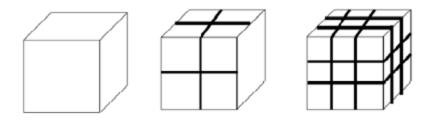
- 1. Increase in surface area to volume ratio
- 2. Quantum confinement effect

#### Increase in surface area to volume ratio:

The ratio of surface area to volume ratio is large for nano materials.

Example 1: To understand this let us consider a spherical material of radius 'r'. Then its surface area to volume ratio is 3/r. Due to decrease of r, the ratio increases predominantly.

Example 2: For one cubic volume, the surface ratio is 6m<sup>2</sup>. When it is divided into eight cubes its surface area becomes 12m<sup>2</sup>. When it is divided into 27 cubes its surface area becomes 18m<sup>2</sup>. Thus, when the given volume is divided into smaller pieces the surface area increases.



Due to increase of surface of surface area, more number of atoms will appear at the surface of compared to those inside. For example, a nano material of size 10nm has 20% of its atoms on its surface and 3nm has 50% of its atoms. This makes the nanomaterials more chemically reactive and affects the properties of nano materials.

# **Quantum confinement effect:**

- According to band theory, the solid atoms have energy bands and isolated atoms possess discrete energy levels. Nano materials are the intermediate state to solids and atoms.
- ➤ When the material size is reduced to nanoscale, the energy levels of electrons change.
- This effect is called quantum confinement effect. This affects the optical, electrical and magnetic properties of nanomaterial's.

## 2. Origin of Nano technology

While the word nano technology is relatively new, the existence of nanostructures and nanodevices is not new. Such structures existed on the earth as life itself. Though it is not known when humans began to use nanosized materials, the first known, Roman glassmakers were fabricated glasses containing nanosized metals. When the material size of the object is reduced to nanoscale, then it exhibits different properties than the same material in bulk form.

**Nanoscience:** Nano science deals with the study of properties of materials at nano scales where properties differ significantly than those at larger scale.

**Nanotechnology:** Nanotechnology deals with the design, characterization, production and applications of nanostructures and Nano devices and Nano systems.

#### Nano materials

All materials are composed of grains. The visibility of grains depends on their size. Conventional materials have grains varying in size from hundreds of microns to millimeters.

The materials processing grains size ranging from 1 to 100 nm, known as nano materials. Nano materials can be produced in different dimensionalities.

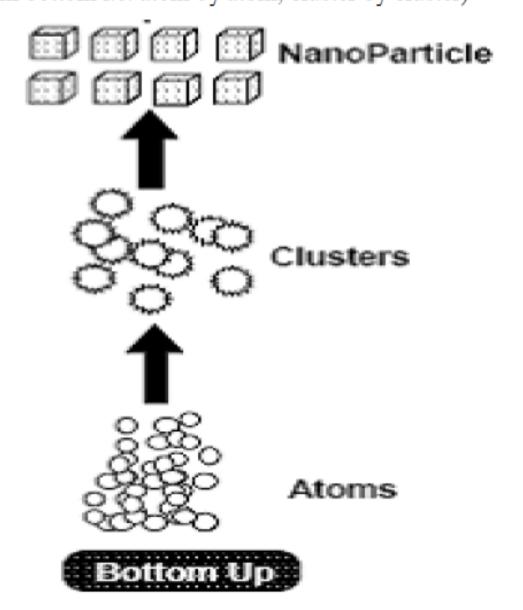
- One dimensional nano material: Surface coatings and thin films.
- > Two dimensional nano materials: nano tubes nano wires, biopolymers
- ➤ Three dimensional nano materials: nano particles, precipitates, colloids, quantum dots, nano crystalline materials, fullerenes or carbon nano-60.

#### **Production of Nanomaterials**

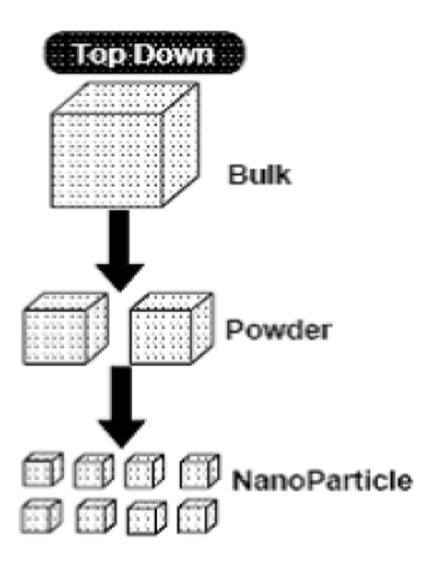
- ✓ Nanomaterials can be produced by a number of ways. Nanomaterials can be synthesized by "top down" techniques, producing very small structures from large pieces of the material. One way of doing this is, mechanically crushing of the solid into fine nanopowder (ball milling).
- ✓ Nanomaterials may also be synthesized by "bottom up" techniques, atom by atom or molecule by molecule. One way of doing this is to allow the atoms or molecules, arrange themselves into a structure, due to their natural properties. Ex: crystal growth.

