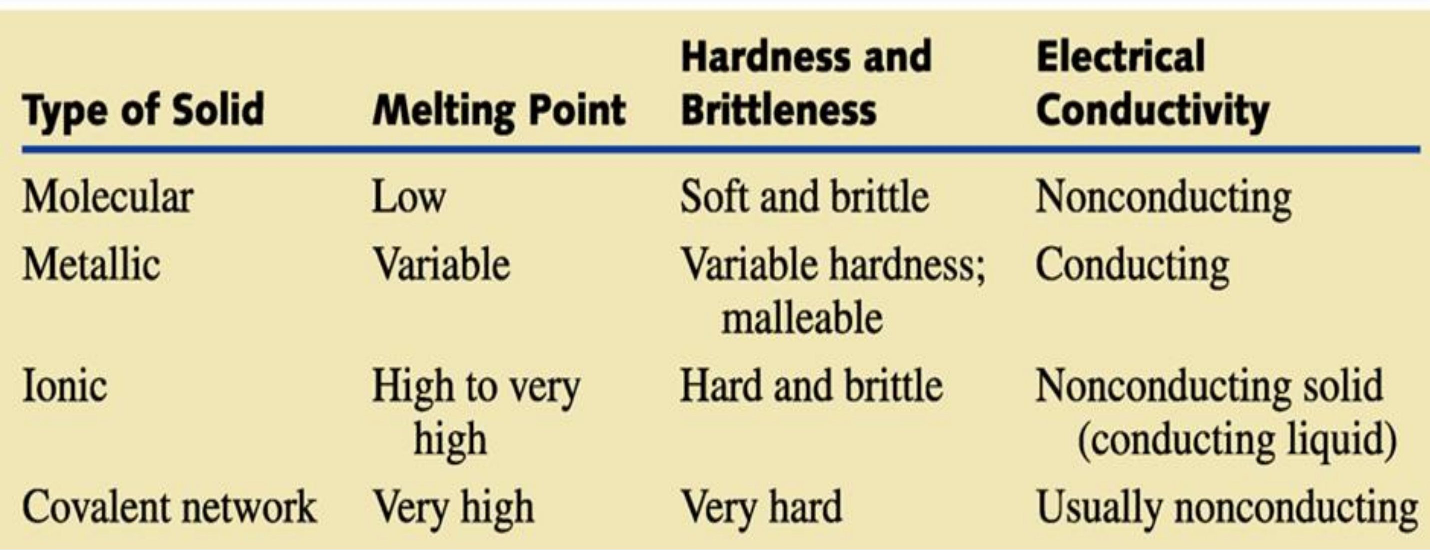
Module:5 Functional materials

- Oxides of AB, AB2, ABO3 type (specific examples)
- Composites - types and properties
- Polymers - thermosetting and thermoplastic polymers – synthesis and application (TEFLON, BAKELITE)
- Conducting polymers- polyacetylene and effect of doping
- Chemistry of display devices specific to OLEDs
- Nanomaterials – introduction, bulk vs. nano (quantum dots)
- Top-down and bottom-up approaches for synthesis, and
- Properties of nano Au.

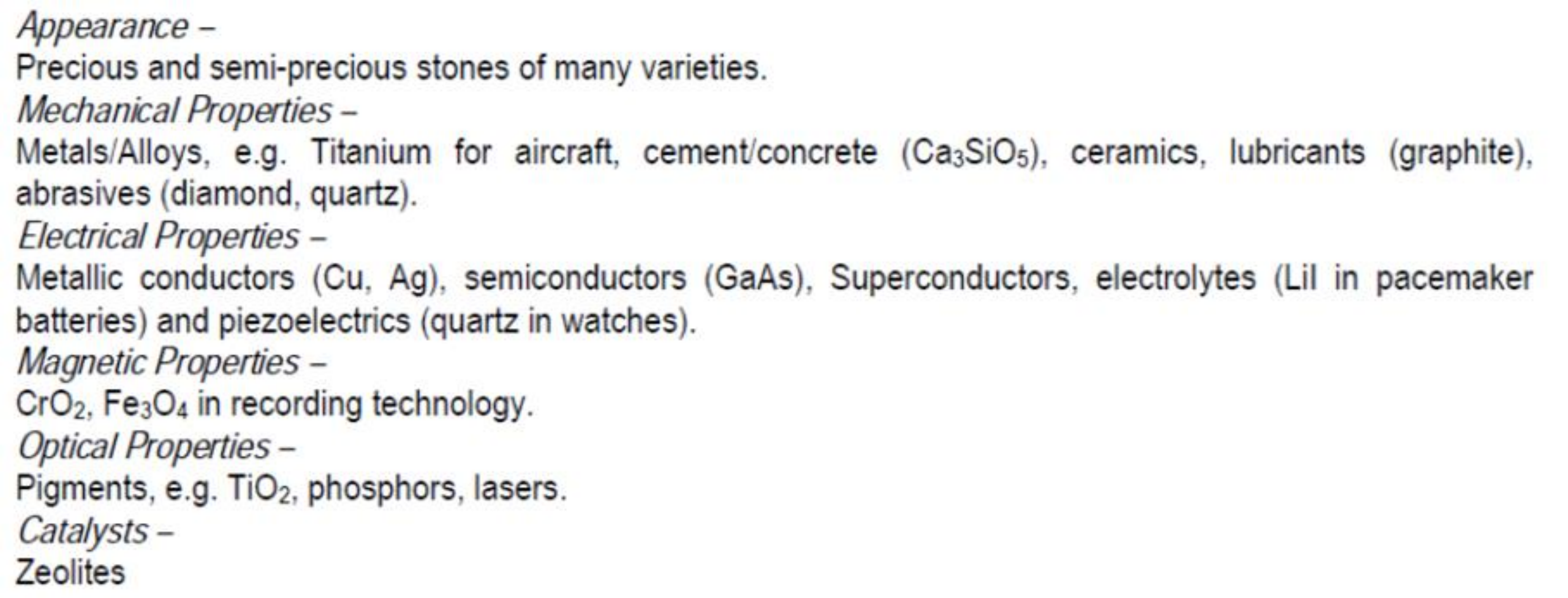
Module 5

Functional Materials

Properties of different type of Solids

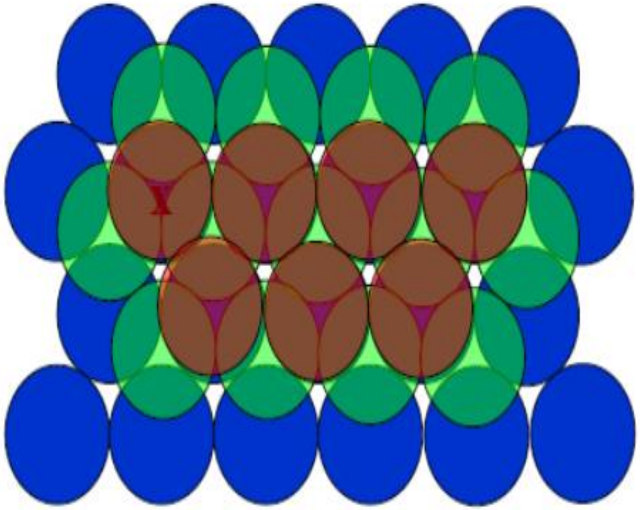


Type of Solid	Melting Point	Hardness and Brittleness	Electrical Conductivity
Molecular	Low	Soft and brittle	Nonconducting
Metallic	Variable	Variable hardness; malleable	Conducting
Ionic	High to very high	Hard and brittle	Nonconducting solid (conducting liquid)
Covalent network	Very high	Very hard	Usually nonconducting



Appearance –
Precious and semi-precious stones of many varieties.
Mechanical Properties –
Metals/Alloys, e.g. Titanium for aircraft, cement/concrete (Ca_3SiO_5), ceramics, lubricants (graphite), abrasives (diamond, quartz).
Electrical Properties –
Metallic conductors (Cu, Ag), semiconductors (GaAs), Superconductors, electrolytes (LiI in pacemaker batteries) and piezoelectrics (quartz in watches).
Magnetic Properties –
CrO_2, Fe_3O_4 in recording technology.
Optical Properties –
Pigments, e.g. TiO_2, phosphors, lasers.
Catalysts –
Zeolites

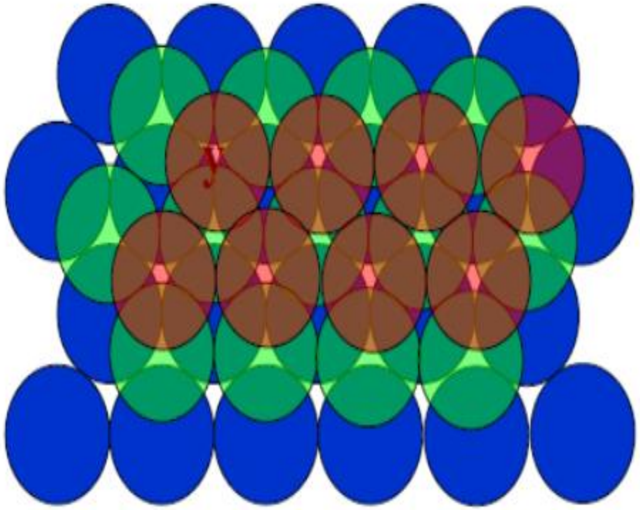
Closest Packing of Spheres



Filling the x sites

ABABAB…. Packing

Hexagonal close packing (HCP)

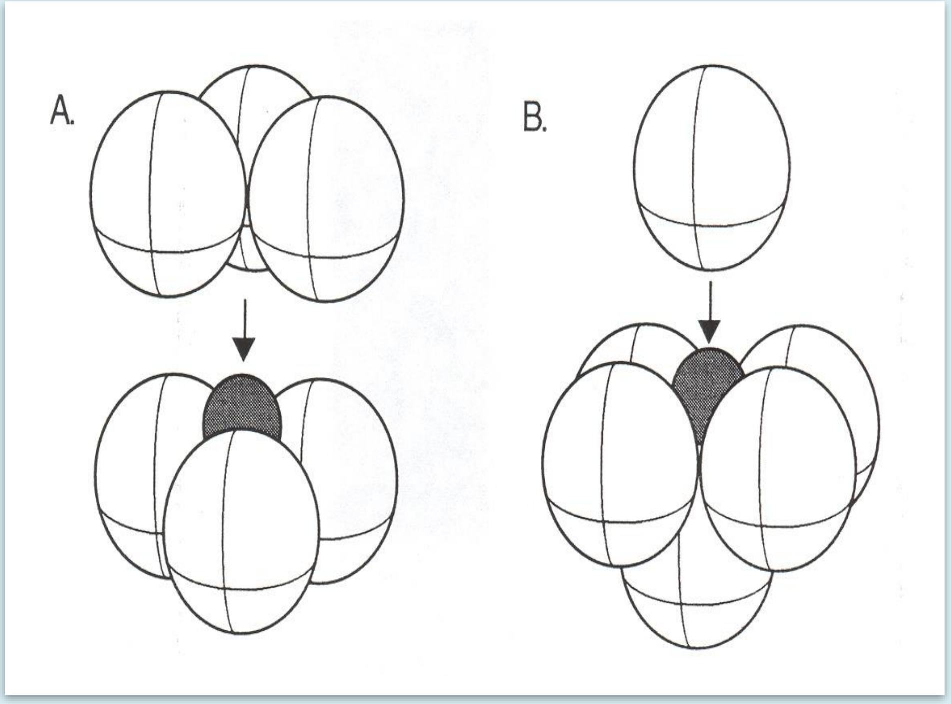


Filling the y sites

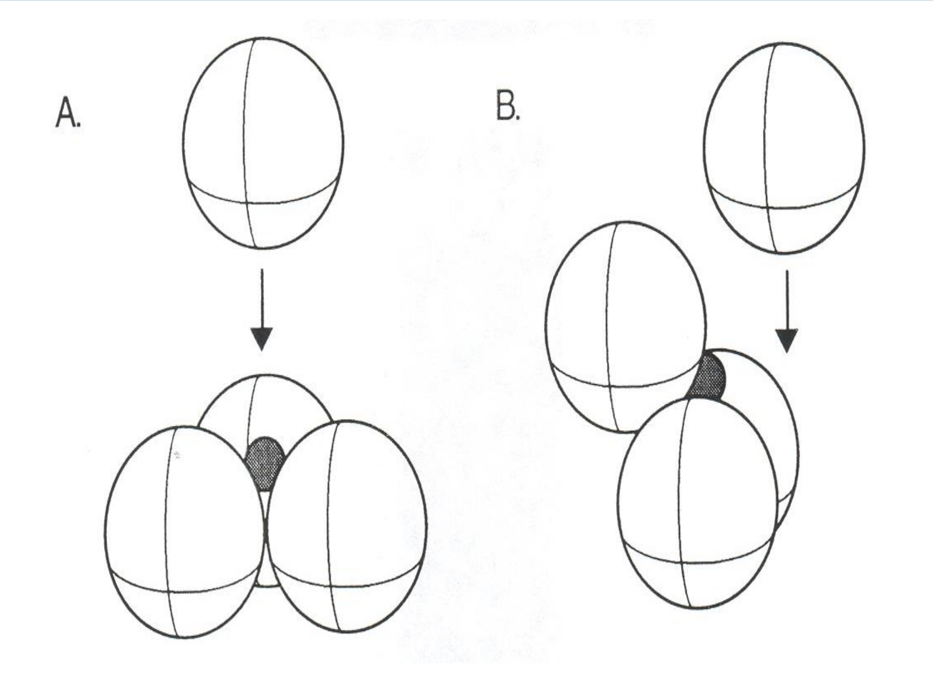
ABCABCABC…. Packing

Cubic close packing (CCP)

OCTAHEDRAL HOLES



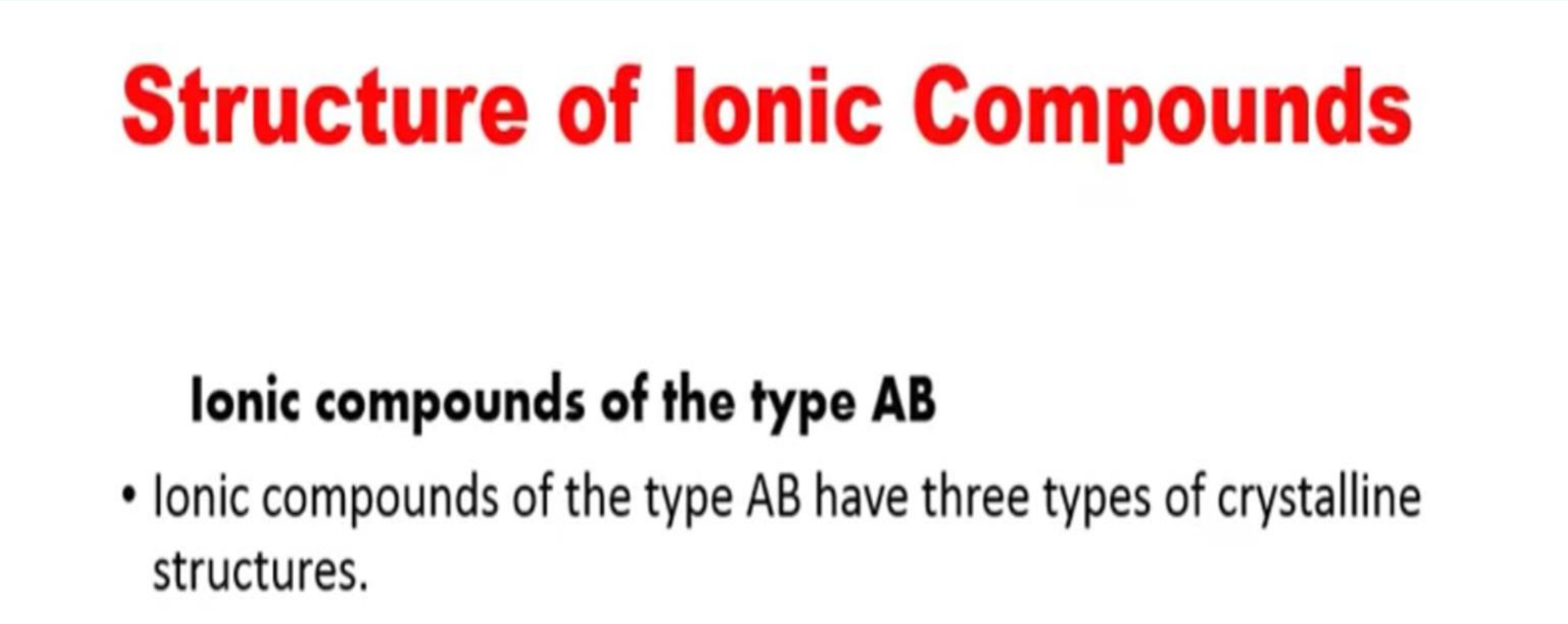
TETRAHEDRAL HOLES



- ✓ Ionic solids are considered as close packing of anions and the cations, occupying the tetrahedral or octahedral sites.

- ✓ Solids can be categorized as mono component (one element A e.g, Cu), binary [two elements AB (e.g, NaCl), or AB_2 (e.g, TiO_2)] and ternary, three elements ABC (e.g, ABO_3)

- ✓ **The structure types are classified as A, AB, AB_2 and ABO_3.**



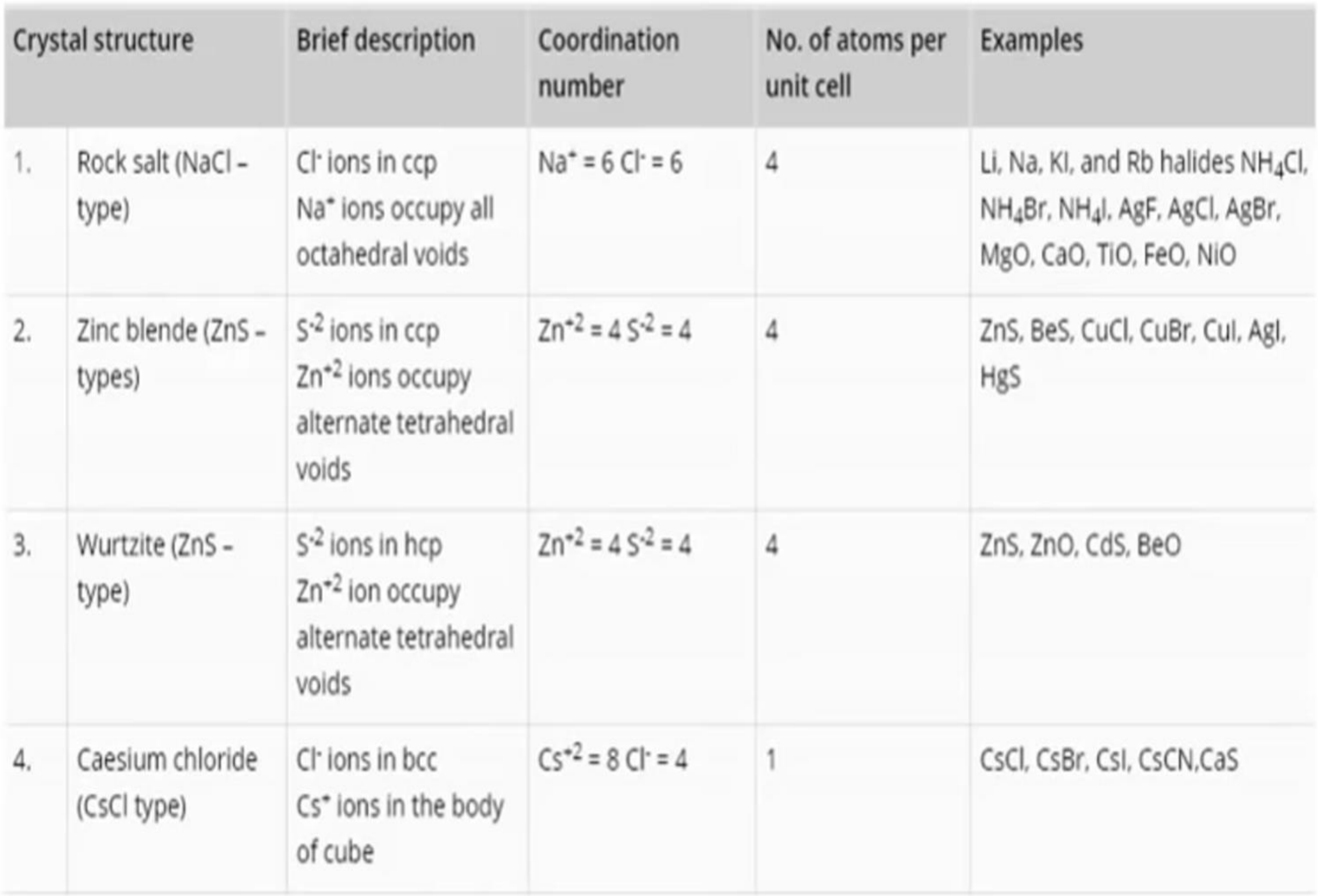
Structure of Ionic Compounds

Ionic compounds of the type AB

- Ionic compounds of the type AB have three types of crystalline structures.

- **NaCl type**
- **ZnS type**
- **CsCl type**

Table for AB type Structures



Crystal structure		Brief description	Coordination number	No. of atoms per unit cell	Examples
1.	Rock salt (NaCl – type)	Cl^- ions in ccp Na^+ ions occupy all octahedral voids	$Na^+ = 6$ $Cl^- = 6$	4	Li, Na, KI, and Rb halides NH_4Cl, NH_4Br, NH_4I, AgF, AgCl, AgBr, MgO, CaO, TiO, FeO, NiO
2.	Zinc blende (ZnS – types)	S^{-2} ions in ccp Zn^{+2} ions occupy alternate tetrahedral voids	$Zn^{+2} = 4$ $S^{-2} = 4$	4	ZnS, BeS, CuCl, CuBr, CuI, AgI, HgS
3.	Wurtzite (ZnS – type)	S^{-2} ions in hcp Zn^{+2} ion occupy alternate tetrahedral voids	$Zn^{+2} = 4$ $S^{-2} = 4$	4	ZnS, ZnO, CdS, BeO
4.	Caesium chloride (CsCl type)	Cl^- ions in bcc Cs^+ ions in the body of cube	$Cs^{+2} = 8$ $Cl^- = 4$	1	CsCl, CsBr, CsI, CsCN,CaS

AB type NaCl Structures

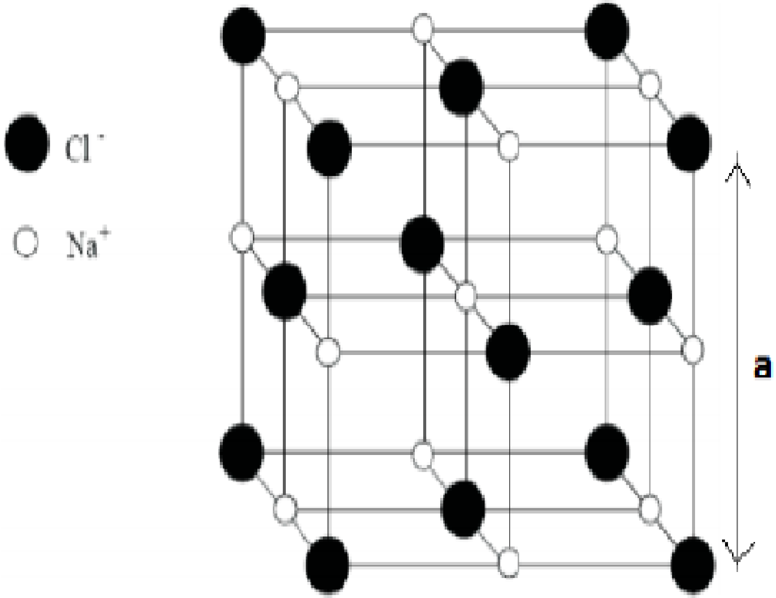


Figure 1.19: Structure of NaCl

Rock salt (NaCl) structure type is AX , anion packing is fcc, here the cation number is 6, anion is 6. A basis consist one Na and one Cl.

position of Cl and Na atoms are:

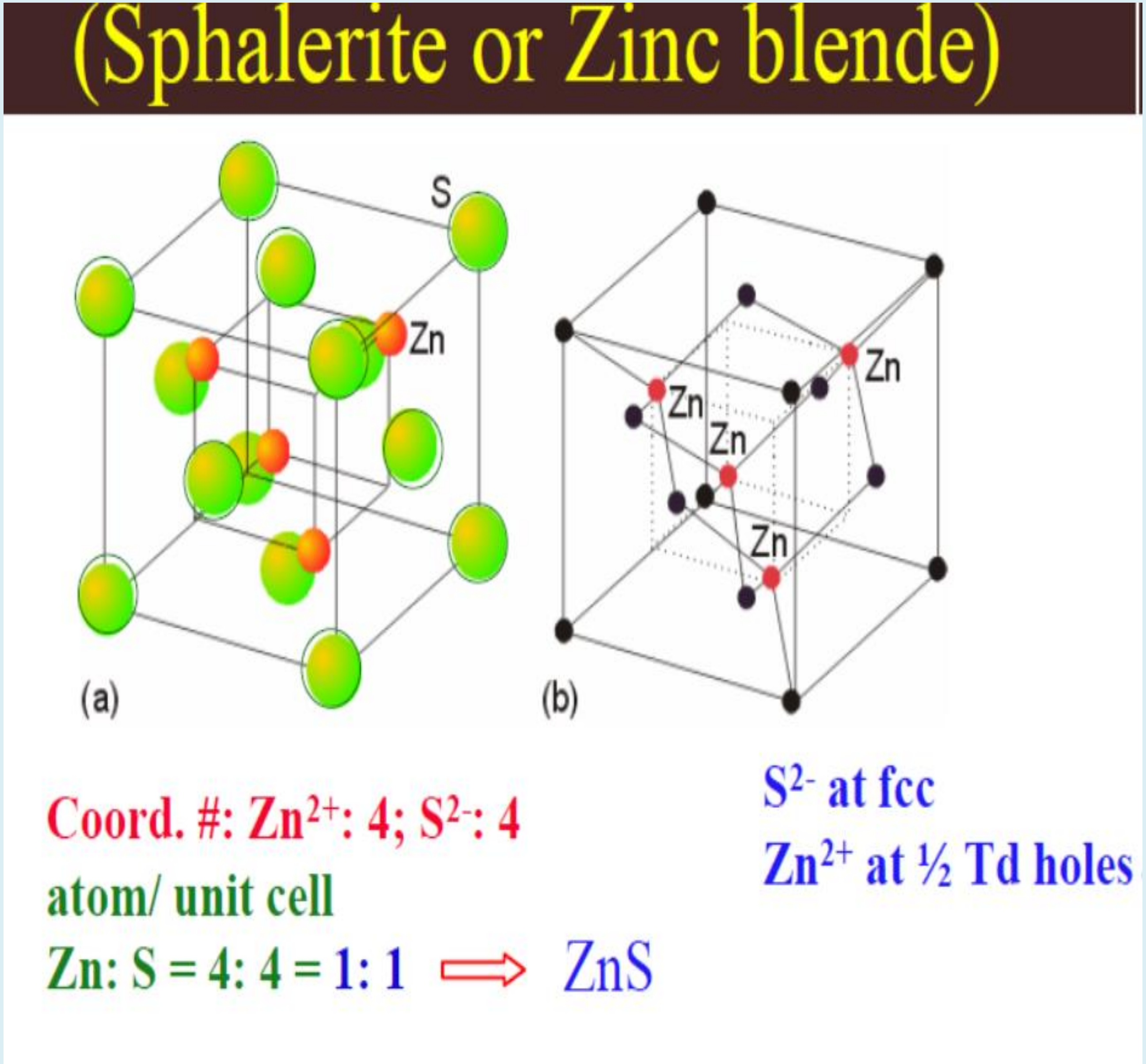
Cl : 0, 0, 0; 1/2,1/2, 0; 1/2, 0, 1/2; 0, 1/2, 1/2;

Na : 1/2, 1/2, 1/2; 0,0, 1/2; 0; 0, 1/2, 1/2; 1/2,0,0

The coordinate number of each Na and Cl atom in this structure is 6.

Other examples of NaCl (AX) type structure are KBr, KCl, MgO, AgBr.

AB type



(Sphalerite or Zinc blende)

Coord. #: Zn^{2+}: 4; S^{2-}: 4

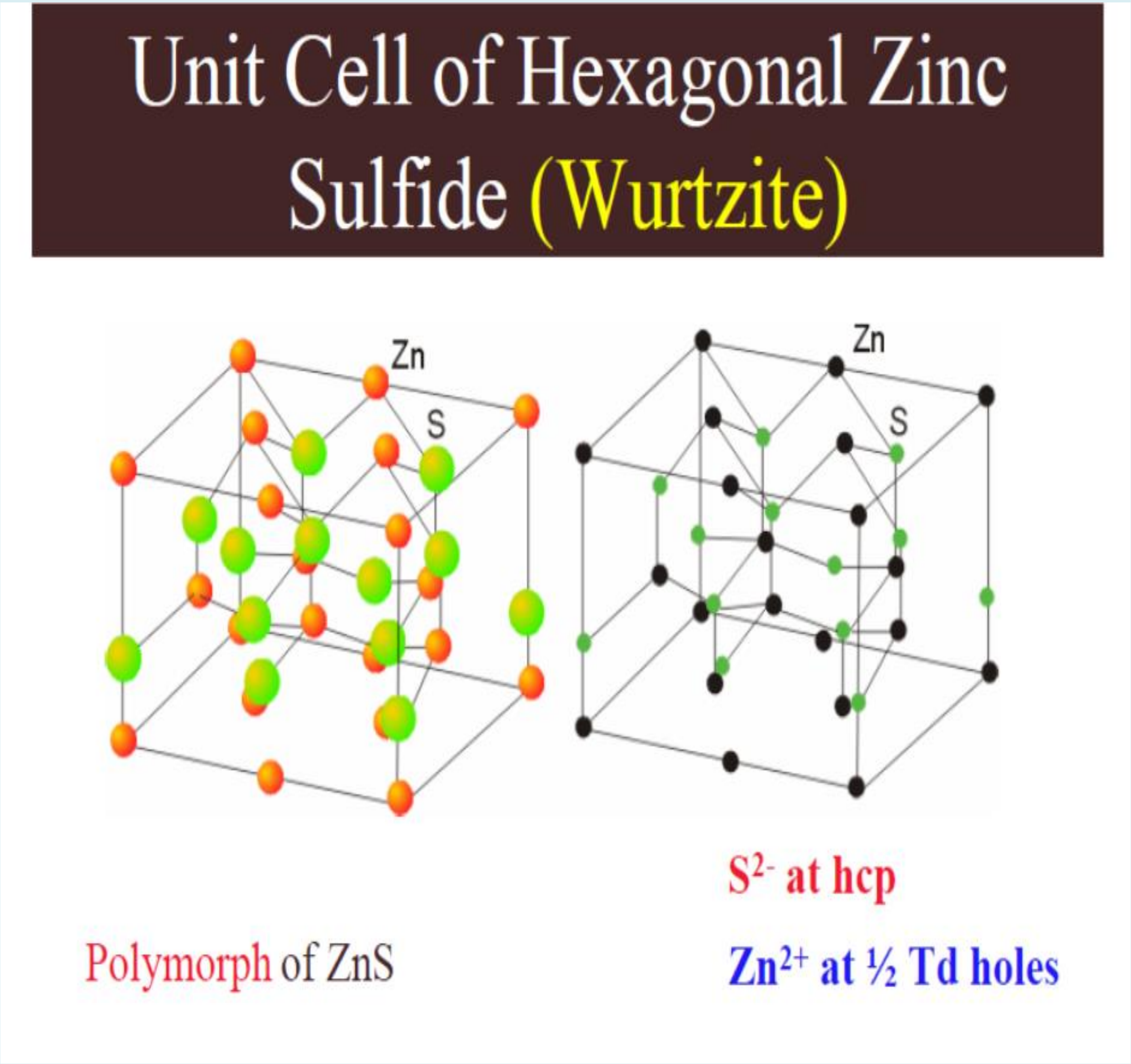
atom/ unit cell

Zn: S = 4: 4 = 1: 1 ⇨ ZnS

S^{2-} at fcc

Zn^{2+} at ½ Td holes

AB type



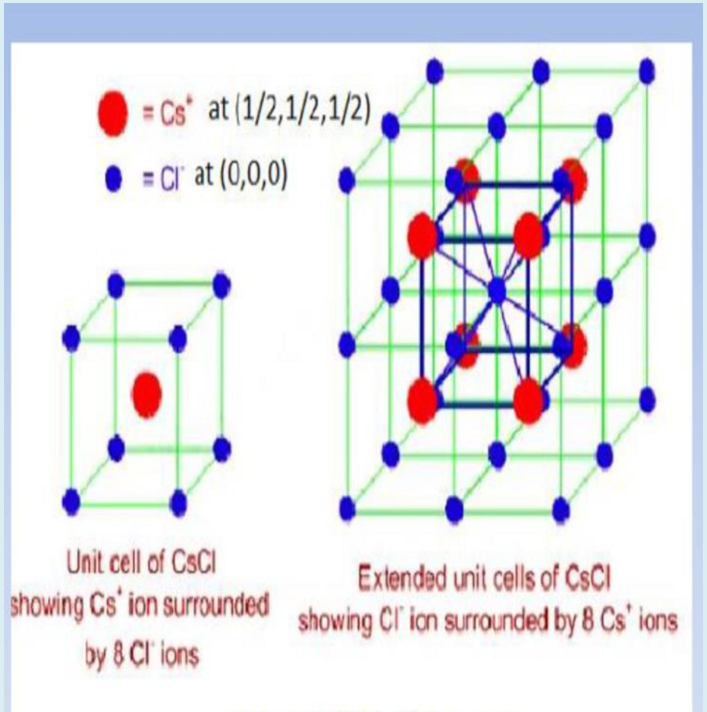
Unit Cell of Hexagonal Zinc Sulfide (Wurtzite)

Polymorph of ZnS

S^{2-} at hcp

Zn^{2+} at ½ Td holes

AB type Cesium Chloride (CsCl) Structure



Unit cell of CsCl showing Cs⁺ ion surrounded by 8 Cl⁻ ions

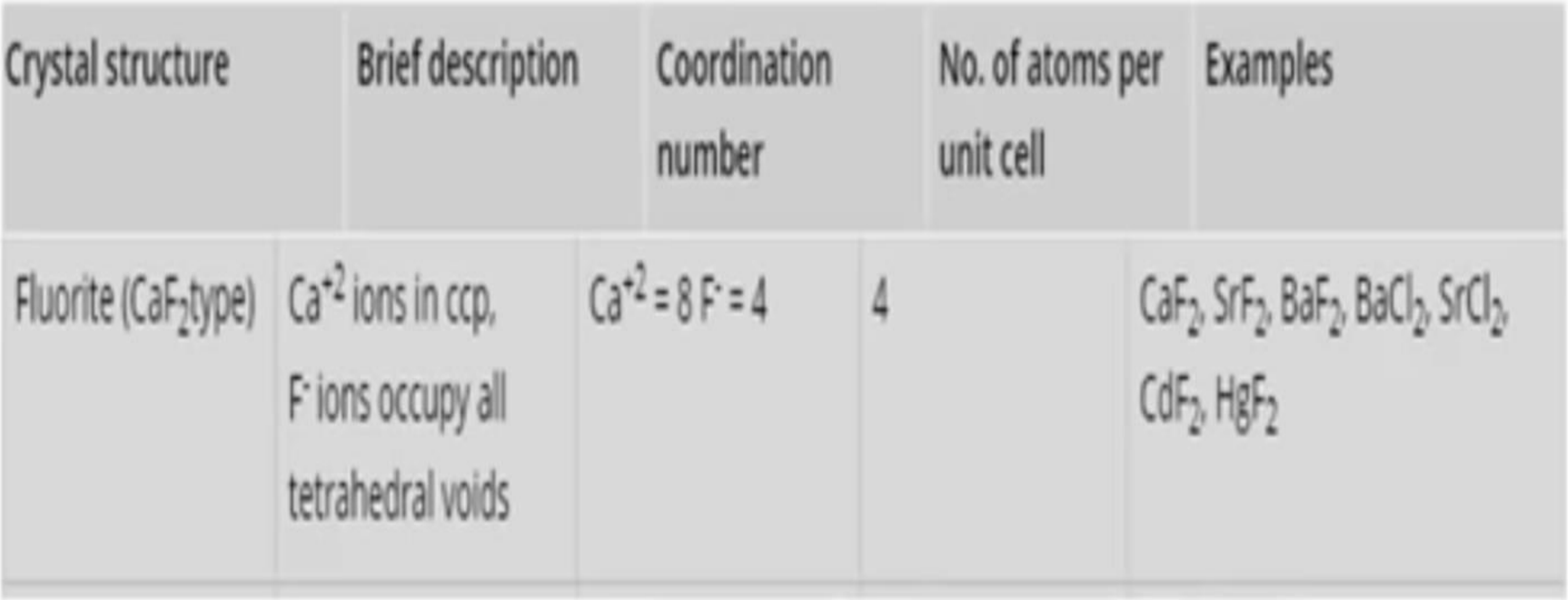
Extended unit cells of CsCl showing Cl⁻ ion surrounded by 8 Cs⁺ ions

Figure 1.20: CsCl Structure

- Cesium chloride (CsCl) structure type is AX at anion packing is body centered cubic.
- two primitive cells in a cubic unit cell. each unit cell has two molecule (basis) of CsCl.
- Positions of Cl ion is at (0, 0, 0) and Cs ion is at (1/2, 1/2,/1/2).
- The Cs is situated at body center and 8 Cl ions at the corner of unit cell. Similarly if we extend the unit cell we can see a Cl ion is surrounded by 8 Cs ions. Thus the coordinate number of CsCl is 8.
- The other examples of CsCl type structure are RbCl, LiHg etc.

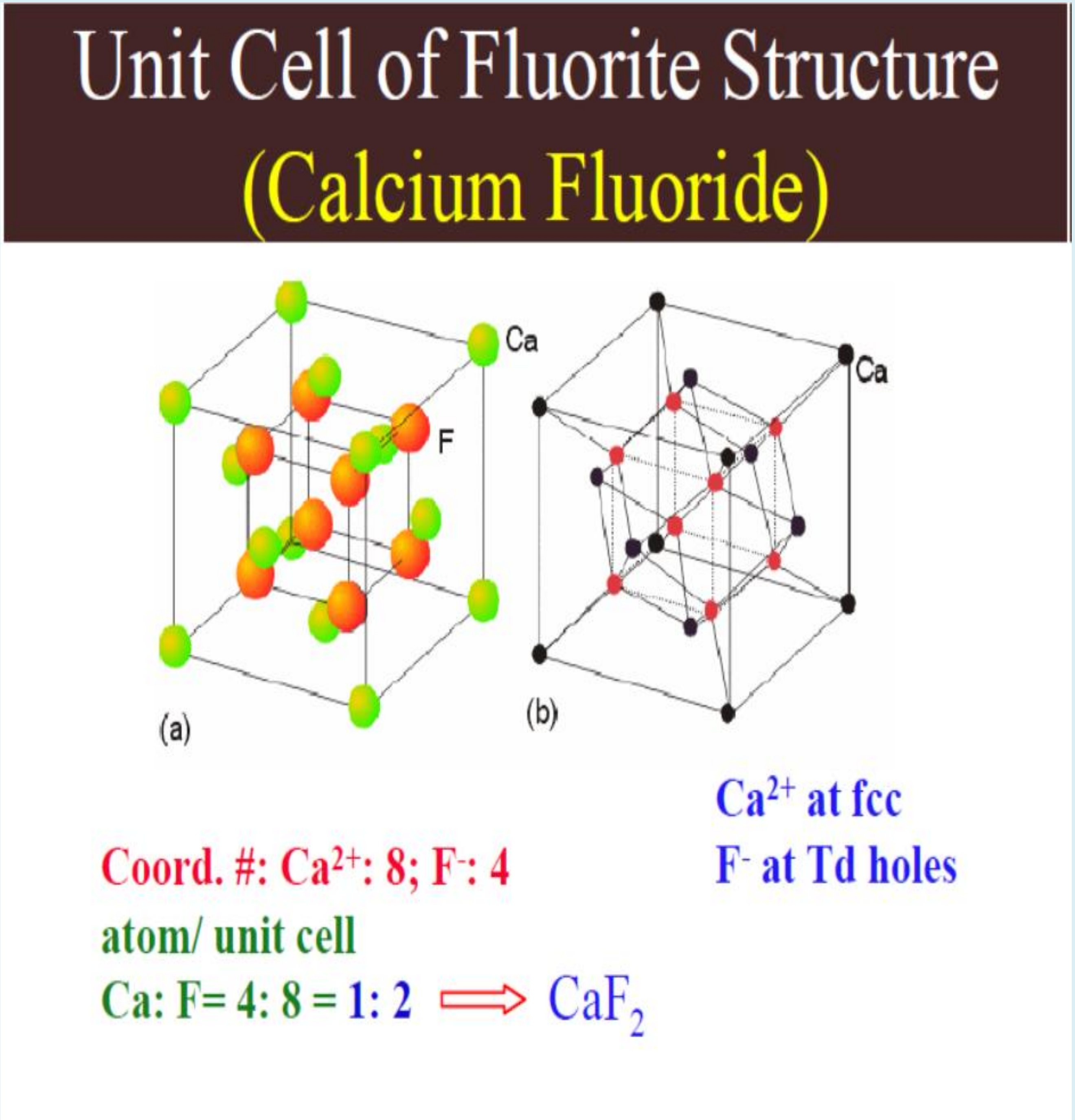
Ionic compound of AB2 type

- Fluorite Structures



Crystal structure	Brief description	Coordination number	No. of atoms per unit cell	Examples
Fluorite (CaF_2type)	Ca^{+2} ions in ccp, F^- ions occupy all tetrahedral voids	Ca^{+2} = 8 F^- = 4	4	CaF_2, SrF_2, BaF_2, $BaCl_2$, $SrCl_2$, CdF_2, HgF_2

AB$_2$ type



Unit Cell of Fluorite Structure (Calcium Fluoride)