There are many known methods to produce nanomaterials. They are

➤ <u>Bottom up:</u> Materials and devices are built from molecular components which assemble chemically using principles of molecular recognition.(Refers to build up Nano material from bottom i.e. atom by atom, cluster by cluster)



**Top down:** Nano objects are constructed from larger entities without atomic level control. (Refers to slicing or successive cutting of Bulk material in to Nano sized particles.)



**Example:** Chemical Vapor Deposition (CVD)

# **Chemical Vapor Deposition (CVD):**

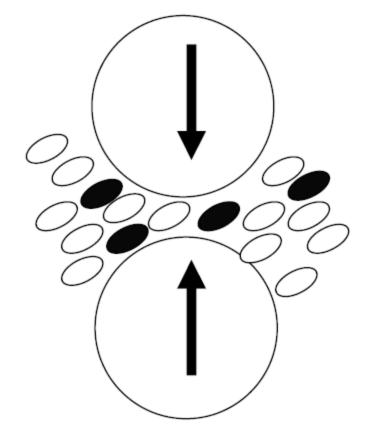
- This is an example for Top-Down approach comes under Physical method.
- In this method, Nano particles are deposited from gas phase. Materials are heated to form a gas and then allowed to deposit on a solid surface, usually under vaccum condition.
- This deposition may be either physical/chemical.
- In deposition by chemical reaction new product is formed. Production of pure metal powders is also possible using this method.
- ➤ CVD can also be used to grow surfaces. The object to be coated is placed inside the chemical vapour and may react with substrate atoms.
- Then the atoms or molecules grow on the surface of the substrate depends on alignment of atoms or molecules of the substrates.

#### **Chemical Vapour Deposition (CVD)**

- In this method, the material is heated to gaseous phase and allowed to condense on a solid surface in vacuum.
- Nanomaterials of metallic oxides or metallic carbides can be formed by heating metal and carbon or metal and oxygen, in a vacuum chamber to gaseous phase, and allowed to deposit on the surface of a solid.
- ➤ Pure metal powders (nanoparticles) are formed by this method. The metal is melted, excited with microwave frequency and vaporized to produce plasma at 1500°c. By cooling this plasma with water in a reaction column, nanoparticles are produced.
- ➤ The grain size of the nanoparticles depends on the concentration of the metal vapour, its rate of flow in the reaction column and temperature. This method can also be used to grow surfaces.

# **Ball milling method**

This method is a very popular, simple inexpensive and scalable method. This is also called crushing method. Ball method is to prepare a wide range of elemental and oxide powders.



Refractory or Steel balls

- This method is to produce nanocrystalline or amorphous materials. When the balls are allowed to rotate with particular rpm inside of a drum the necessary energy is transferred to the powder which in turn reduces the powder grain-sized structure to ultrafine or nano range particles.
- > Depending on the material either refractory balls or steel balls or plastic balls are used.
- The energy transferred to the poser from the balls depends on many factors such as rotational speed of the balls, number of balls, milling time and the milling medium. Generally, a hard material will be selected to synthesize softer material.

# **Applications of nanomaterials**

Nano materials posses unique and beneficial, physical, chemical and mechanical properties, they can be used for a wide verity of applications.

# Material technology

- Nanocrystalline aerogel are light weight and porous, so they are used for insulation in offices homes, etc,.
- Cutting tools made of nanocrystalline materials are much harder, much more wear- resistance, and last stranger.
- ➤ Nanocrystalline material sensors are used for smoke detectors, ice detectors on air craft wings, etc,.
- Nanocrystalline materials are used for high energy density storage batteries.
- Nanosized titanium dioxide and zinc dioxide are used in sunscreens to absorb and reflect ultraviolet rays.

Nan coating of highly activated titanium dioxide acts as water repellent and antibacterial.

- ➤ The hardness of metals can be predominately enhanced by using nanoparticles.
- Nanoparticles in paints change colour in response to change in temperature or chemical environment, and reduce the infrared absorption and heat loss.
- Nanocrystalline ceramics are used in automotive industry as high strength springs, ball bearings and valve lifters.

#### Information technology

- Nanoscale fabricated magnetic materials are used in data storage
- Nano computer chips reduce the size of the computer.
- Nanocrystalline starting light emitting phosphors are used for flat panel displays.
- > Nanoparticles are used for information storage.
- Nanophotonic crystals are used in chemical optical computers.

#### **Biomedicals**

- Biosensitive nanomaterials are used for ragging of DNA and DNA chips.
- In the medical field, nanomaterials are used for disease diagnosis, drug deliveryaand molecular imaging.
- Nanocrystalline silicon carbide is used for artificial heart valves due to its low weight and high strength.

## Energy storage

- Nanoparticles are used hydrogen storage.
- Nano particles are used in magnetic refrigeration.
- Metal nanoparticles are useful in fabrication of ionic batteries.