Ca^{2+} at fcc

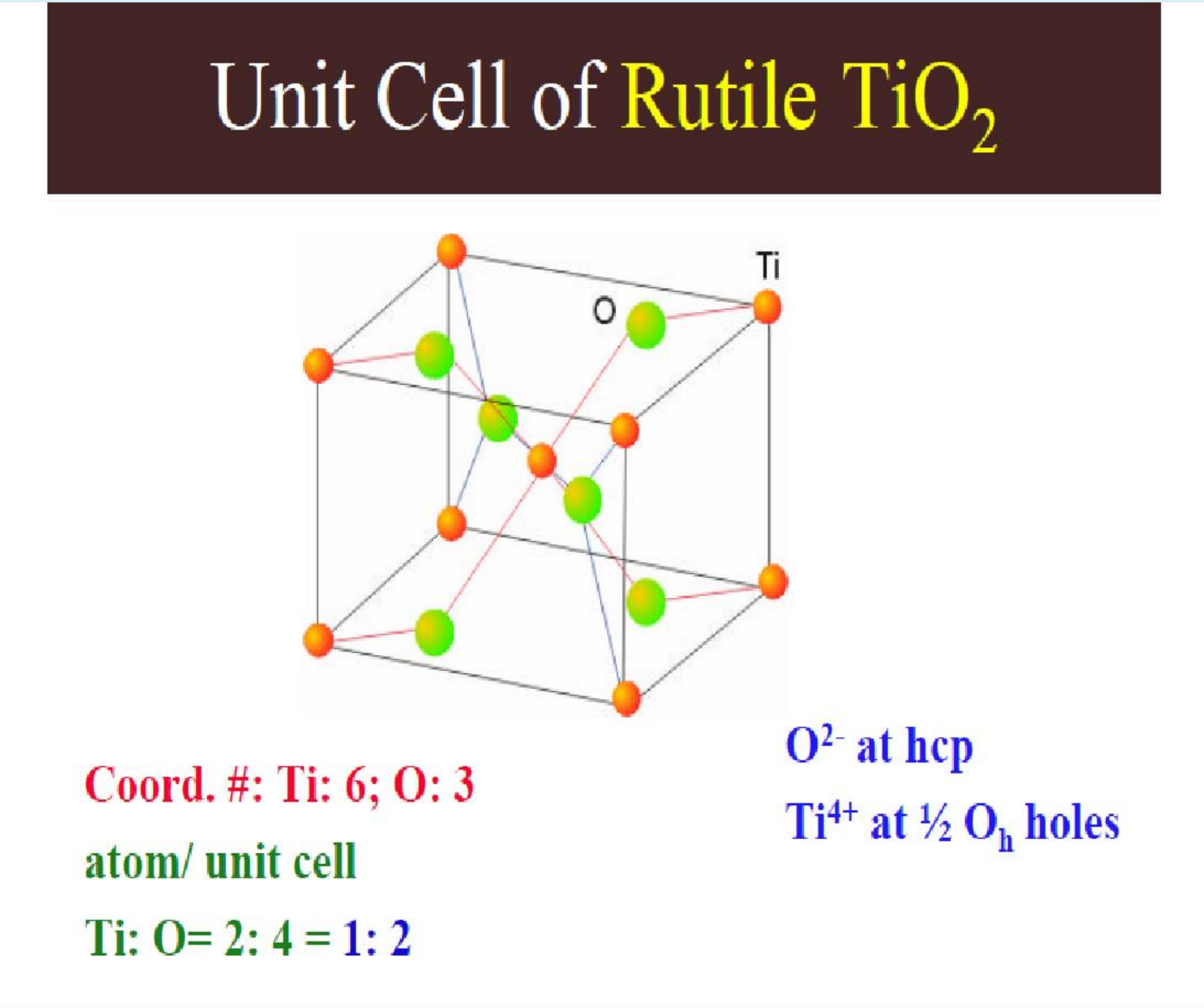
F$^-$ at Td holes

Coord. #: Ca^{2+}: 8; F$^-$: 4

atom/ unit cell

Ca: F= 4: 8 = 1: 2 $\Longrightarrow$ CaF$_2$

AB$_2$ type



Unit Cell of Rutile TiO_2

Coord. #: Ti: 6; O: 3

atom/ unit cell

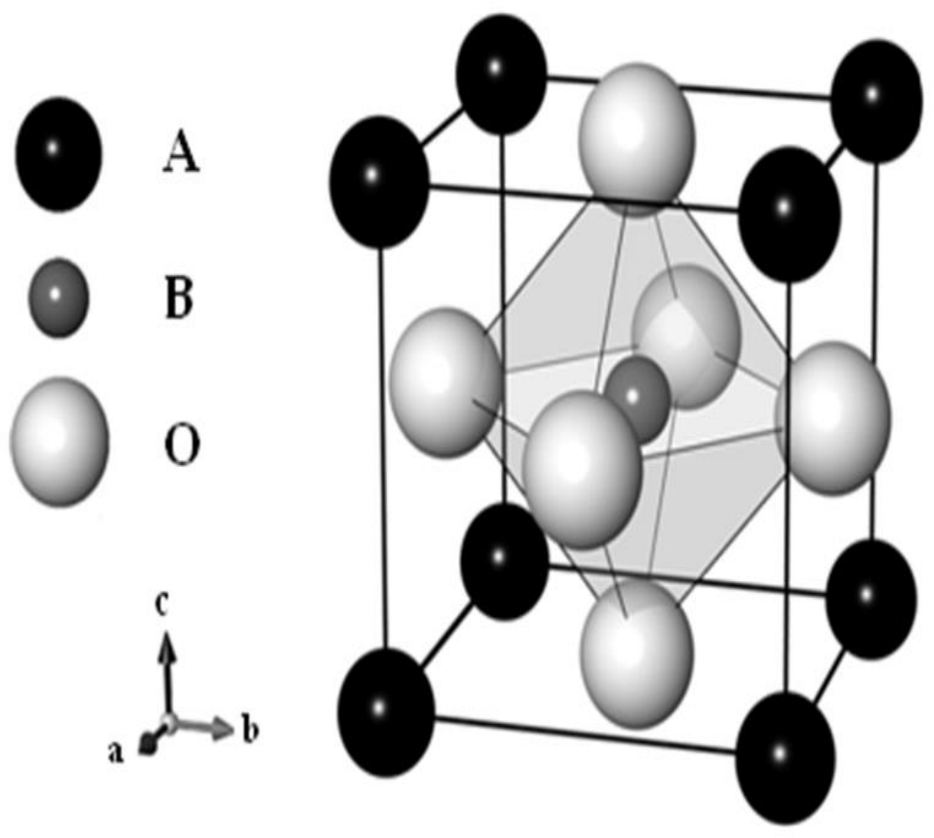
Ti: O= 2: 4 = 1: 2

O^{2-} at hcp

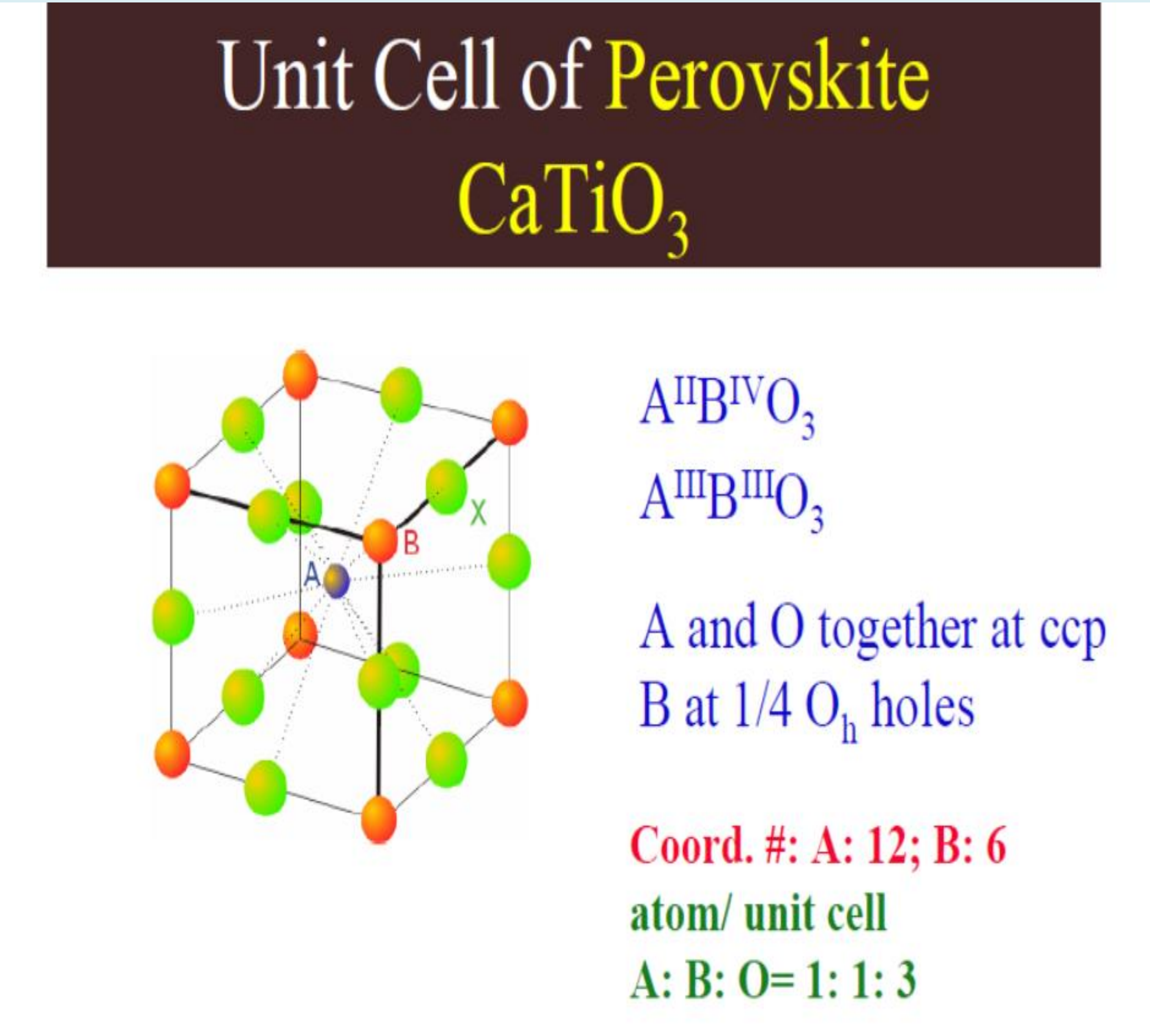
Ti^{4+} at ½ O_h holes

Ionic Compound of ABO_3 type

- ✓ General chemical formula is ABO_3, where 'A' and 'B' are two cations of very different sizes, and O is an anion.



ABO_3 type



Unit Cell of Perovskite $CaTiO_3$

$A^{II}B^{IV}O_3$

$A^{III}B^{III}O_3$

A and O together at ccp

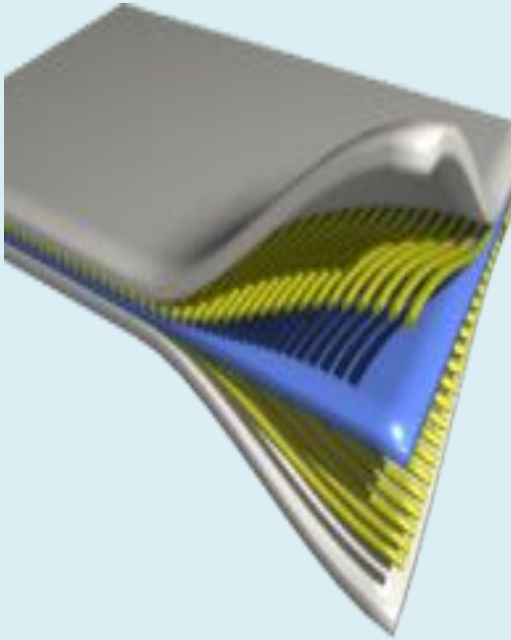
B at 1/4 O_h holes

Coord. #: A: 12; B: 6

atom/ unit cell

A: B: O= 1: 1: 3

What is a Composite Material?



- A composite material is a combination of two materials with different physical and chemical properties.
- The materials combined to produce a new material which is specific to a definite work, for instance, to become stronger, lighter, or resistant to electricity and also improve strength and stiffness.
- The components maintain their identity within the composite, i.e. they do not dissolve or completely merge into one another, though they act in concert.

Example for composites showing superior properties

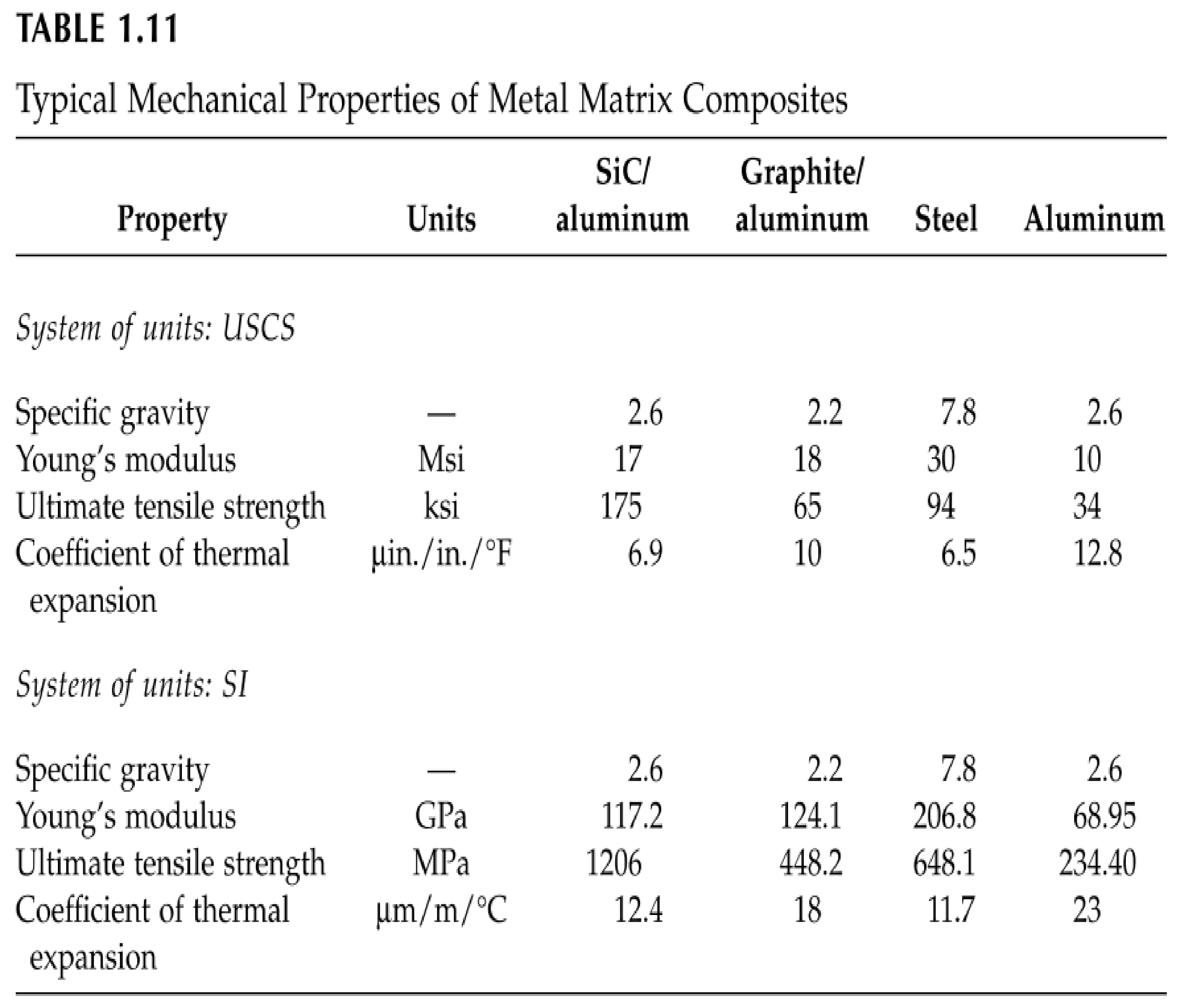


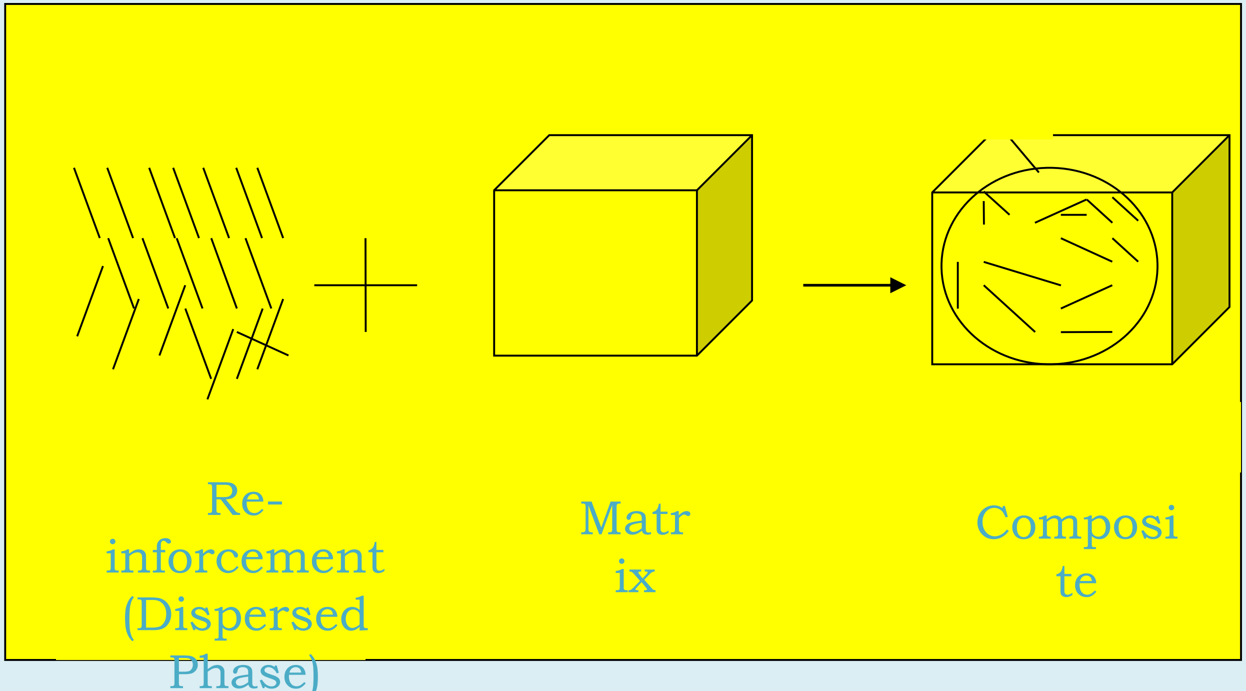
TABLE 1.11

Typical Mechanical Properties of Metal Matrix Composites

Property	Units	SiC/ aluminum	Graphite/ aluminum	Steel	Aluminum
System of units: USCS					
Specific gravity	—	2.6	2.2	7.8	2.6
Young's modulus	Msi	17	18	30	10
Ultimate tensile strength	ksi	175	65	94	34
Coefficient of thermal expansion	μin./in./°F	6.9	10	6.5	12.8
System of units: SI					
Specific gravity	—	2.6	2.2	7.8	2.6
Young's modulus	GPa	117.2	124.1	206.8	68.95
Ultimate tensile strength	MPa	1206	448.2	648.1	234.40
Coefficient of thermal expansion	μm/m/°C	12.4	18	11.7	23

Constituents of composites

- **Matrix (Continuous phase) : Continuous or bulk material**
- **Reinforcement (Dispersed Phase) : Added primarily to increase the strength and stiffness of matrix**
- **The reinforcement is generally can be in the form of fibres, particles, whiskers or flakes**



Functions (requirements) of the matrix:

1. Keep the fibers in place in the structure;
2. Help to distribute or transfer loads;
3. Protect the fillers, both in the structure and before and during fabrication;
4. Control the electrical and chemical properties of the composite;
5. Carry interlaminar shear.

Types of composites

Natural Composites
(Exist in animal and plants)
Wood = Cellulose + Lignin
Bone= Hydroxyapatite + Collagen

Synthetic composites
(Man-Made)
Mud Bricks = Mud+ Straw
Reinforced Concrete
Fibre glass etc.

Classification of composite materials

Based on the matrix materials

- Polymer matrix composite (PMCs)
- Metal Matrix composite (MMCs)
- Ceramic matrix composite (CMCs)
- Carbon/carbon composites (c/Cs)

Based on the geometry of reinforcement

- Particulate reinforced composites
- Whisker /Flakes reinforced composites
- Fibre reinforced composites

Polymer matrix Composites

- Polymers constitute the most important matrix materials and are used in more than 95% of the composite products in use today.

- **Polymer**
  - **Resin**
    - **Thermosets**
    - **Thermoplastic**
  - **Elastomer**

Polymer matrix composites

Thermoplastic polymer matrices

- Thermoplastics are incorporated in the composite system by melting and solidifying by cooling.
- The physical reaction being reversible in nature.
- Thermoplastics have low creep resistance and low thermal stability compared to thermosetting resins.

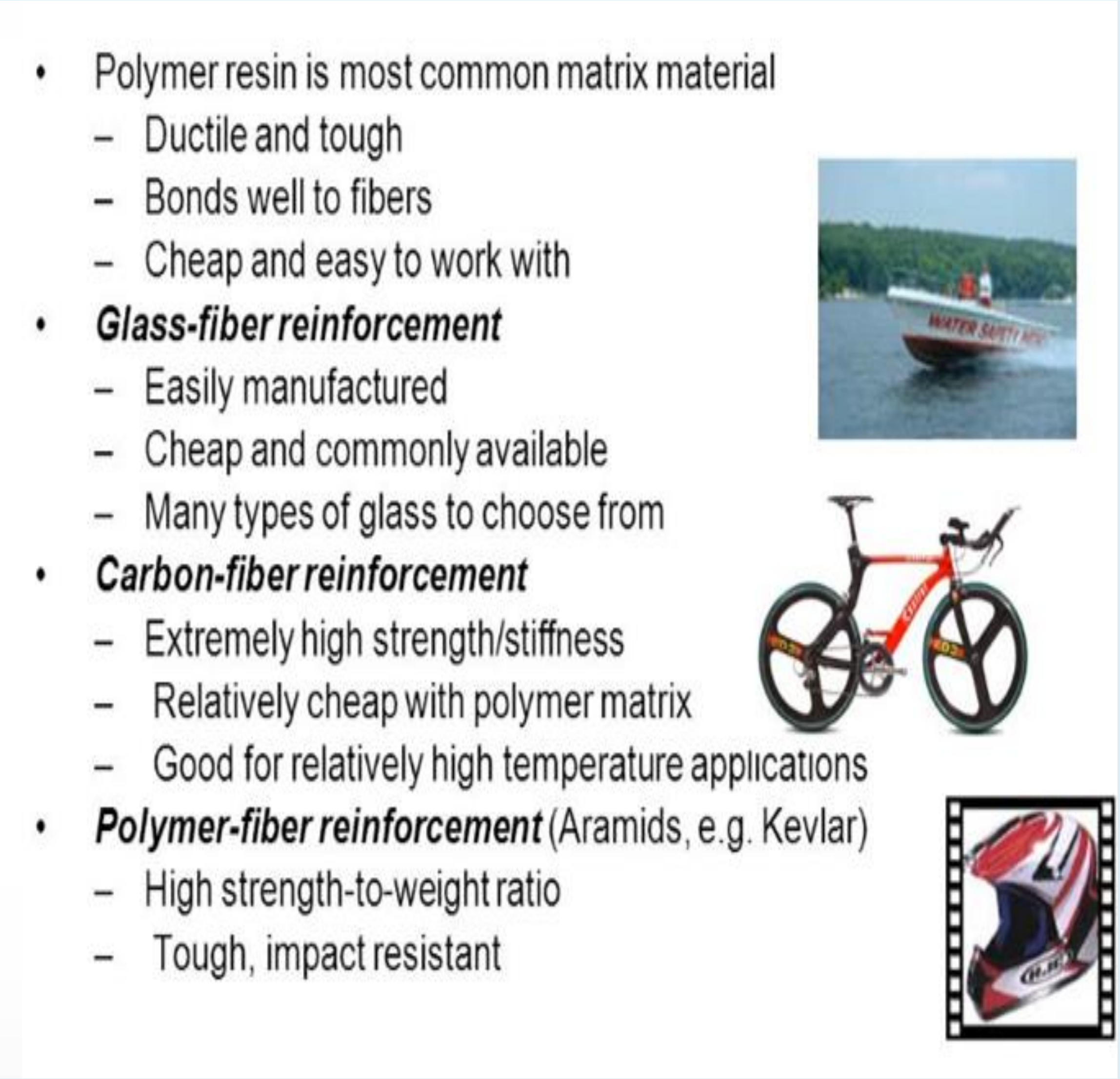
Thermoset polymer matrices

- Thermosetting resins are more common for the development of composite systems.
- Solidification from the liquid phase takes place by the action of an irreversible chemical cross- linking reaction, generally in the presence of heat and pressure.

Elastomer based composites

- The greater extensibility and high-energy storing capacity make them a suitable continuous phase for composite materials.
- Unlike plastics, a wide variety of flexible products can be made using elastomers as the matrix phase.
- They offer elastic strain higher than that of metals and can be stretched rapidly, even under small loads.

Applications of Polymer matrix composites (PMC)



- Polymer resin is most common matrix material
  - Ductile and tough
  - Bonds well to fibers
  - Cheap and easy to work with
- ***Glass-fiber reinforcement***
  - Easily manufactured
  - Cheap and commonly available
  - Many types of glass to choose from
- ***Carbon-fiber reinforcement***
  - Extremely high strength/stiffness
  - Relatively cheap with polymer matrix
  - Good for relatively high temperature applications
- ***Polymer-fiber reinforcement*** (Aramids, e.g. Kevlar)
  - High strength-to-weight ratio
  - Tough, impact resistant

The Fiber-line Bridges,Denmark

Metal- matrix composites (MMC)

- Metal Matrix Composites are composed of a metallic matrix (Al,Mg,Fe,Cu etc) and a dispersed ceramic (oxide, carbides) or metallic phase(Pb,Mo,W etc).

- Ceramic reinforcement may be silicon carbide, boron, alumina, silicon nitride, boron carbide, boron nitride etc.,whereas metallic reinforcement may be tungsten, beryllium etc.

- From a material point of view, when compared to polymer matrix composites, the advantages of MMCs lie in their retention of strength and stiffness at elevated temperature, good abrasion and creep resistance properties.

- Most MMCs are still in the development stage or the early stages of production and are not so widely established as polymer matrix composites. The biggest disadvantages of MMCs are their high costs of fabrication.

- There are also advantages in some of the physical attributes of MMCs such as no significant moisture absorption properties, non-inflammability and resistance to most radiations.

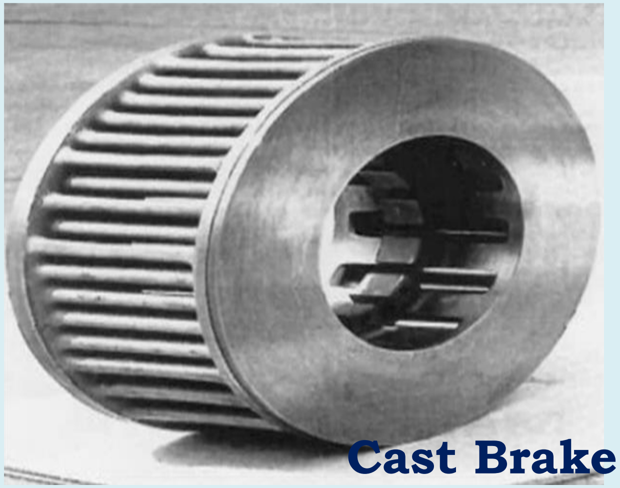
Metal- matrix composites (MMC)

- Only light metals are responsive, with their low density proving an advantage. Titanium, aluminium and magnesium are the popular matrix metals currently in vogue, which are particularly useful for aircraft applications.
- If metallic matrix materials have to offer high strength, they require high modulus reinforcements.
- The strength-to-weight ratios of resulting composites can be higher than most alloys.
- The melting point, physical and mechanical properties of the composite at various temperatures determine the service temperature of composites.
- They can withstand elevated temperature in corrosive environment than polymer composites. However, practically, the choices for low temperature applications are not many.
- The choice of reinforcements becomes more stunted with increase in the melting temperature of matrix materials.

Applications of Metal matrix composites (MMC)

- Carbide drills are often made from a tough cobalt matrix with hard tungsten carbide particles inside.
- Modern high-performance sport cars, such as those built by Porsche, use rotors made of carbon fiber within a silicon carbide matrix.
- Metal Matrix Composite (MMC) are used in Diesel Piston, disk break
- The F-16 Fighting Falcon uses monofilament silicon carbide fibres in a titanium matrix for a structural component of the jet's landing gear.
- Today these applications are found most often in aircraft components, space systems and high-end or "boutique" sports equipment.
- MMCs are used for Space Shuttle, commercial airliners, electronic substrates, bicycles, automobiles, golf clubs and a variety of other applications.

Diesel Piston



Cast Brake Disk

Ceramic Matrix composite (CMC)

- A given ceramic matrix can be reinforced with either discontinuous reinforcements, such as particles, whiskers or chopped fibres, particulates having compositions of Si_3N_4, SiC, AlN, titanium diboride, boron carbide, and boron nitride or with continuous fibres.

- Characteristics of CMC
  - High-temperature stability
  - High thermal shock resistance
  - High hardness
  - High corrosion resistance
  - Light weight
  - Nonmagnetic and nonconductive properties
  - Versatility in providing unique engineering solutions

Ceramic matrix composites (CMC)

- Ceramic-matrix composite development has continued to focus on achieving useful structural and environmental properties at the highest operating temperatures. The high risk associated with this task foreshadows the relatively small number of commercial products.

- However, development of CMCs for other uses has also been pursued, and significant commercial products now exist.

- Ceramics can be described as solid materials which exhibit very strong ionic bonding in general and in few cases covalent bonding.

- High melting points, good corrosion resistance, stability at elevated temperatures and high compressive strength, render ceramic-based matrix materials a favourite for applications requiring a structural material that doesn’t give way at temperatures above 1500°C.

- Naturally, ceramic matrices are the obvious choice for high temperature applications.

Applications:

- CMCs find promising applications in the area of cutting tools and in heat engines where the components should withstand aggressive environments.

- In Aircraft engines - use of stator vanes formed of CMC in the hot section of the F136 turbofan engine is under consideration.

Applications of CMC

- Exhaust nozzle flaps and seals in the F414 engine of the Navy F-18 E/F.

  The exhaust temperature of the F414 is over 80^0C (145^0F) higher than the F404 engine used in the previous version of the F-18. As a result, the metal flaps and seals were failing in tens of hours. The CMC parts consist of a Nicalon (Dow Corning Corp.) fiber with an inhibited carbon matrix. A thick SiC overcoat and glaze provide protection from oxidation.

  Insertion of the CMC flaps and seals has produced a weight savings of nearly 1 kg (2 lb) per engine relative to the metal parts. Because this mass is at the very back of the aircraft, additional weight savings can be obtained by removing ballast to shift the center of gravity of the aircraft. The CMC flaps have a useful life that is at least double the design requirement of 500 hours.

Applications of CMC

- Ceramic-matrix composites are now also commercially available as brake rotors for automobiles.

✓ The new Porsche braking system uses an MMC brake pad.

✓ Ceramic-matrix composite brake rotors have also been demonstrated for the Inter-City Express high-speed trains in Germany, where a total weight savings of 5.5 metric tons is obtained per train set.

Types of Plastics

Plastics are classified into two types………..

1. Thermoplastic
2. Thermosetting resins

1. Thermoplastic

Thermoplastics are the plastics that do not undergo chemical change in their composition when heated and can be molded again and again.

- ✓ **They are prepared by addition polymerisation.**
- ✓ **They are straight chain (or) slightly branched polymers and**
- ✓ **Various chains are held together by weak vanderwaal's forces of attraction.**
- ✓ **It can be softened on heating and hardened on cooling reversibly.**
- ✓ **They are generally soluble in organic solvents**

Examples: Polyethylene, Polyvinylchloride

- ✓ **Common thermoplastics range from 20,000 to 500,000 amu**
- ✓ **Each polymer chain will have several thousand repeating units.**

They can be recycled and reused many times by heating and cooling process.

2. Thermosetting resins or Thermosets

- ✓ Thermosetting resins can melt and take shape once; after they have solidified, they stay solid.
- ✓ They are prepared by condensation polymerisation.
- ✓ Various polymer chains are held together by strong covalent bonds (cross links)
- ✓ These plastics get harden on heating and once harden, they cannot be softened again.
- ✓ They are almost insoluble in organic solvents.

Examples: Bakelite, Polyester

Thermoset Polymers whose individual chains have been chemically cross linked by covalent bonds and form a 3-D cross linked structure.

- ➢ Therefore, they resist heat softening and solvent attack.
- ➢ These are hardened during the molding process and once they are cured, they cannot be softened and they cannot be recycled and reused

Eg. Phenol-formaldehyde resins, urea-formaldehyde paints.

Difference between Thermoplastic and Thermosetting Polymers………

Thermoplastic polymers	Thermosetting polymers
Consists of long-chain linear polymers with negligible cross-links.	Have 3-Dimensional network structures joined by strong covalent bonds.
Soften on heating readily because secondary forces between the individual chain can break easily by heat or pressure.	Do not soften on heating; On prolonged heating, they are charred.
By re-heating to a suitable temperature, they can be softened, reshaped and thus reused.	Retain their shape and structure even on heating. Hence, cannot be reshaped.
Usually soft, weak and less brittle.	Usually, hard, strong and brittle.
Can be reclaimed from wastes.	Cannot be reclaimed from wastes.
Usually soluble in some organic solvents.	Due to strong bonds and cross-linking, they are insoluble in almost all organic solvents.

Properties and engineering applications

Types of Thermoplastic resins:

Vinyl resins

(i) PVC
(ii) TEFLON or FLUON
(iii) ABS (Acrylonitrile Butadiene Styrene)

Types of Thermosetting resins:

Phenolic resins or phenoplasts

(i) Bakelite
(ii) Novolac

(ii) TEFLON or FLUON (polytetrafuloroethylene) PTFE

$$n(CF_2=CF_2) \xrightarrow{\text{Polymerize}} \left[-\underset{F}{\overset{F}{C}}-\underset{F}{\overset{F}{C}}- \right]_n$$

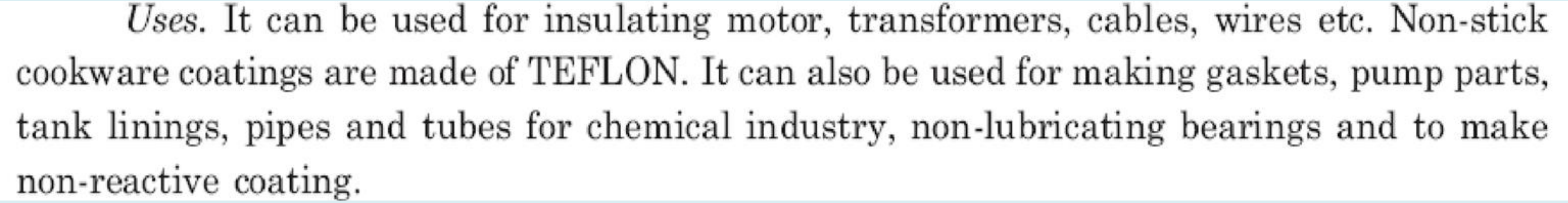
- ✓ Teflon is obtained by polymerization of tetrafluoro ethylene under pressure in the presence of **benzoyl peroxide** as catalyst.

Properties:

- ✓ This polymer is a hard, strong, extreme toughness, High chemical resistance with a high m.pt. and very low surface friction.
- ✓ High softening point (350 C), waxy touch, good mechanical and electrical properties.

Due to all these qualities, the polymeric material can be machined.

- ✓ Its softens at about (350 C), hence at this high temperature it can be moulded applying high pressure.

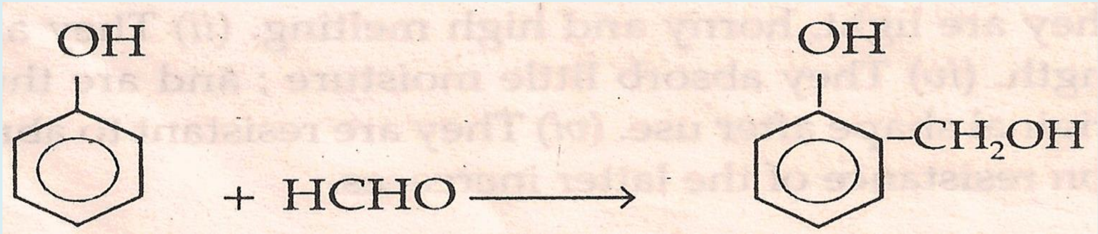


Uses. It can be used for insulating motor, transformers, cables, wires etc. Non-stick cookware coatings are made of TEFLON. It can also be used for making gaskets, pump parts, tank linings, pipes and tubes for chemical industry, non-lubricating bearings and to make non-reactive coating.

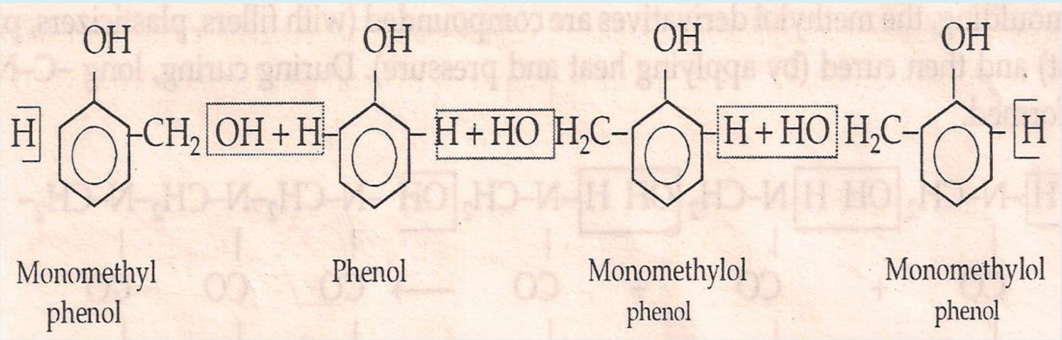
Thermosetting Plastics:

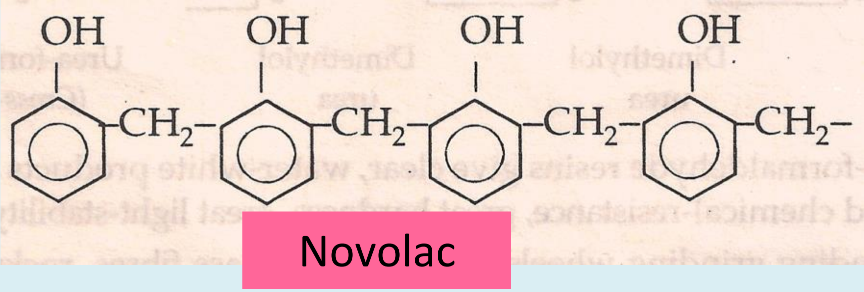
(a) Phenolic resins or Phenoplasts : Novoloc and Bakelite

Phenolic resins are condensation polymerization products of phenol derivatives and aldehydes.



At first, Phenol reacts with Formaldehyde in presence of acidic / alkaline catalyst to form Monomethylnol phenol.





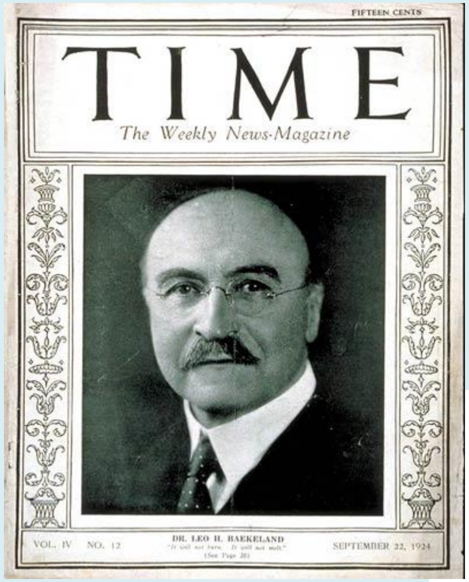
Novolac

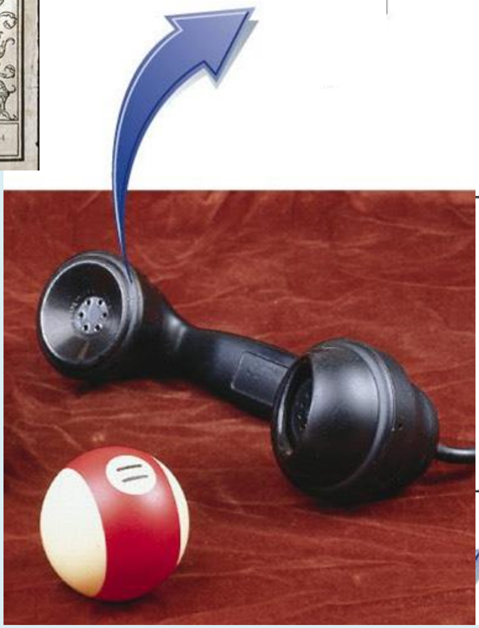
Monomethylol phenol further reacts with Phenol to form a linear polymer “Novolac”.

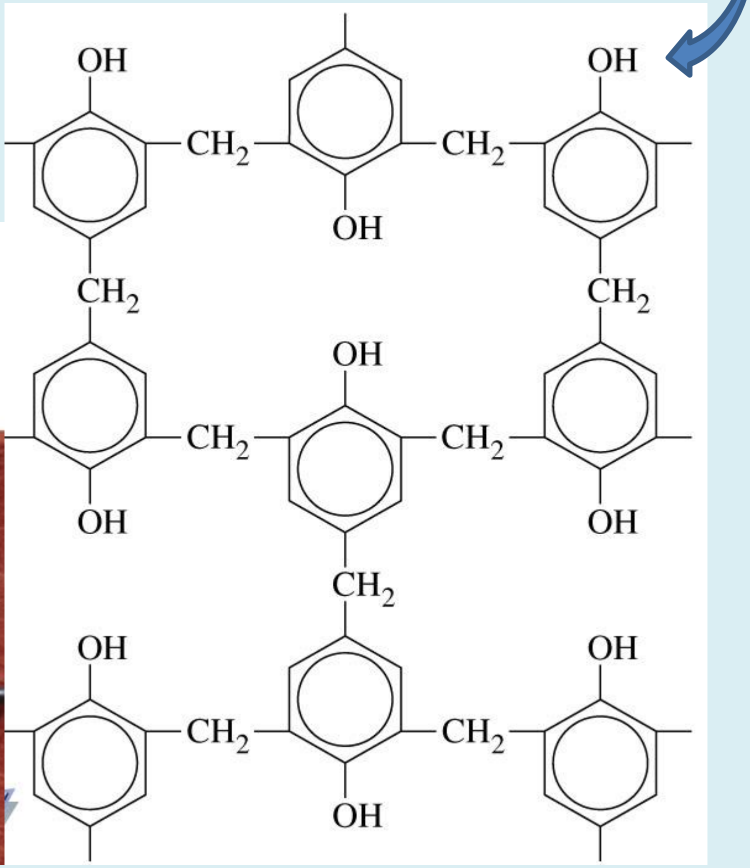
Water is removed as the by-product.

Bakelite

Leo Baekeland



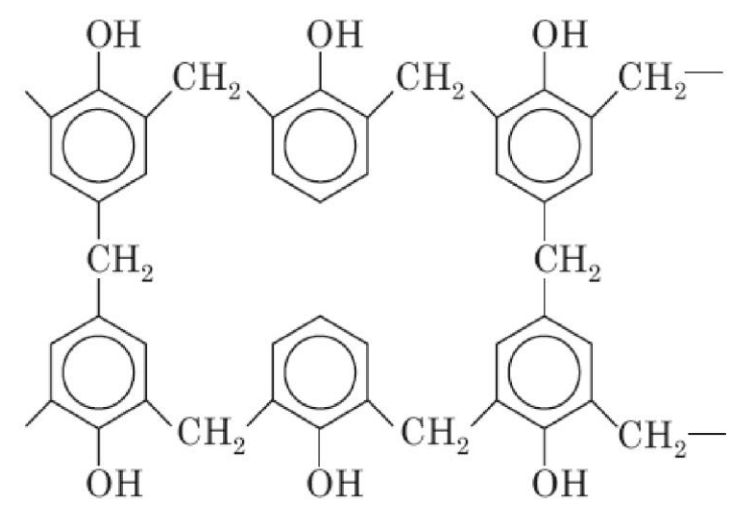




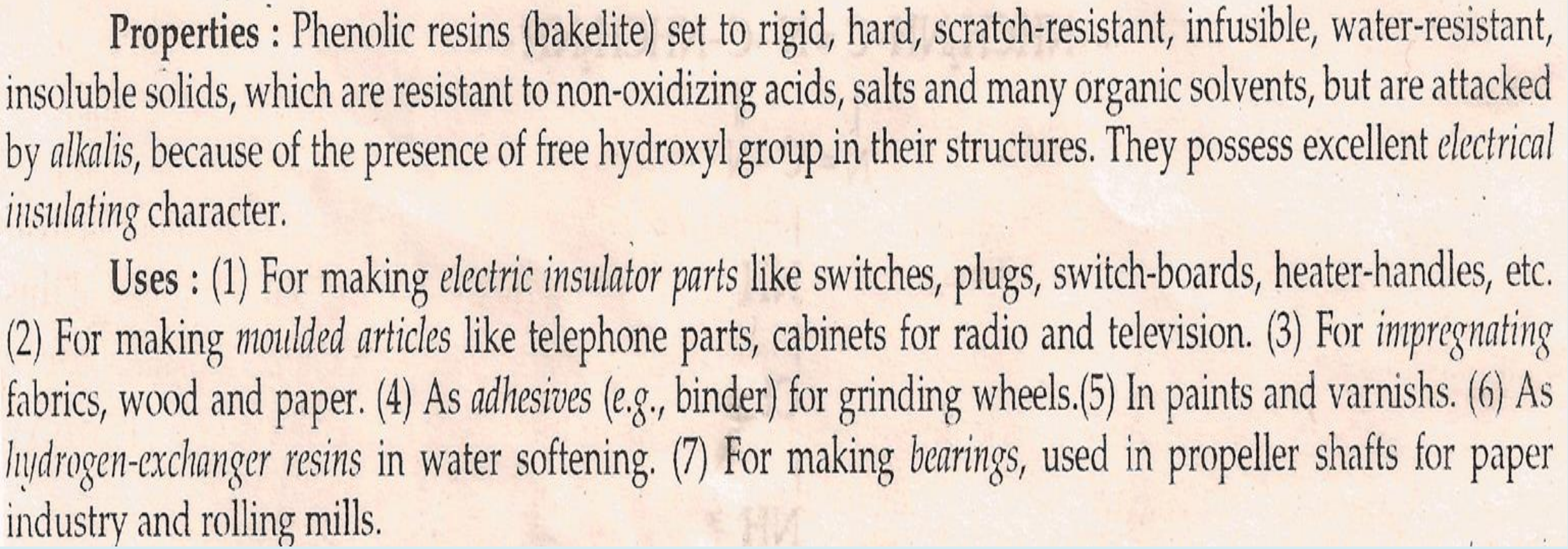
✓ **bakelite** is a cross- linked polymer of phenol and formaldehyde

Thermosetting Plastics: Bakelite

- ✓ **Further addition of HCHO at high temperature and pressure converts Novolac (soft and soluble) into cross-linked "Bakelite" (hard and insoluble).**



Bakelite



Properties : Phenolic resins (bakelite) set to rigid, hard, scratch-resistant, infusible, water-resistant, insoluble solids, which are resistant to non-oxidizing acids, salts and many organic solvents, but are attacked by *alkalis*, because of the presence of free hydroxyl group in their structures. They possess excellent *electrical insulating* character.

Uses : (1) For making *electric insulator parts* like switches, plugs, switch-boards, heater-handles, etc. (2) For making *moulded articles* like telephone parts, cabinets for radio and television. (3) For *impregnating* fabrics, wood and paper. (4) As *adhesives* (*e.g.*, binder) for grinding wheels.(5) In paints and varnishs. (6) As *hydrogen-exchanger resins* in water softening. (7) For making *bearings*, used in propeller shafts for paper industry and rolling mills.

Bakelite

Properties:

- ✓ Bakelite is resistant to acids, salts and most organic solvents, but it is attacked by alkalis because of the presence of –OH groups.
- ✓ It possesses excellent electrical insulating property.
- ✓ As thermoset it is difficult to recycle.

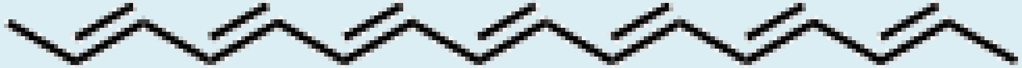
Uses:

- ✓ Bakelite is used as an adhesive in plywood laminations & grinding wheels, etc
- ✓ It is also widely used in paints, varnishes,
- ✓ It is used for making electrical insulator parts like plugs, switches, heater handles, paper laminated products, thermally insulation foams etc.

Conducting Polymers

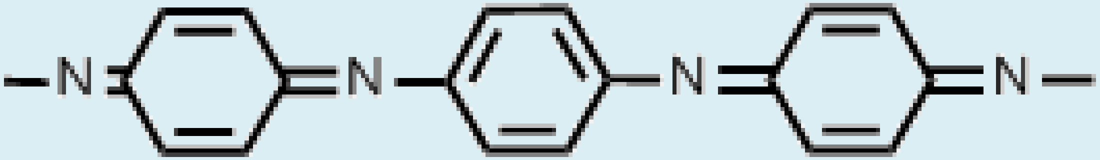
- Polymers, particularly those with a conjugated p-bond structure often show higher conductivity when doped with conductive materials.
- But the use of conductive polymers is limited since they have poor mechanical strength.
- Hence, a combination of mechanical and electrical properties can only find good applications in conductive polymers area.
- Sometimes, in a polymer blend, a bifunctional linker is doped to increase the conductivity of Polyaniline (PANI) (having conductivity) and polycaprolactum (PCL) (having mechanical strength) blend.
- Conductive polymers can be made using simple procedures like melt blending, solution blending etc., and can be used for antistatic and electromagnetic shielding applications.

Some Examples of Conductive Polymers

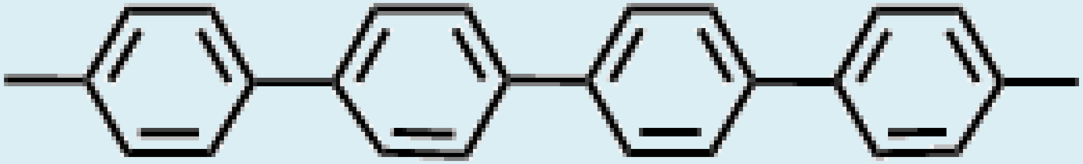


trans-polyacetylene

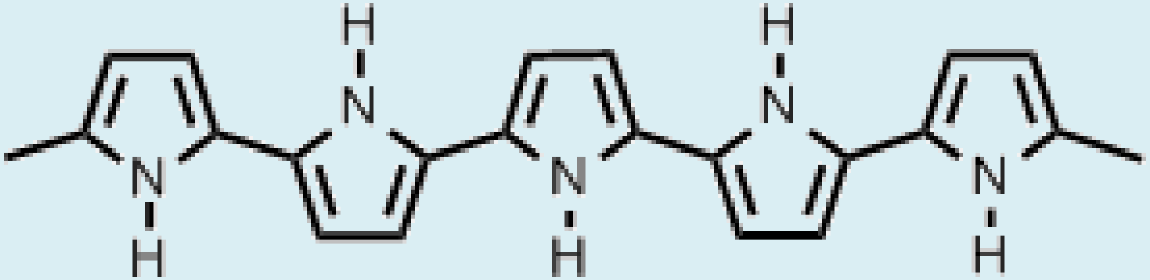
polythiophene



polyaniline

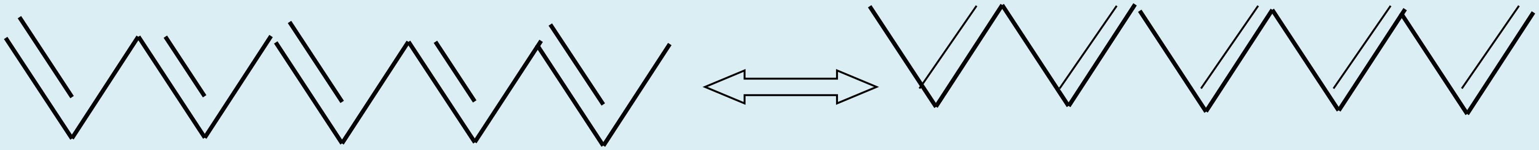


poly(p-phenylene)



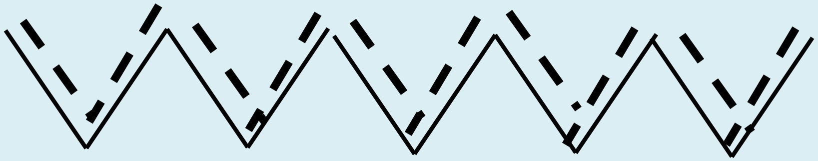
polypyrrole

Mechanism of Conduction in Polymers

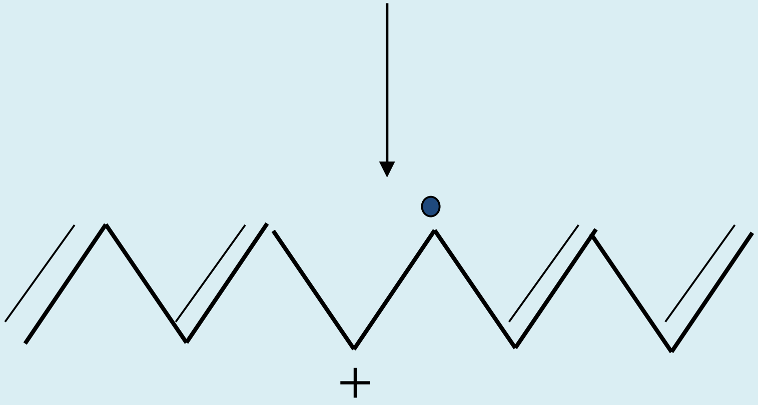


Conjugation of π-electrons

Undoped



Insulating



Doped

Conducting

A-

Dopant anion for charge neutrality

Different Types of Conducting Polymers:

1. Intrinsically conducting polymers (ICP)
2. Doped Conducting polymers
3. Extrinsically conducting polymers (ECP)

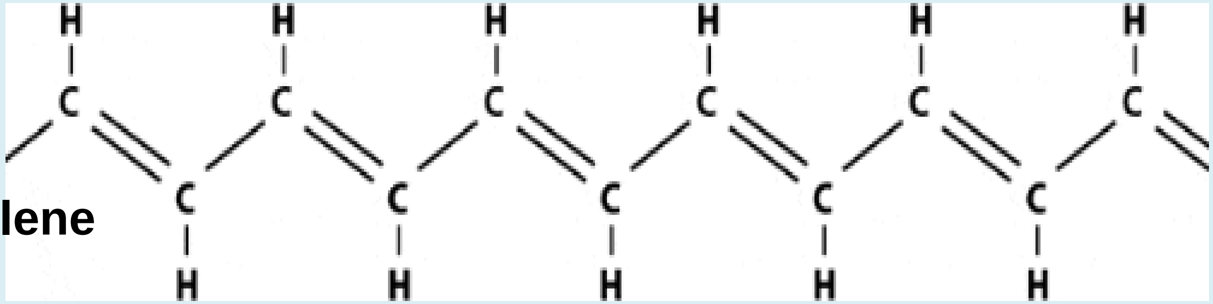
Factors that affect the conductivity:

1. Density of charge carriers
2. Their mobility
3. The direction
4. Presence of doping materials (additives that facilitate the polymer conductivity in a better way)
5. Temperature

1. Intrinsically Conducting Polymers (ICPs)

- Polymer consisting of alternating single and double bonds is called conjugated double bonds.
- In conjugation, the bonds between the carbon atoms are alternately single and double. Every bond contains a localised “sigma” (σ) bond which forms a strong chemical bond.
- In addition, every double bond also contains a less strongly localised “pi” (π) bond which is weaker.
- Conjugation of sigma and pi-electrons over the entire backbone, forms valence bands and conduction bands.

Eg: Poly-acetylene, poly-p-phenylene, polyaniline, polypyrrole polymers



Polyacetylene

2. Doped Conducting Polymers

It is obtained by exposing a polymer to a charge transfer agent either in gas or solution phase. ICPs possess low conductivity (10^{-10} S or Mho/cm), but they possess low ionisation potential and high electron affinity. So they can be easily oxidised or reduced.

DOPING:

The conductivity of ICPs can be increased by creating positive charges (oxidation) or by negative charges (reduction) on the polymer backbone. This technique is called DOPING .

In otherwords….

The polymer structure has to be disturbed - either by removing electrons (oxidation) from or inserting them (reduction) into the materials. The process is known as Doping.

There are two types of doping:

1. Oxidation with halogen (*p*-doping).
2. Reduction with alkali metal (*n*-doping).

(i) p-Doping:

- It involves treating an ICP with a **Lewis acid** which leads to **oxidation process** and positive charges on the polymer backbone are created.

- Some of the p-dopants are I_2, Br_2, AsF_5, PF_5 etc.

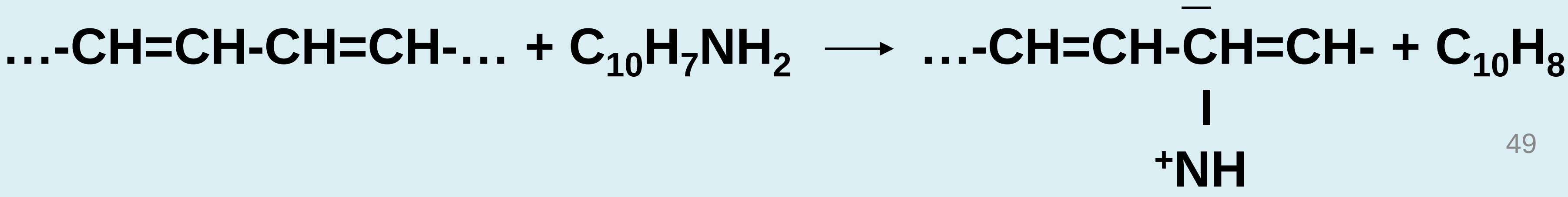
$$2(C_2H_2)_n \quad + \quad 3I_2 \xrightarrow{\qquad\qquad} 2[(C_2H_2)_n^{+} I_3^{-}$$

polyacetylene Lewis acid

(ii) n-Doping:

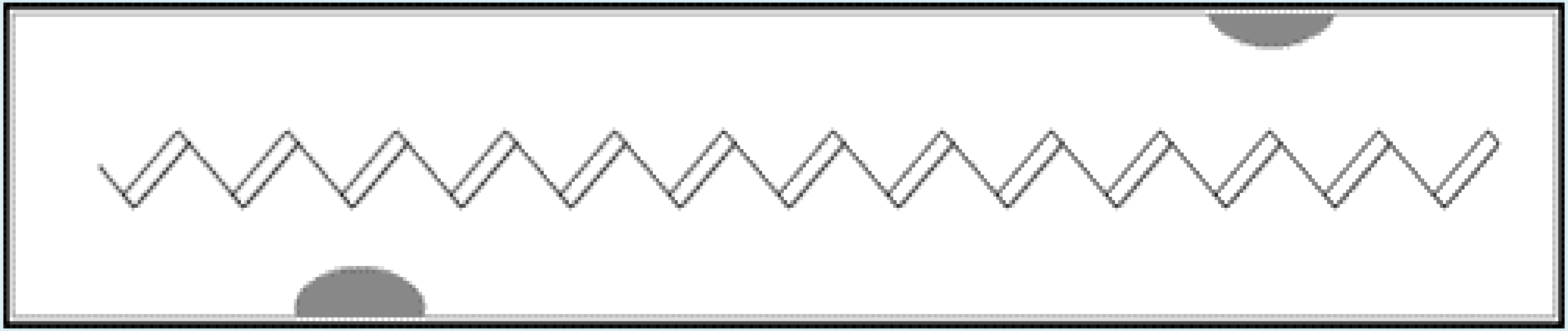
- It involves treating an ICP with a **Lewis base** which leads to **reduction process** and negative charges on the polymer backbone are created.

- Some of the n-dopants are Li, Na, Ca, $FeCl_3$, naphthylamine etc.



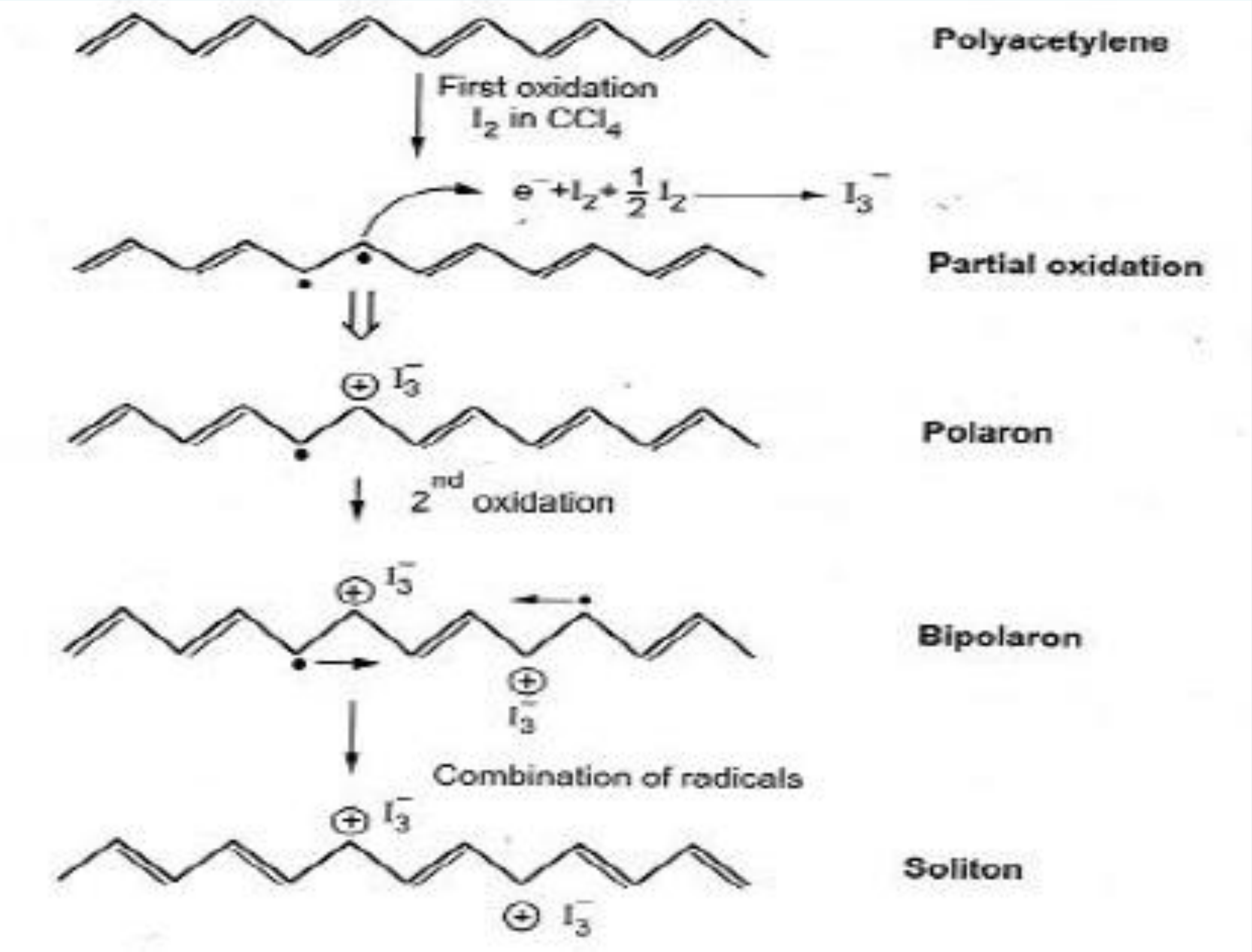
$$\ldots\text{-CH=CH-CH=CH-}\ldots + C_{10}H_7NH_2 \longrightarrow \ldots\text{-CH=CH-}\underset{\underset{{}^{+}NH}{|}}{\overset{-}{C}}\text{H=CH-} + C_{10}H_8$$

- <u>**In p-type doping**</u>**, the dopant (Iodine, I_2) attracts an electron from the polyacetylene chain to form (I_3^-) leaving a positive soliton (carbenium ion) in the polymer chain that can move along its length.**
- **The lonely electron of the double bond, from which an electron was removed, can move easily.**
- **As a consequence, the double bond successively moves along the molecule, and the polymer is stabilized by having the charge spread over the polymer chain.**



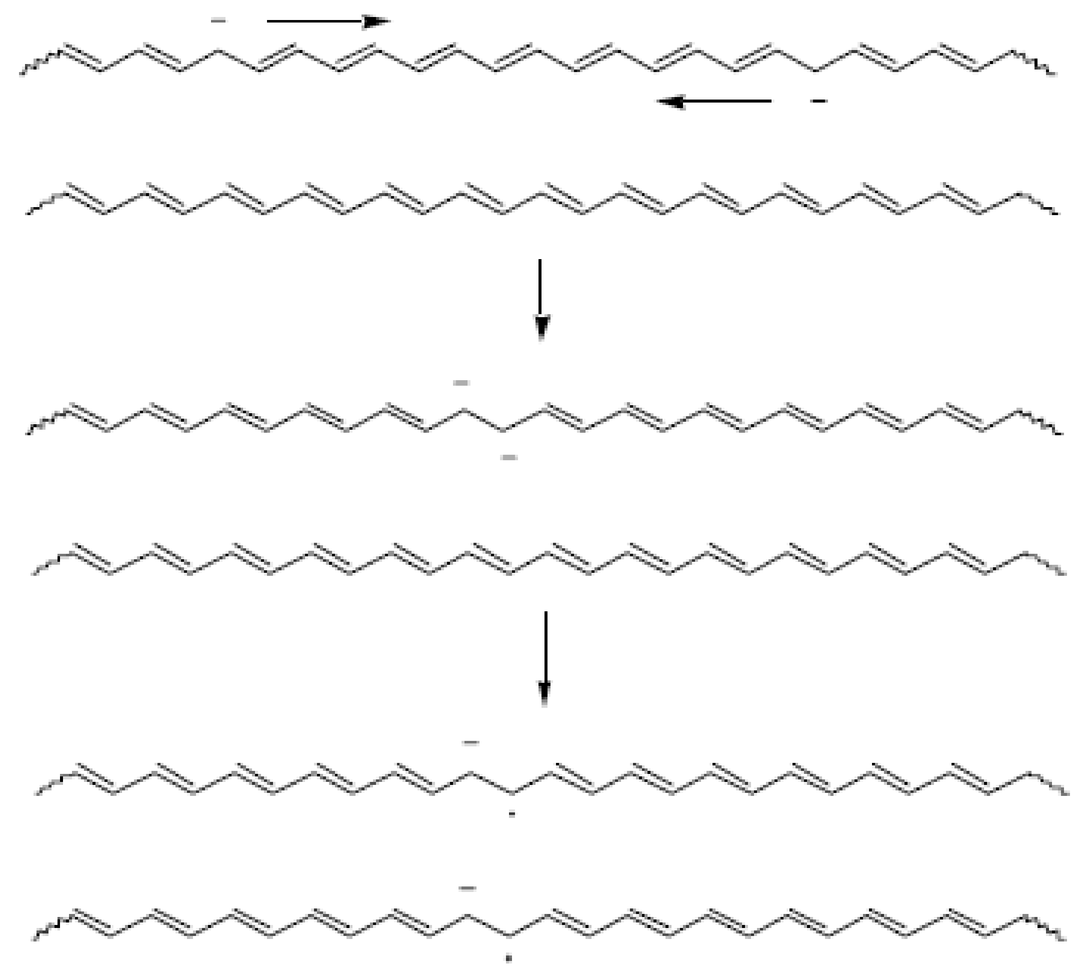
Doping in Trans-Polyacetylene

Mechanism of Conduction in Polyacetylene



Conductivity Mechanism in Polyacetylene:

- The mechanism followed by **polyacetylene** for the transfer of charge from one chain to another is called **intersoliton hopping**.
- **What is a soliton?** The soliton is a charged or a neutral defect in the polyacetylene chain that propagates down the chain, thereby reducing the barrier for interconversion.



- In n-type doping (This can be done by dipping the film in THF solution of an alkali metal) soliton is a resonance-stabilized polyenyl anion of approximately 29-31 CH units in length, with highest amplitude at the centre of the defect.
- The solitons (**anions**) transfer electrons to a neutral soliton (**radical**) in a neighboring chain through an isoenergetic process.
- The charged solitons are responsible for making polyacetylene a conductor.

3. Extrinsically Conducting Polymers

These are those polymers whose conductivity is due to the presence of externally added ingredients in them.

Two types:

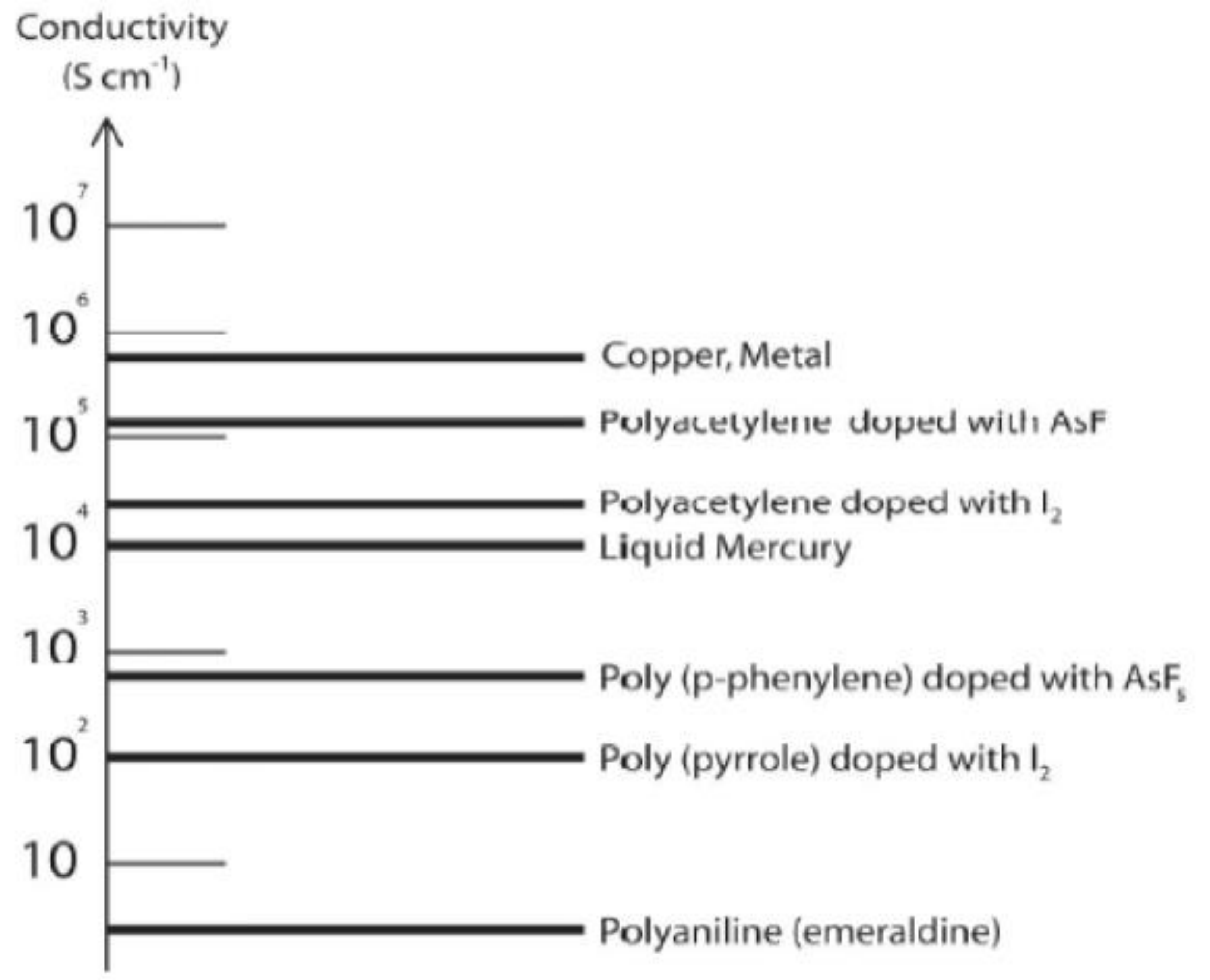
(1) Conductive element filled polymer:

- **It is a resin/polymer filled with carbon black, metallic fibres, metal oxides etc. Polymer acts as a binder to those elements.**
- **These have good bulk conductivity and are low in cost, light weight, strong and durable. They can be in different forms, shapes and sizes.**

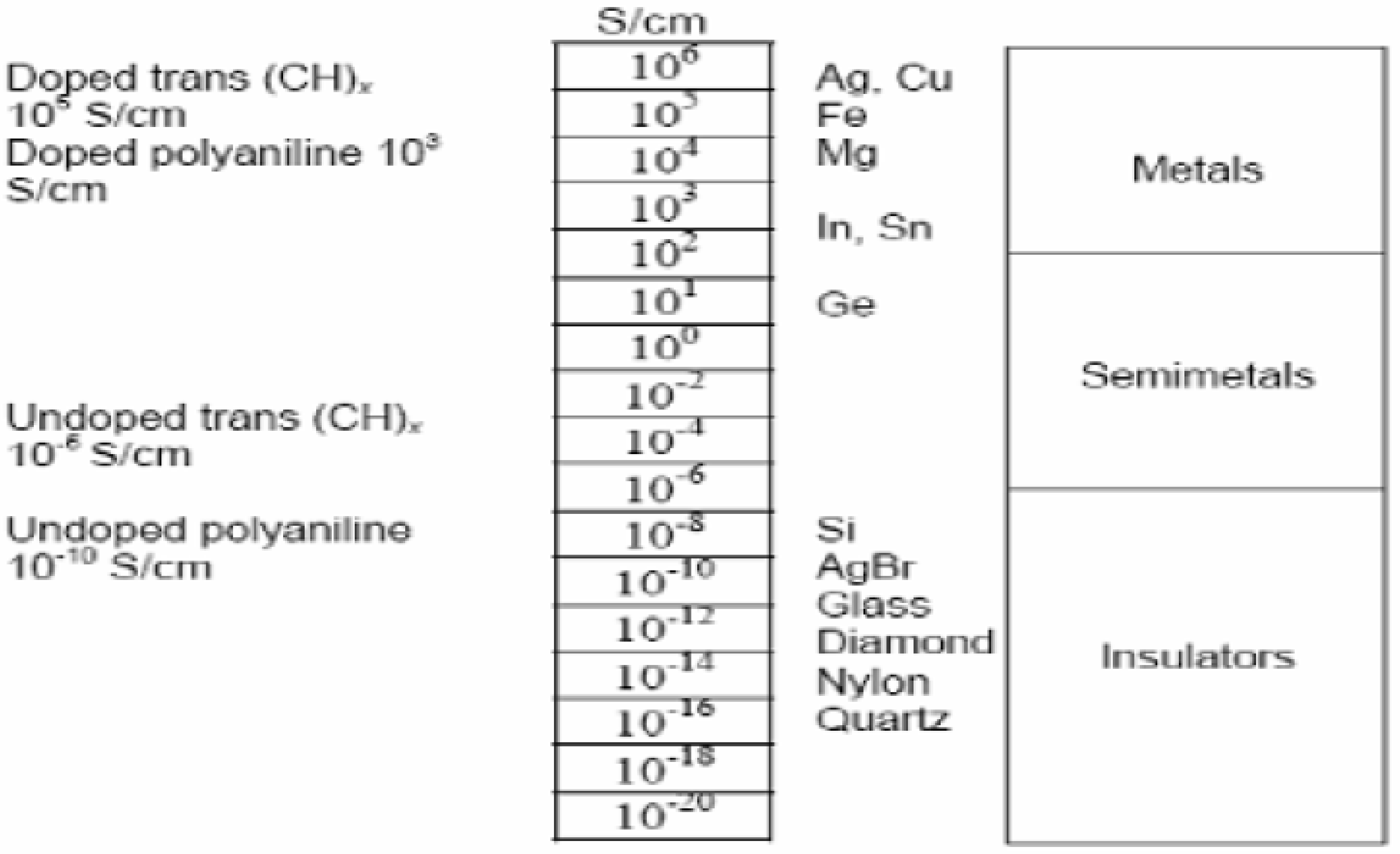
(2) Blended Conducting Polymers:

- **It is the product obtained by blending a conventional polymer with a conducting polymer either by physical or chemical change.**
- **Such polymers can be processed and possess better physical, chemical and mechanical strength.**

Conductivity of Polymers and Metals

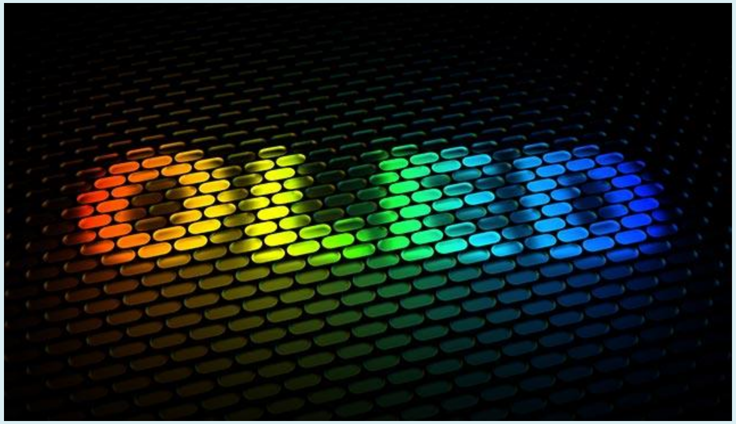


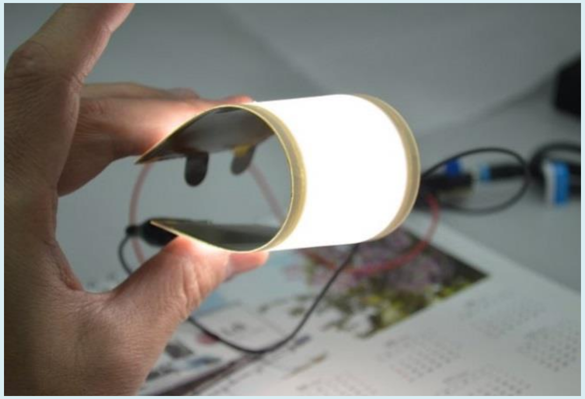
Conductivity Comparison between Conductive Polymers and Other Materials

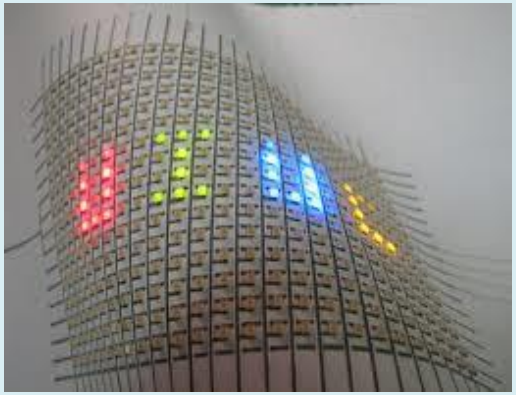


Chemistry of display devices specific to OLEDs

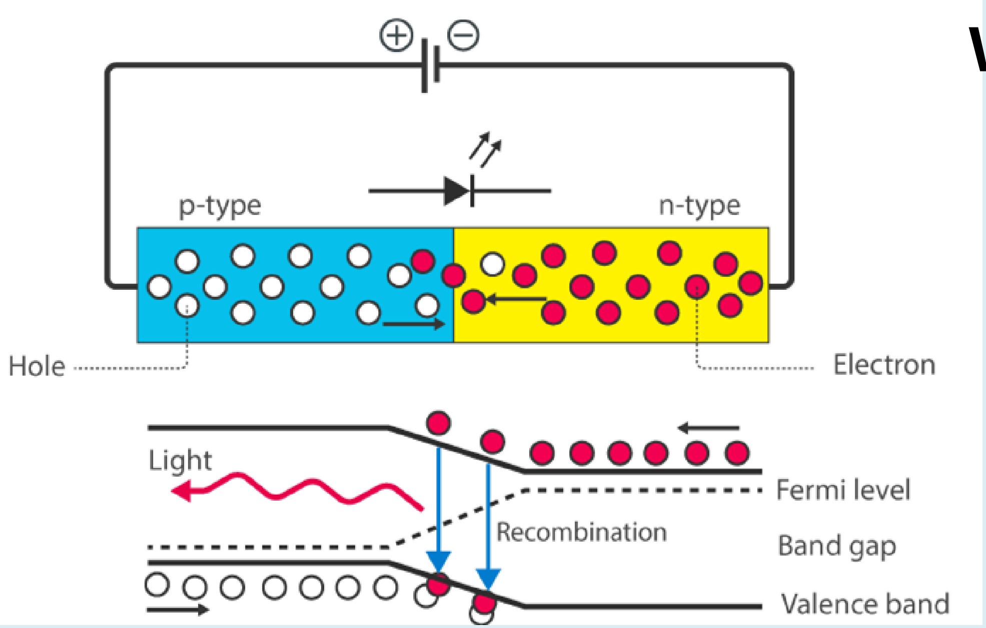
An organic light-emitting diode (OLED or organic LED), also known as organic electroluminescent (organic EL) diode, is a light-emitting diode (LED) in which the emissive electroluminescent (EL) layer is a film of organic compound that emits light in response to an electric current.

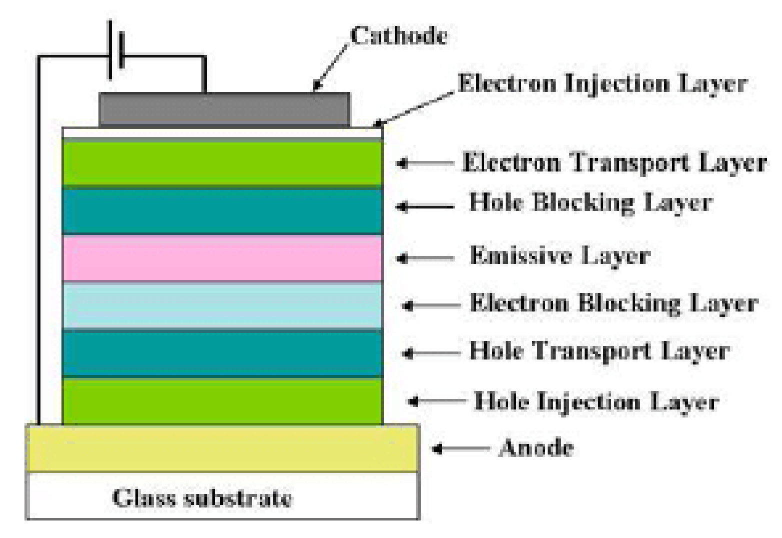






Working principle of OLEDs

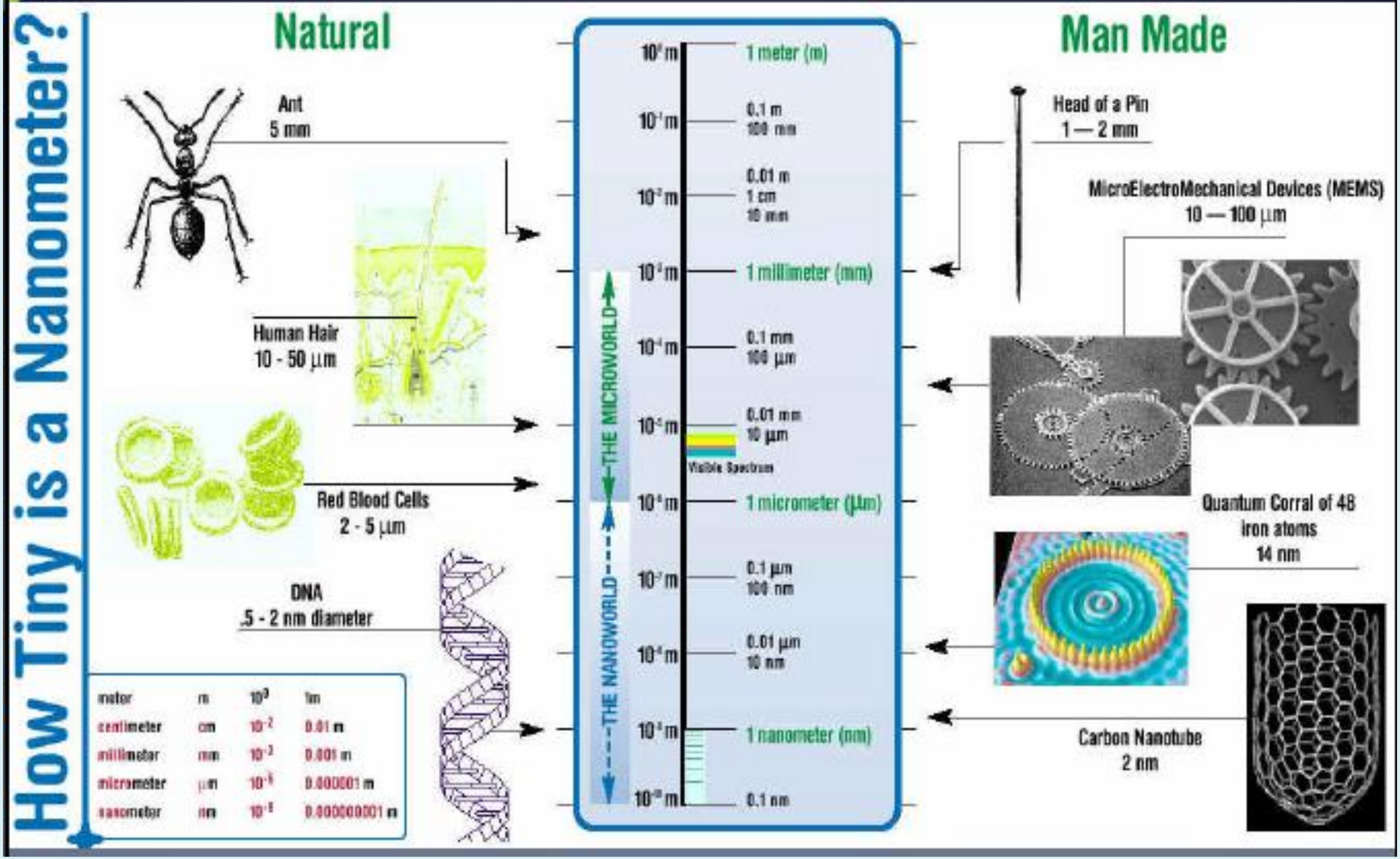




- The holes lie in the valence band, while the free electrons are in the conduction band of material.
- When there is a forward bias in the p-n junction, the electron which is a part of the n-type semiconductor material would overrun the p-n junction and join with the holes in the p-type semiconductor material. Therefore, regarding the holes, the free electrons would be at the higher energy bands.
- When this movement of free electron and hole takes place, there is a change in the energy level as the voltage drops from the conduction band to the valance band.
- There is a release of energy due to the motion of the electron.
- In standard diodes, the release of energy in the manner of heat. But in LED the release of energy in the form of photons would emit light energy.
- This entire process is known as electroluminescence, and the diodes are known as a light-emitting diode.

What is Nano?

Greek = Dwarf



meter	m	10^0	1m
centimeter	cm	10^{-2}	0.01 m
millimeter	mm	10^{-3}	0.001 m
micrometer	µm	10^{-6}	0.000001 m
nanometer	nm	10^{-9}	0.000000001 m

§ Introduction to Nanomaterials

- A nanoparticle is an entity with a width of a few nanometers to a few hundred, containing tens to thousands of atoms. Their defining characteristic is a very small feature size in the range of 1-100 (nm).

- **Nano size:**

One nanometre is a millionth part of the size of the tip of a needle.

1 nm = 10^{-6} mm = 10^{-9} m

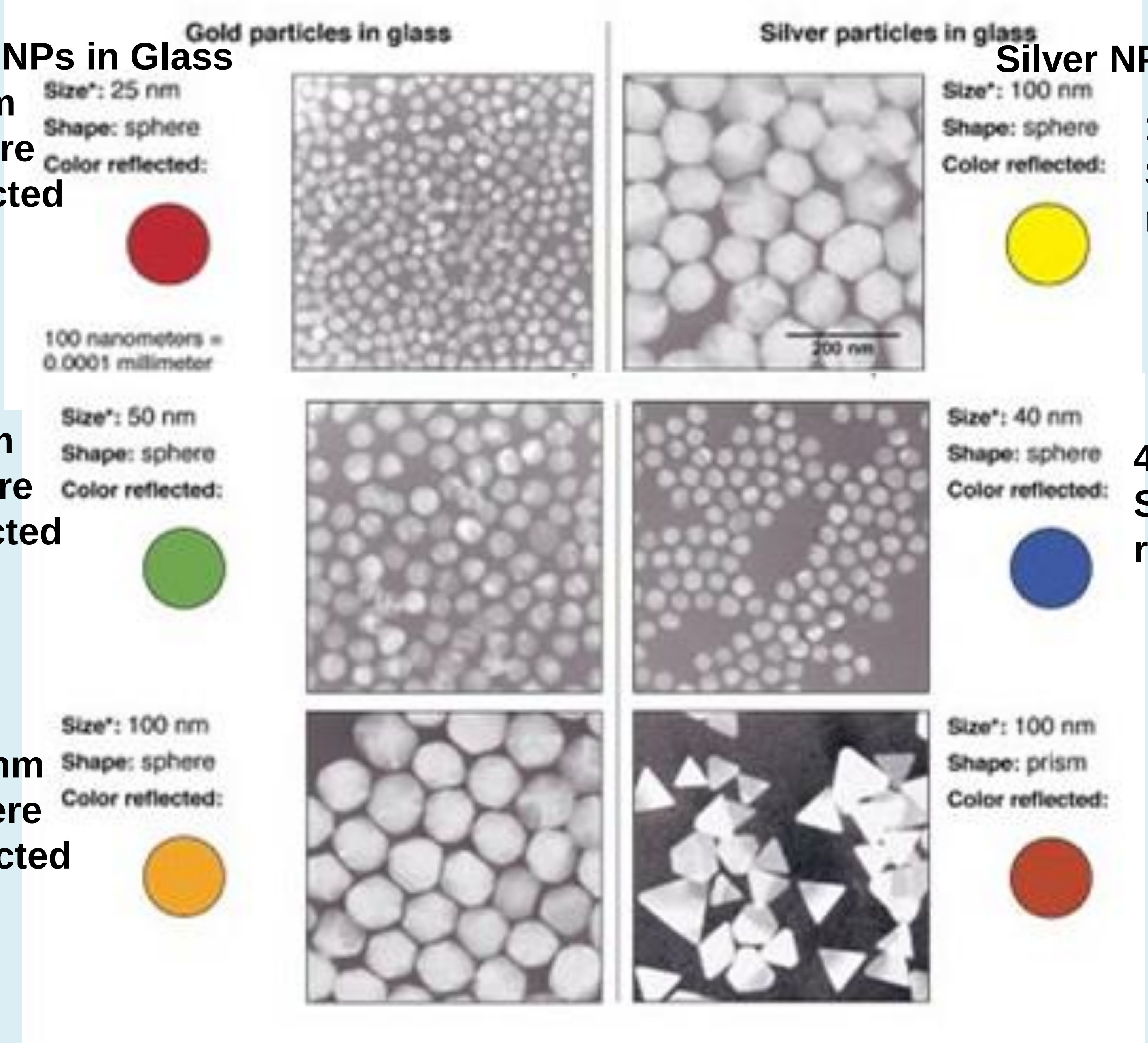
Table 1. Some examples of size from macro to molecular

Size (nm)	**Examples**	**Terminology**
0.1-0.5	Individual chemical bonds	Molecular/atomic
0.5-1.0	Small molecules, pores in zeolites	Molecular
1-1000	Proteins, DNA, inorganic nanoparticles	Nano
10^3-10^4	living cells, human hair	Micro
>10^4	Normal bulk matter	Macro

Bulk Gold

From: USDA's roadmap of nanotechnology.

Size and shape dependent colors of Au and Ag nanoparticles



Gold NPs in Glass

25 nm
Sphere
reflected

50 nm
Sphere
reflected

100 nm
Sphere
reflected

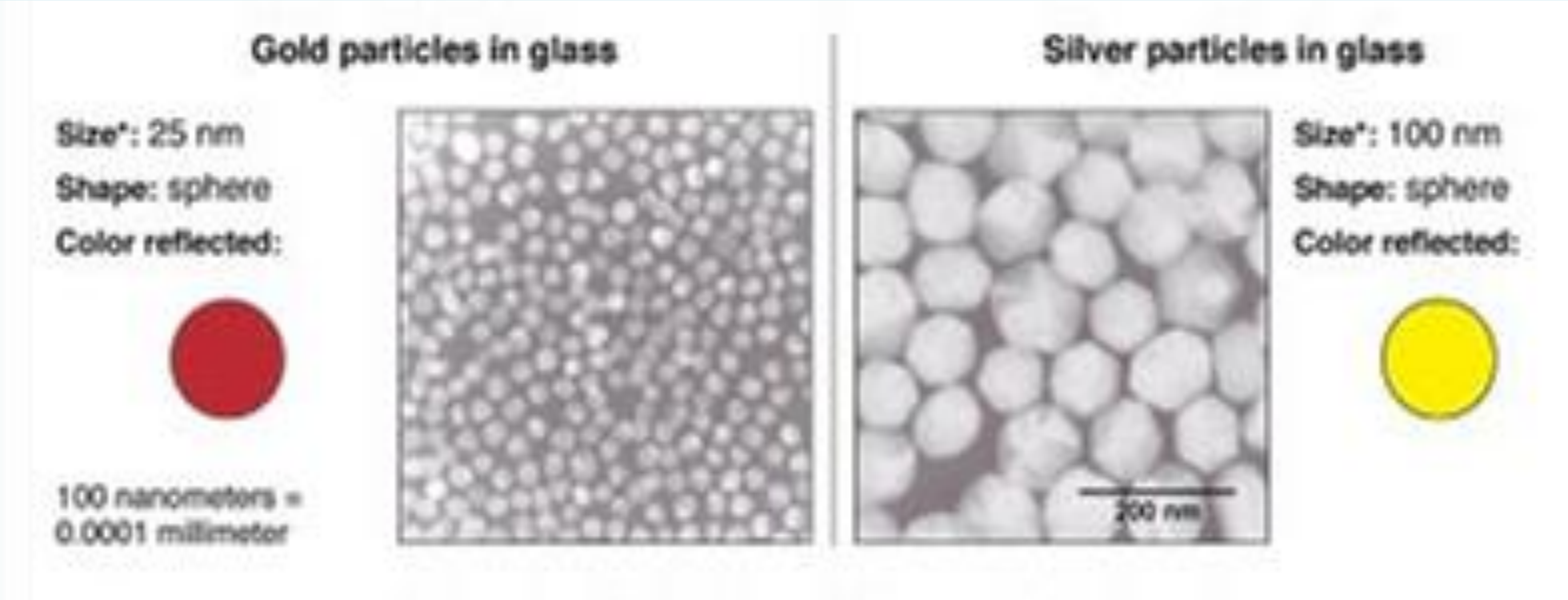
Silver NPs in Glass

100 nm
Sphere
reflected

40 nm
Sphere
reflected

100 nm
prism
reflected

Size and shape dependent colors of Au and Ag nanoparticles



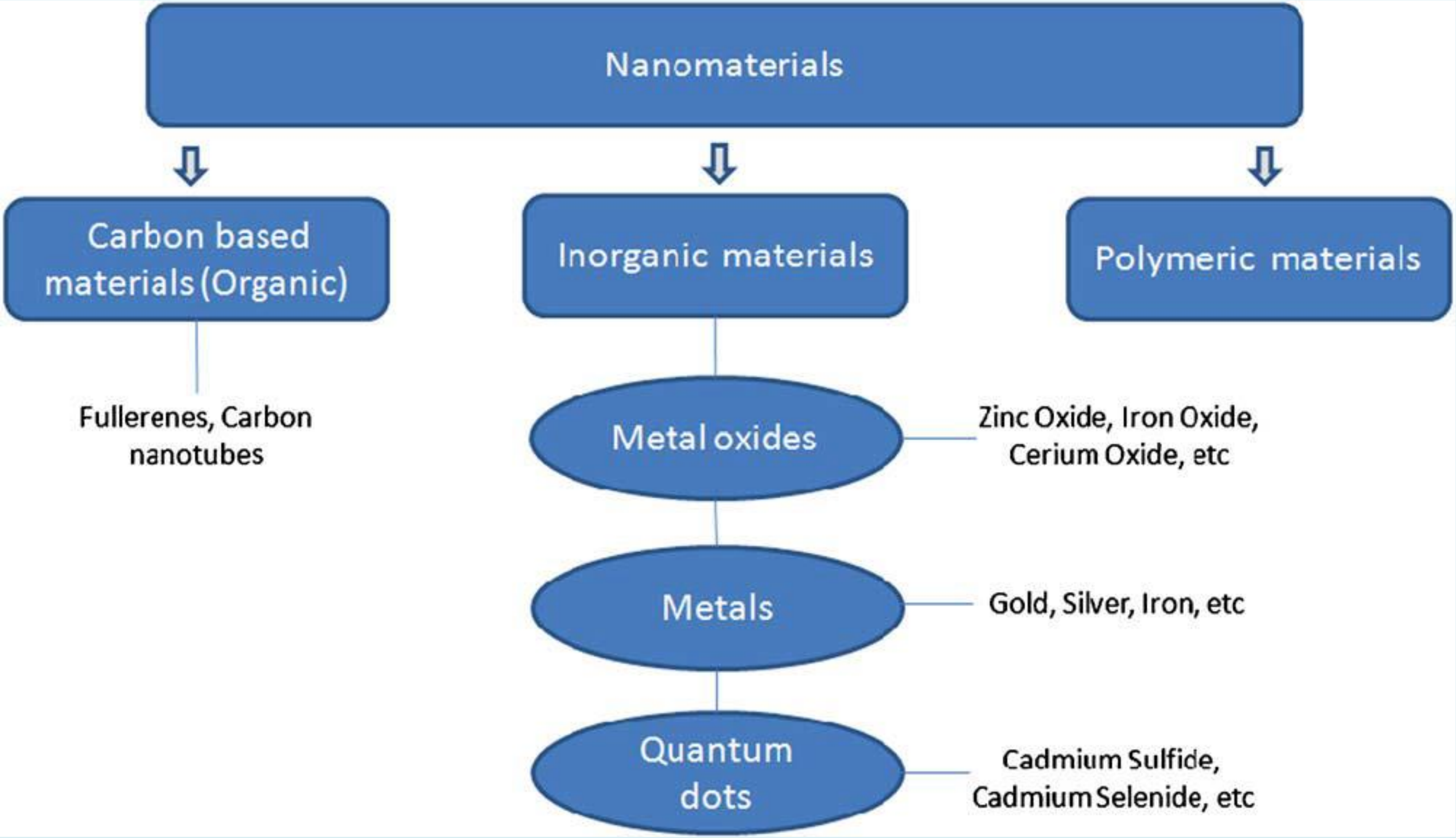
Note: **nanomaterials scatter visible light rather than absorb**

- **Distance between particles also effects colour**

Surface plasmon resonance: Excitation of surface plasmons by light (visible or infra red) is denoted as a surface plasmon resonance

Localized surface plasmon resonance (LSPR) for nanometer-sized metallic structures

Categories of Nanomaterials



Nanomaterials

Carbon based materials (Organic)

Fullerenes, Carbon nanotubes

Inorganic materials

Metal oxides

Zinc Oxide, Iron Oxide, Cerium Oxide, etc

Metals

Gold, Silver, Iron, etc

Quantum dots

Cadmium Sulfide, Cadmium Selenide, etc

Polymeric materials

Properties of Semiconductor Nanomaterials

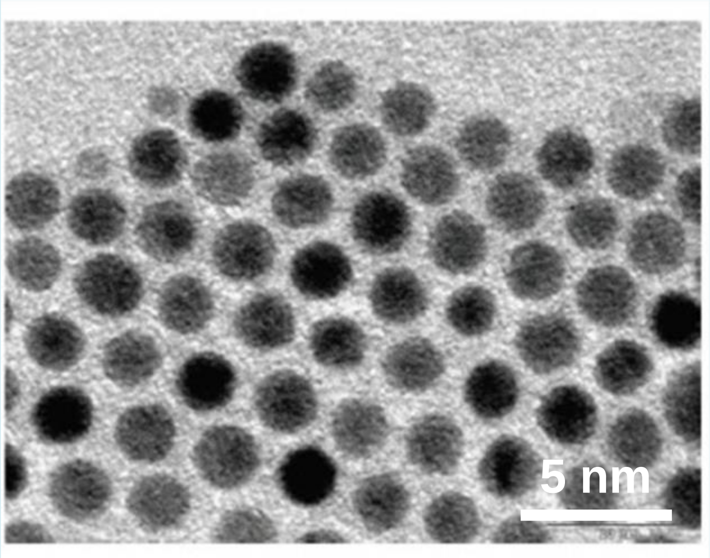
- The properties of nanosized semiconductor particles depend very sensitively on the particle size .
- The physical properties of semiconductor nanocrystals are dominated by the spatial confinement of excitations (electronic and vibrational).
- Quantum confinement that manifests itself in widening of HOMO-LUMO gap or the bandgap increase with decreasing crystallite size and its implications on the electronic structure and photophysics of the crystallites has generated considerable interest.

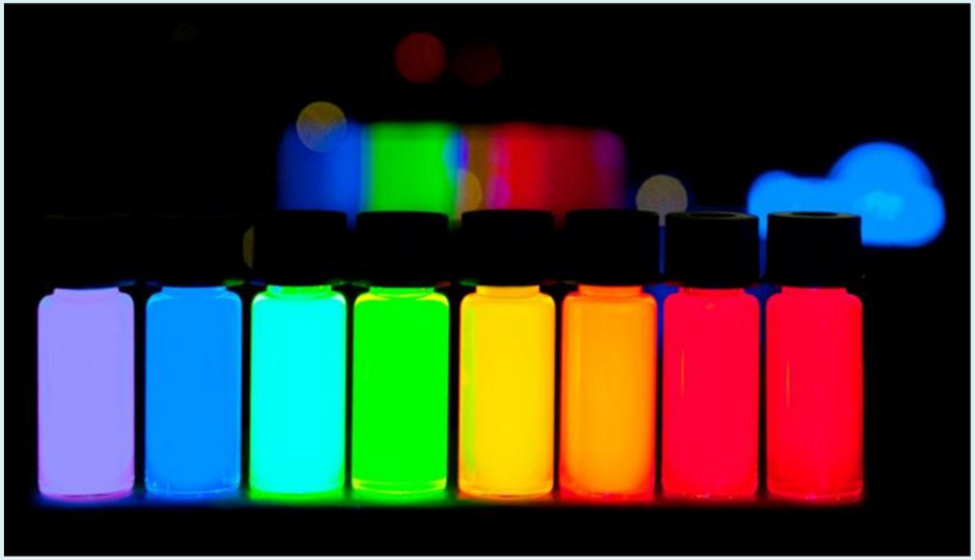
Quantum Confinement

- In the nanoparticles with **some of its dimensions smaller than 10nm**, show new effects, since the laws of classical physics no longer valid and we need quantum physics to explain them.
- For example, the **minimum potential energy** of an electron confined in a nanoparticle is higher than expected in classical physics and energy levels of different electronic states are **discrete**.
- Due to **quantum confinement**, the particle size has a drastic effect on the **density of electronic states** and thus on the **optical response**

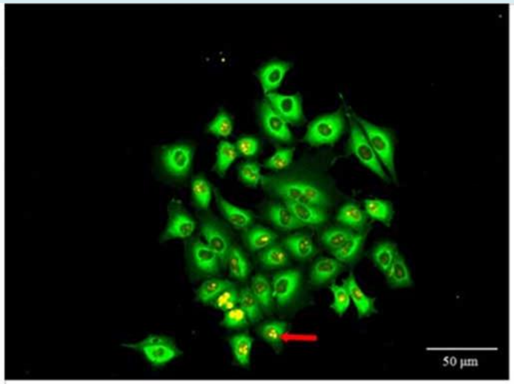
Quantum Dots and applications

Quantum dots (QDs) are semiconductor particles of few nanometers (<10 nm) in size, having optical and electronic properties that differ from larger particles.

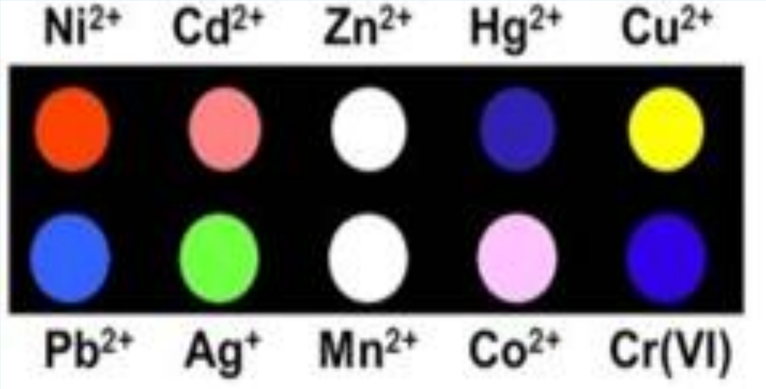




Cancer cell imaging

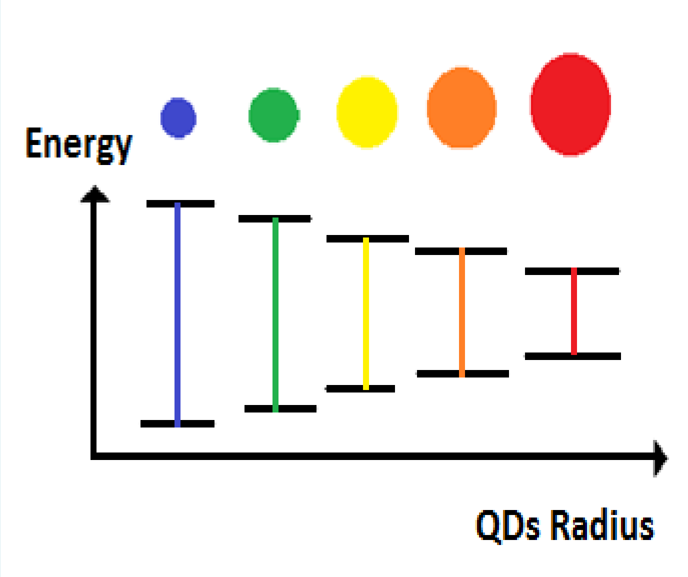


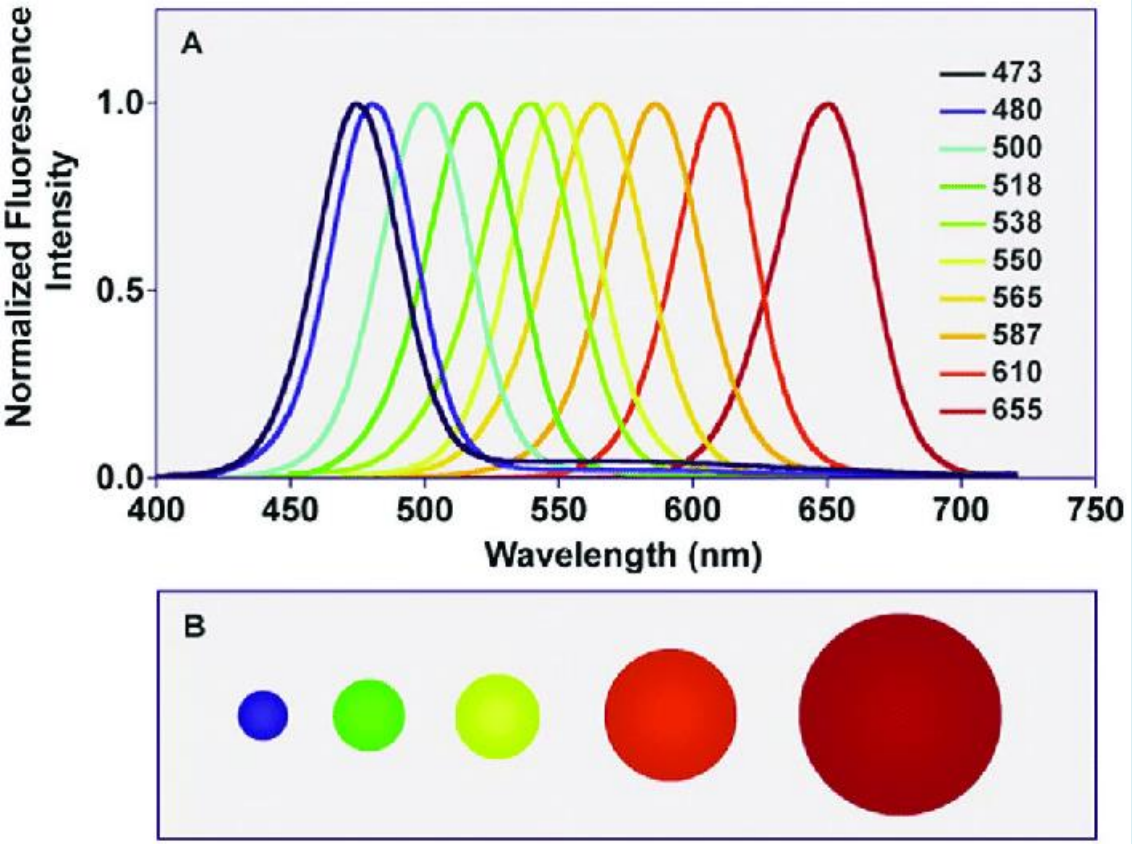
Metal ions sensing



Light emitting diode

Emission properties of Quantum Dots

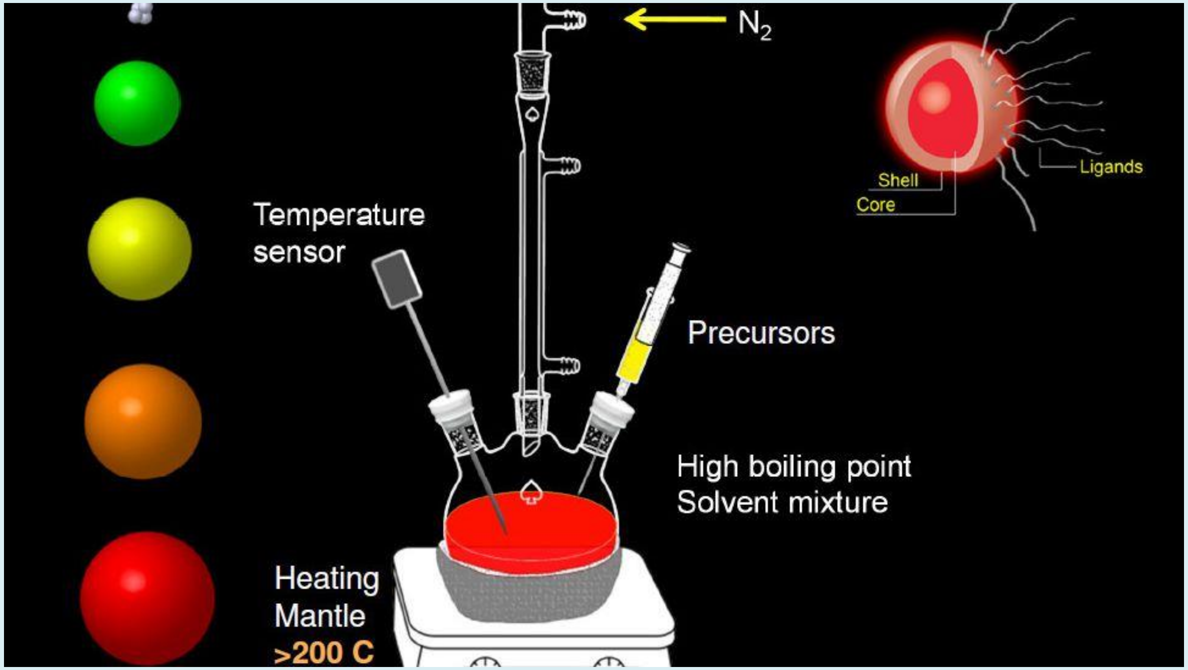




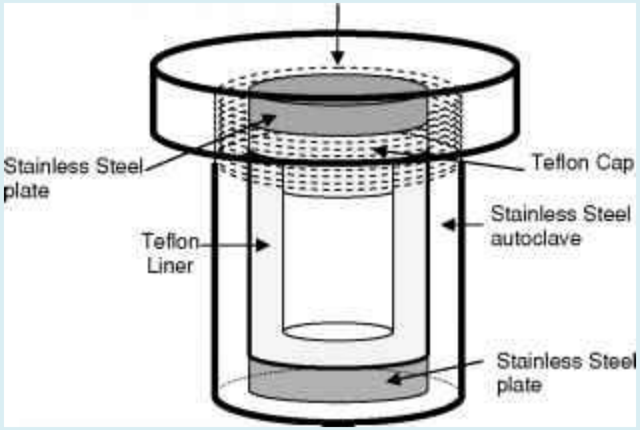
1. Band gap decreases as the QDs size increases
2. Emission wavelength becomes red shifted with increase in size of QDs

Synthetic Procedures of Quantum Dots

1. High temperature synthesis



2. Hydrothermal synthesis



3. Microwave synthesis

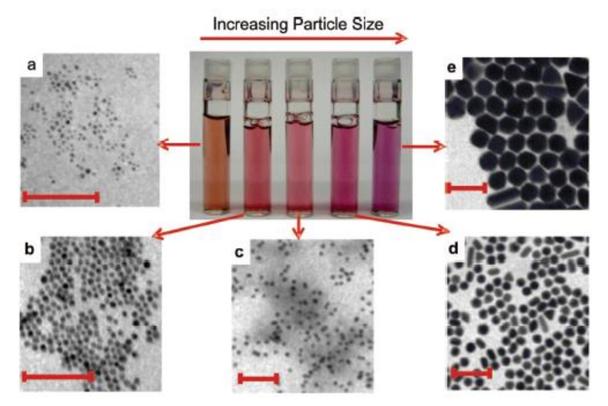
4. Ultrasonication synthesis

- **Nanomaterials show unusual**
  - **Mechanical**
  - **Electrical**
  - **Optical**
  - **Magnetic properties.**

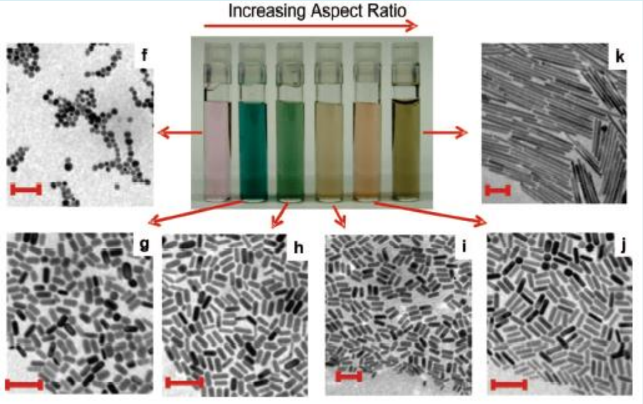
Hence it has potential applications in

- **Different industries**
- **Biomedical**
- **Electronic applications.**
- **For example, long lasting medical implants of biocompatible nanostructured ceramic and carbides,**
- **Biocompatible coating**
- **Drug delivery**
- **Protection coatings**
- **Composite materials**
- **Anti fogging coatings for spectacles and car windows etc.**

- At the nanomaterial level, some material properties are affected by the laws of atomic physics, rather than behaving as traditional bulk materials.
- Nanomaterials can be metals, ceramics, polymeric materials, or composite materials.
- The beautiful ruby red color of some glass is due to gold nanoparticles (Au NPs) trapped in the glass matrix.
- The decorative glaze known as luster, found on some medieval pottery, contains metallic spherical nanoparticles dispersed in a complex way in the glaze.



Spherical AuNPs



Rod shaped nano Au

What makes these nanomaterials so different and so intriguing?

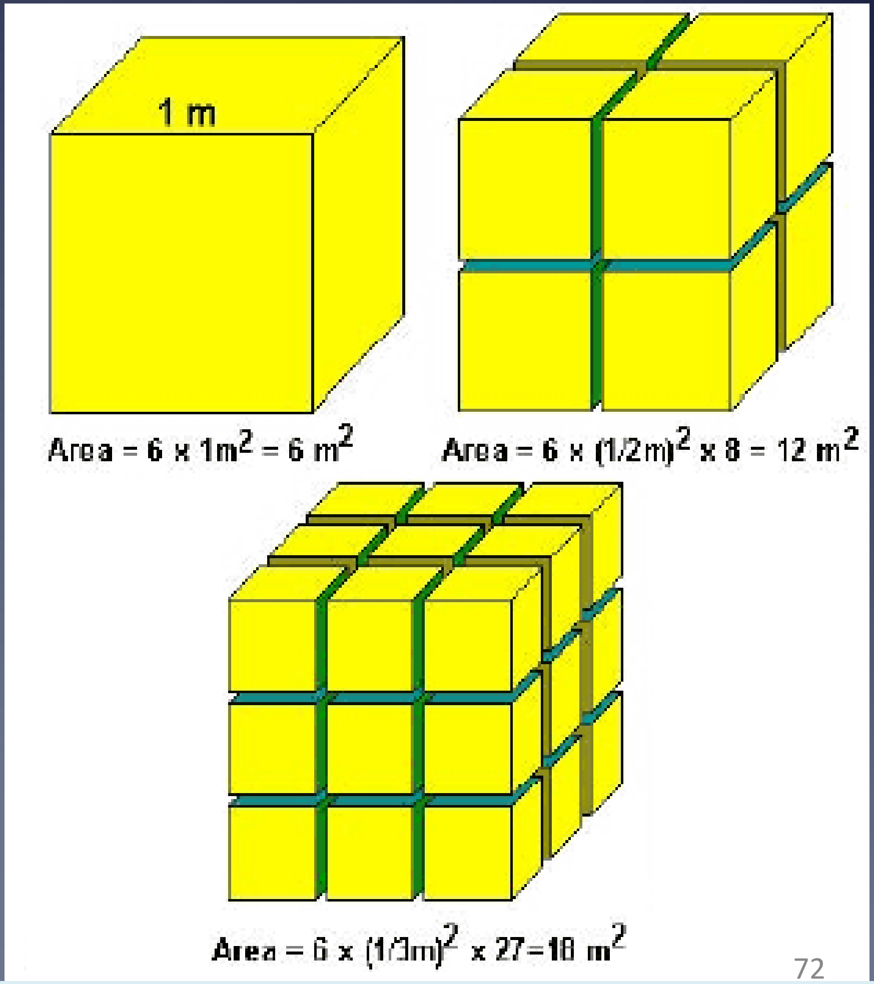
- Deviation from the reduced size and dimensionality of the nanometer-sized building blocks (crystallites), the numerous **interfaces between adjacent crystallites, grain boundaries and surfaces**
- These building blocks have different crystallographic orientation that may lead to **incoherent or coherent interfaces between them**
- Lead to **inherent heterogeneous structure** on a nanometer scale.
- Grain boundaries make up a major portion of the material at nanoscales, and strongly affect properties and processing.
- Surfaces and interfaces- half or more than half atoms near to interfaces
- Hence, surface properties such as **energy levels**, **electronic structure**, and **reactivity** are different from bulk materials

Gold : Bulk vs. Nano

	Bulk Gold	Nano Gold
1	Lustrous–they have a shiny surface when polished	Are never gold in colour but found in a range of colours
2	Malleable–they can be hammered, bent or rolled into any desired shape	Size & Shape of the nanoparticles determines the colour
3	Ductile–they can be drawn out into wires 	For example, Gold particles in glass 25 nm > red reflected 50 nm > green reflected 100 nm > orange reflected
4	Is metallic, with a yellow colour when in a mass	Are not "metals" but are semiconductors (Band gap energy = 3.4 eV)
5	Good conductors of heat and electricity	Are very good catalysts
6	Generally have high densities	
7	Have high melting point (~1080^{o}C)	Melts at relatively low temp (~940º C)
8	Are often hard and tough with high tensile strength	
9	Having high resistance to the stresses of being stretched or drawn out	
10	Not easily breakable	
11	Inert-unaffected by air & most reagents	

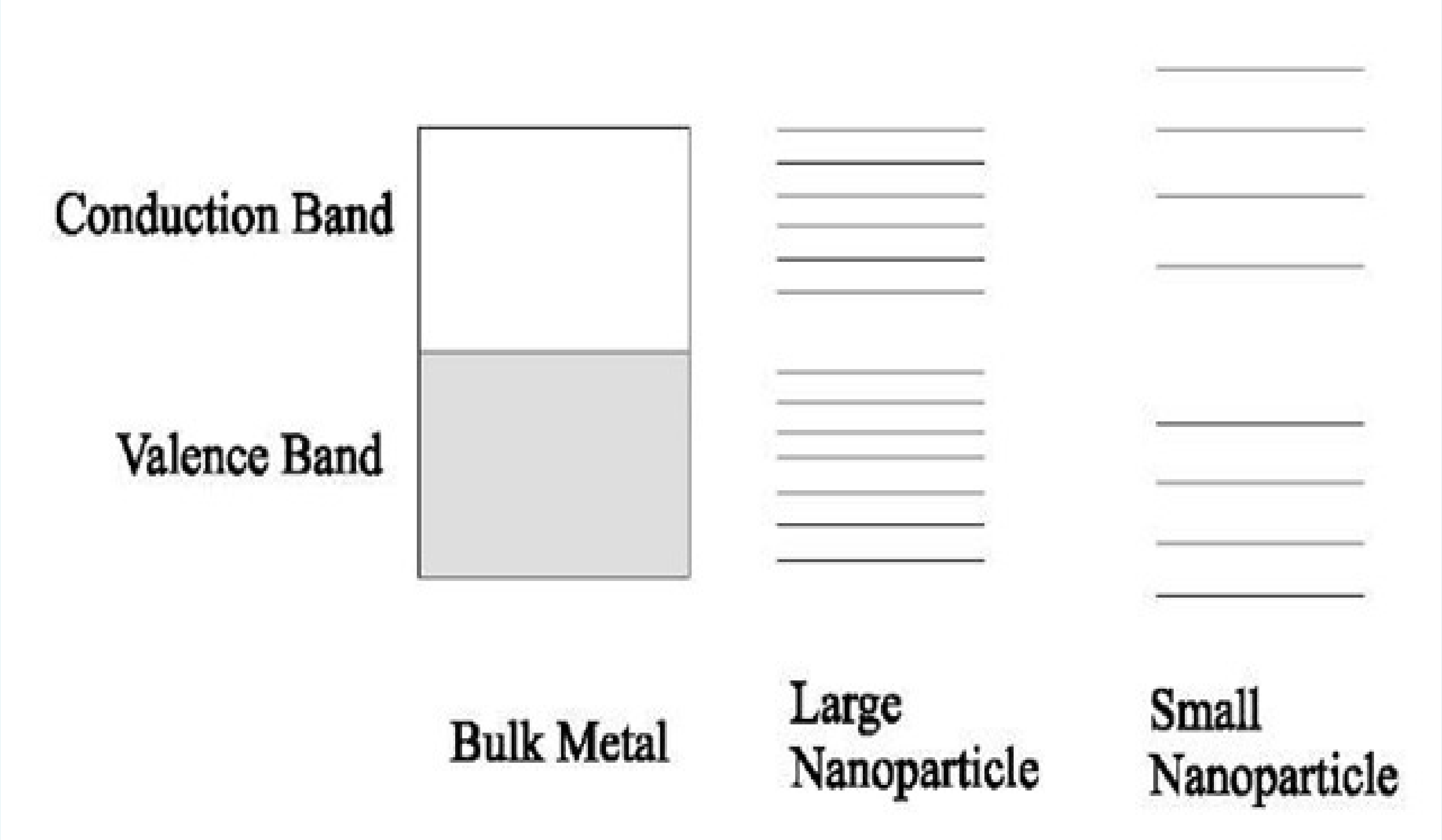
Surface Area to Volume Ratio Increases

- **As surface area to volume ratio increases**
    - A greater amount of a substance comes in contact with surrounding material
    - This results in better catalysts, since a greater proportion of the material is exposed for potential reaction

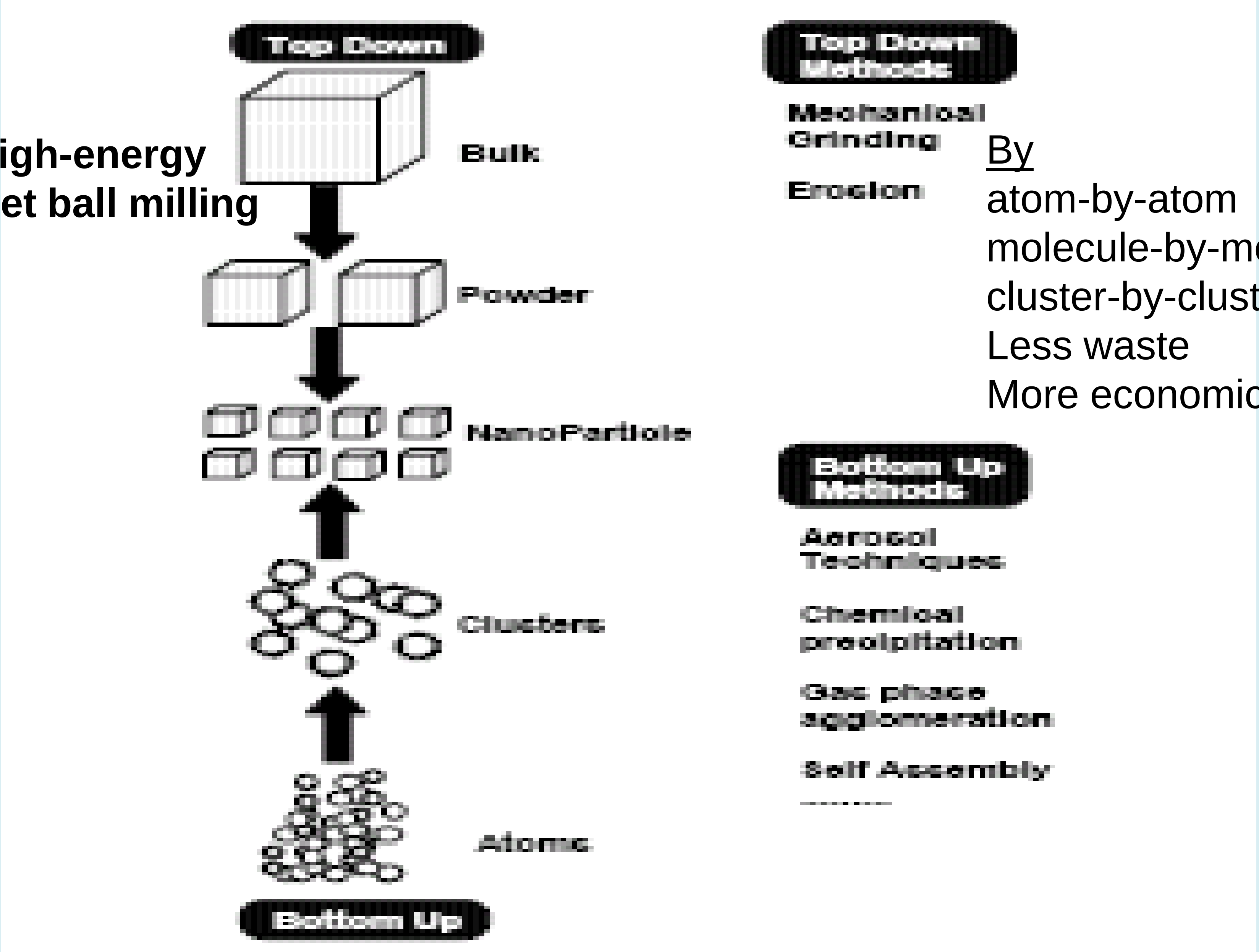


BAND GAP IN NANO AND BULK MATERIALS

- Band Gap



Schematic representation of the ‘bottom up’ and top down’ synthesis processes of nanomaterials



High-energy wet ball milling

By
atom-by-atom
molecule-by-molecule
cluster-by-cluster
Less waste
More economical

Any fabrication technique should provide the followings:

- Identical size of all particles (also called mono sized or with uniform size distribution
- Identical shape or morphology
- Identical chemical composition and crystal structure
- Individually dispersed or mono dispersed i.e., no agglomeration

Nanoparticles preparation:

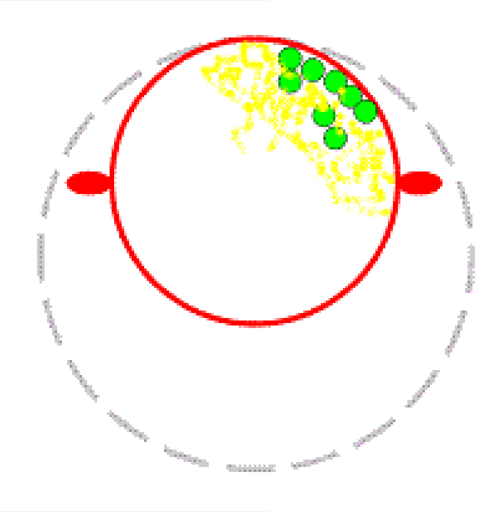
❖ **Top-down approaches**

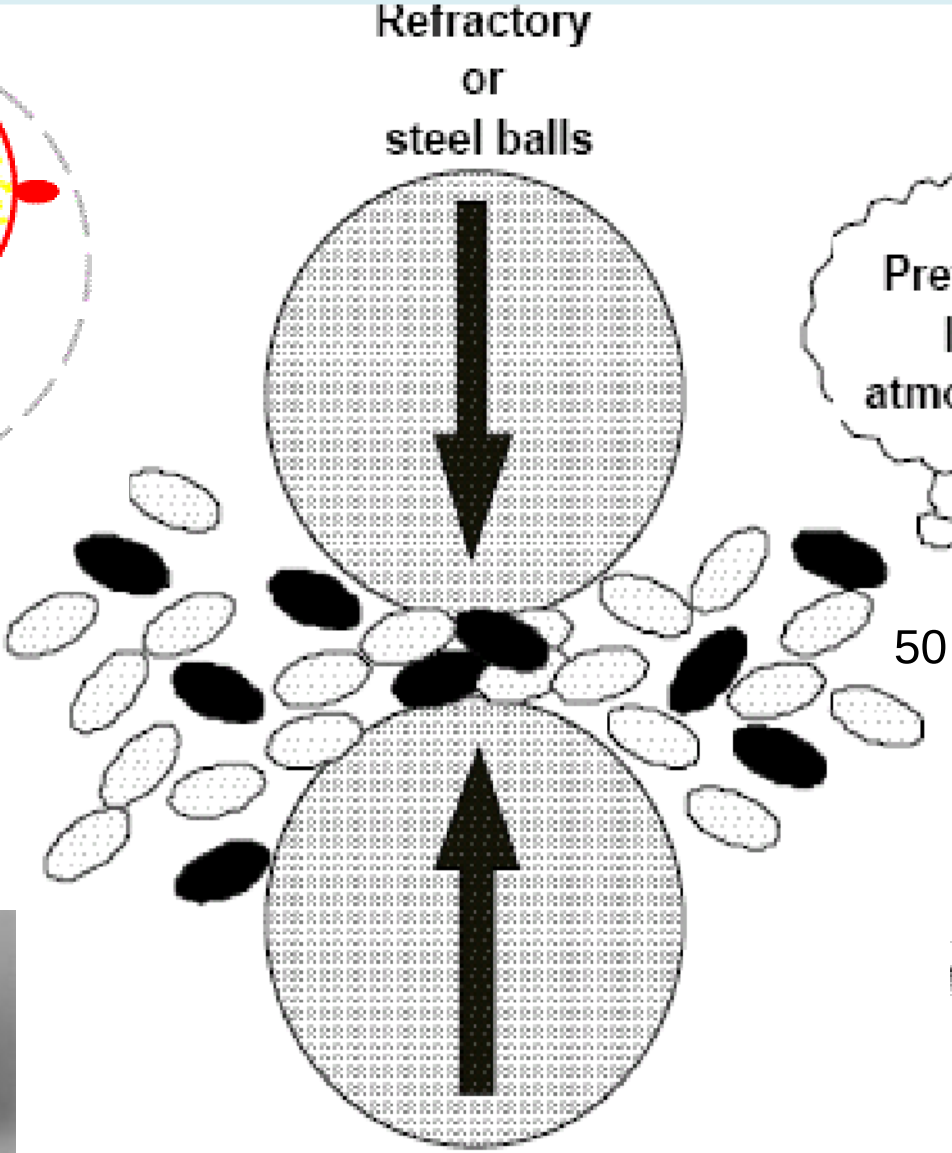
- High-energy ball milling/Machining
- Chemical Oxidation Process (CNTs to QDs)
- Electrochemical Oxidation Process (Graphite rod to QDs)
- Lithography (photo- and electrochemical)
- Etching/Cutting
- Coating
- Atomization

❖ **Bottom-up approaches**

- Gas Condensation Processing (GCP)/Aerosol Based Processes
- Chemical Vapour Condensation (CVC)
- Atomic or Molecular Condensation
- Laser ablation
- Supercritical Fluid Synthesis
- Wet Chemical Synthesis of nanomaterials (Sol-gel process)
- Precipitation method
- Spinning
- Self-Assembly
- DNA Origami

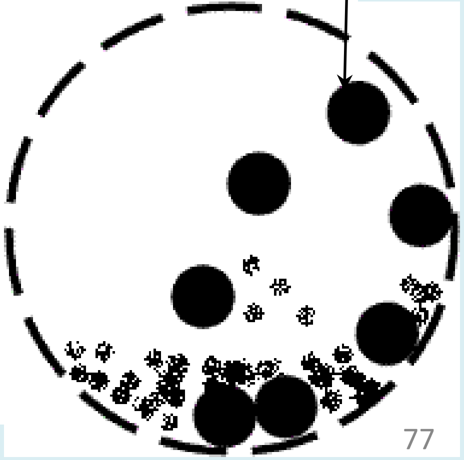
Schematic representation of the principle of mechanical milling





50 µm powder

WC coated ball



Mineral, ceramic processing, and powder metallurgy industry

❖ Procedure of milling process

- Particle size reduction, solid-state alloying, mixing or blending, and particle shape changes
- Restricted to relatively hard, brittle materials which fracture and/or deform and cold weld during the milling operation
- To produce nonequilibrium structures including nanocrystalline, amorphous and quasicrystalline materials
- Users are tumbler mills, attrition mills, shaker mills, vibratory mills, planetary mills etc
- Powders diameters of about **50 µm** with a number of hardened steel or tungsten carbide (WC) coated balls in a sealed container which is shaken or violently agitated. The most effective ratio for the ball to powder mass is 5 : 10.

- Shaker mills (e.g. SPEX model 8000) uses small batches of powder (approximately 10 cm^3 is sufficient

❖ **Advantage**: **High production rates**

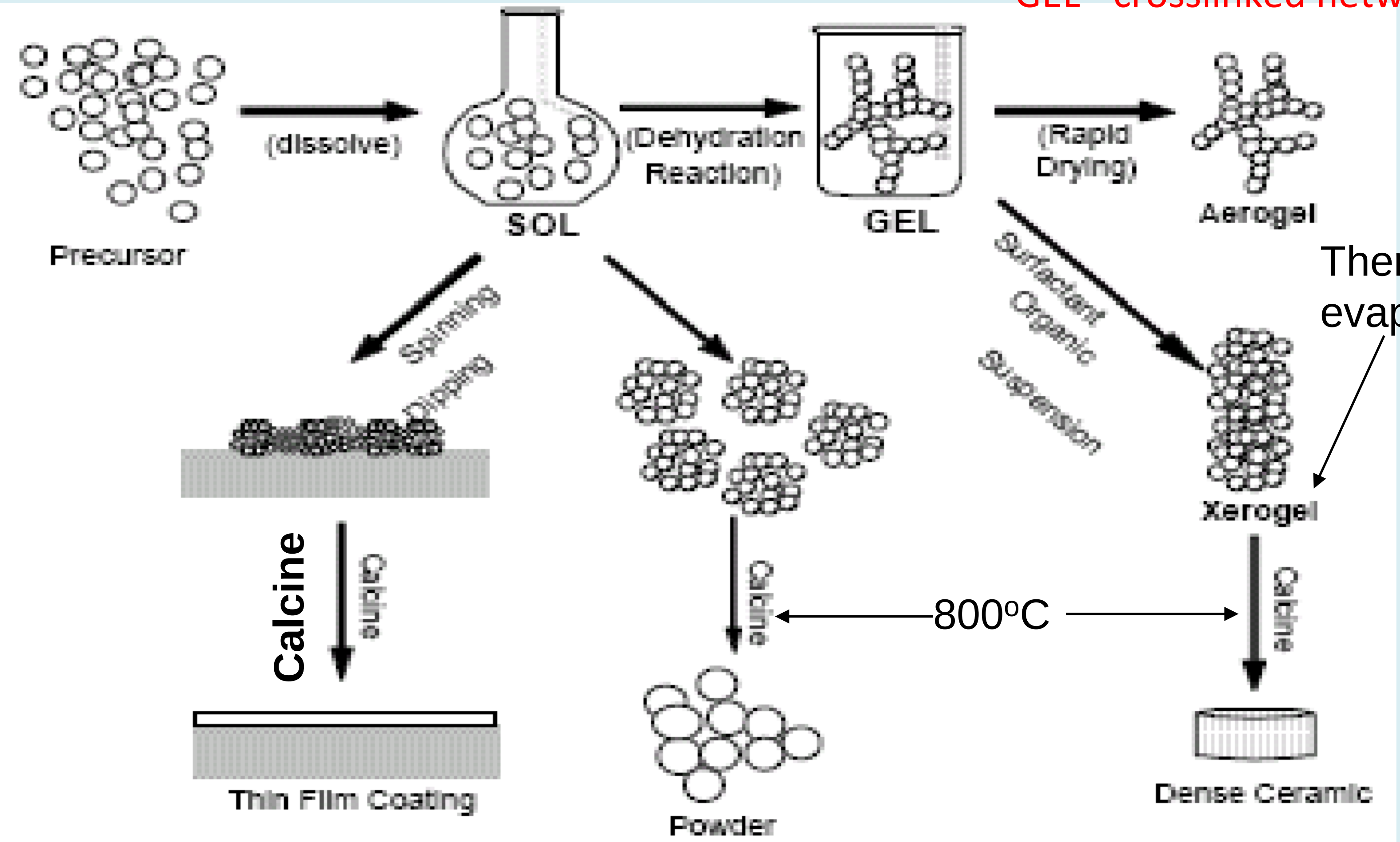
❖ **Limitation**

- ➢ Severe plastic deformation associated with mechanical attrition due to generation of high temp in the interphase, 100 to 200 ^oC.
- ➢ Difficulty in broken down to the required particle size
- ➢ Contamination by the milling tools (**Fe**) and atmosphere (trace elements of **O_2, N_2 in rare gases**) can be a problem (inert condition necessary like **Glove Box**)(Fe <1-2% and Trace elements<300 ppm)
- ➢ Protective coating to reduce milling tools contamination (MTC) increases cost of the process
- ➢ Working duration (>30 h) increases MTC (>10%)

Wet Chemical Synthesis of nanomaterials (Sol-gel process)

SOL - nanoparticle dispersion

GEL - crosslinked network



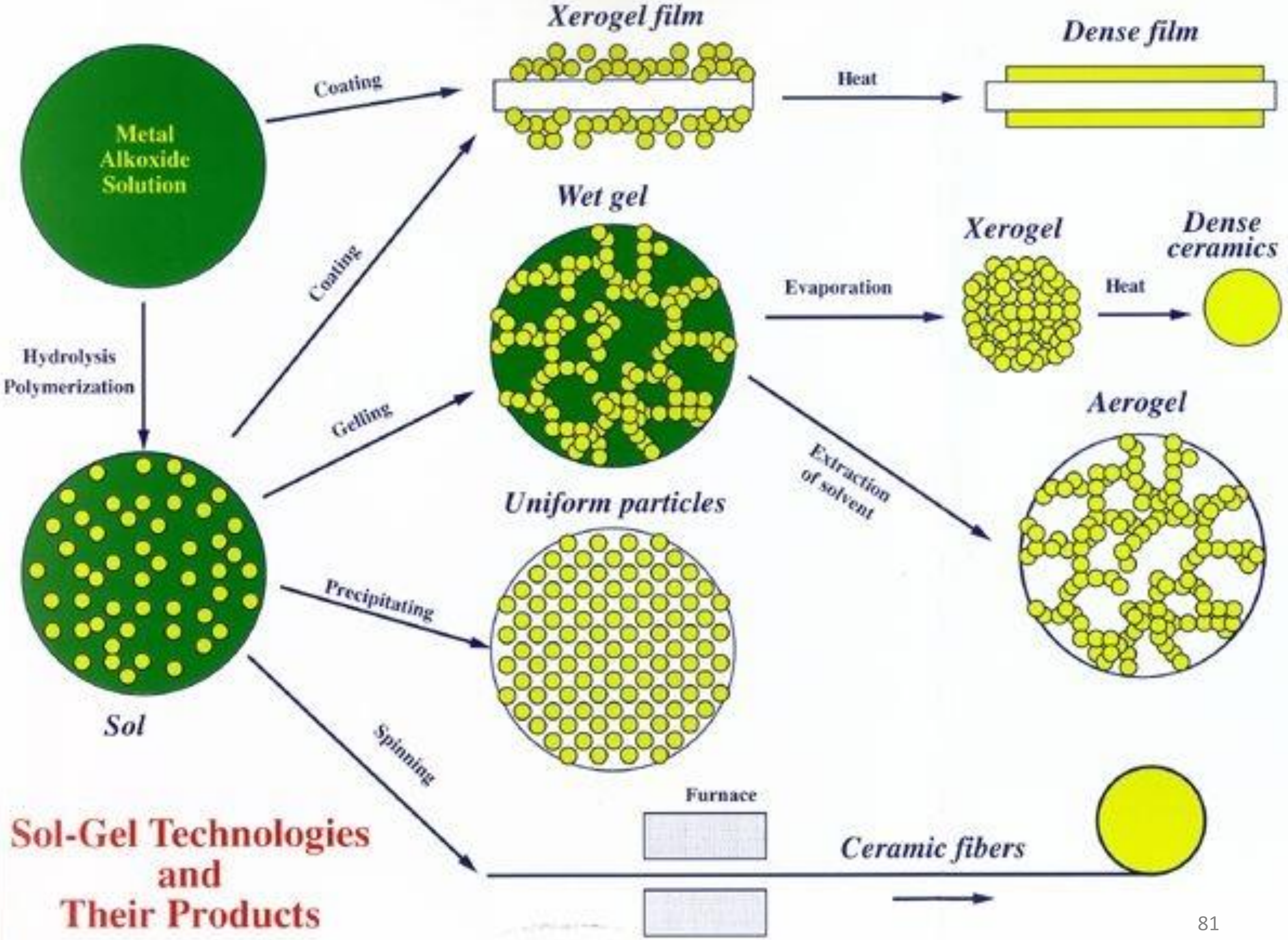
Thermal evaporation

Calcine

800°C

Schematic representation of sol-gel process of synthesis of nanomaterials.

Sol-Gel Technologies and Their Products



Sol-Gel Processing

- Creation of Sol (solid particles in solution)
- Followed by the following two generic sol-gel processes (assuming as a precursor a metal alkoxide MOR):

hydrolysis: $-\mathrm{MOR} + \mathrm{H2O} \rightarrow -\mathrm{MOH} + \mathrm{ROH}$

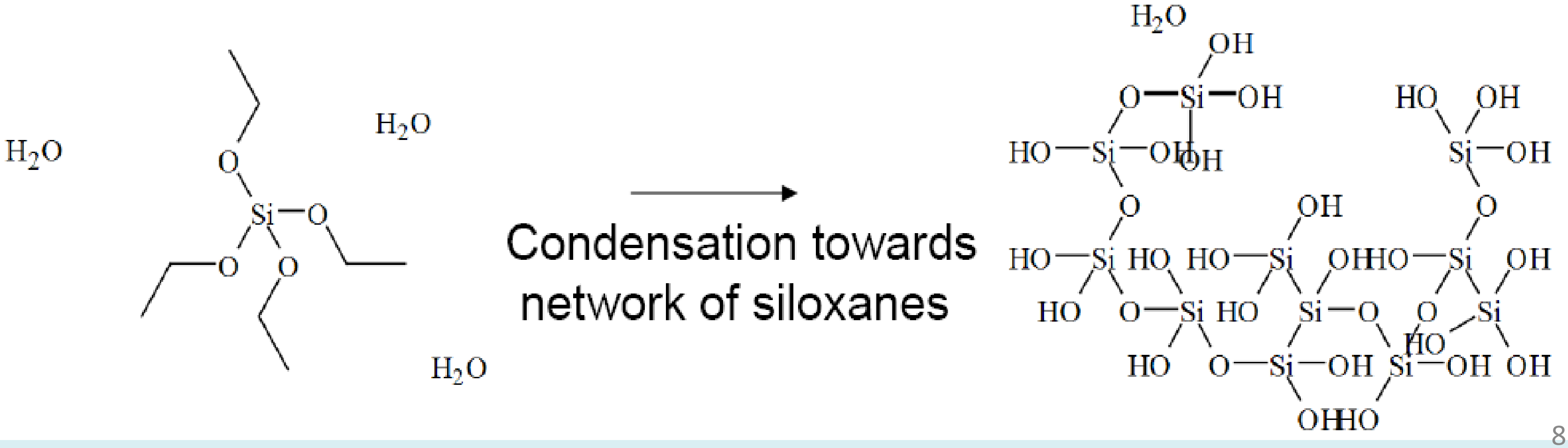
Ex.: $\mathrm{Si(OR)_4} + 4\,\mathrm{H_2O} \rightarrow \mathrm{Si(OH)_4} + 4\,\mathrm{R\text{-}OH}$

condensation: $-\mathrm{MOH} + \mathrm{ROM}- \rightarrow -\mathrm{MOM}- + \mathrm{ROH}$

$\mathrm{(OR)_3\text{–}Si\text{-}OH} + \mathrm{HO\text{–}Si\text{-}(OR)_3} \rightarrow [\mathrm{(OR)_3Si\text{–}O\text{–}Si(OR)_3}] + \mathrm{H\text{-}O\text{-}H}$

or $-\mathrm{MOH} + \mathrm{HOM}- \rightarrow -\mathrm{MOM}- + \mathrm{H2O}$

$\mathrm{(OR)3\text{–}Si\text{-}OR} + \mathrm{HO\text{–}Si\text{-}(OR)3} \rightarrow [\mathrm{(OR)3Si\text{–}O\text{–}Si(OR)3}] + \mathrm{R\text{-}OH}$



Condensation towards network of siloxanes

- **Overall Steps:**
- **Step 1:** Formation of different stable solutions of the alkoxide (the sol).
- **Step 2:** Gelation resulting from the formation of an oxide- or alcohol-bridged network (the gel) by a polycondensation or polyesterification reaction
- **Step 3:** Aging of the gel, during which the polycondensation reactions continue until the gel transforms into a solid mass, accompanied by contraction of the gel network and expulsion of solvent from gel pores.
- **Step 4:** Drying of the gel, when water and other volatile liquids are removed from the gel network.
  - **If isolated by thermal evaporation, the resulting monolith is termed a *xerogel*.**
  - **If the solvent (such as water) is extracted under supercritical or near super critical conditions, the product is an *aerogel*.**
- **Step 5:** Dehydration, during which surface- bound M-OH groups are removed, thereby stabilizing the gel against **rehydration**. This is normally achieved by calcining the monolith at temperatures up to 800^0C.
- **Step 6:** Densification and decomposition of the gels at high temperatures ($T>800^0$C). The pores of the gel network are collapsed, and remaining organic species are volatilized. The typical steps that are involved in sol-gel processing are shown in the schematic diagram above.

- Sol/gel transition controls the particle size and shape. Calcination of the gel produces the product (eg. Oxide).
- Sol-gel processing > hydrolysis and condensation of alkoxide-based precursors such as $\mathrm{Si(OEt)_4}$ (tetraethyl orthosilicate, or TEOS).
- The reactions are as follows:

$\mathrm{MOR + H_2O \rightarrow MOH + ROH}$ (hydrolysis)

$\mathrm{MOH+ROM \rightarrow M\text{-}O\text{-}M+ROH}$ (condensation)

- If the aging process of gels exceeds 7 days it is critical to prevent the cracks in gels that have been cast
- Steps are:

Sol → Gel → Ageing → Drying → Dehydration → Densification & Decomposition → Product

Advantages

- Synthesizing nonmetallic inorganic materials like glasses, glass ceramics or ceramic materials at very low temperatures compared to melting glass or firing ceramics
- Monosized nanoparticles possible by this bottom up approach.

Disadvantages

- Controlling the growth of the particles and then stopping the newly formed particles from agglomerating.
- Difficult to ensure complete reaction so that no unwanted reactant is left on the product
- Completely removal of any growth aids
- Also production rates of nanopowders are very slow by this process