

Module-2

Atomic Structures, Interatomic Bonding and Structure of Crystalline Solids

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- 1) Atomic Structure and Atomic bonding in solids
- 2) Crystal structures, Crystalline and Non-crystalline materials
- 3) Miller indices, Anisotropic elasticity and Elastic behavior of Composites
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Atomic structure

- Every atom consists of a small nucleus composed of protons and neutrons, which is encircled by moving electrons in their *orbitals*, specific energy levels.
- The top most orbital electrons, valence electrons, affect most material properties that are of interest to engineer. **E.g.:** chemical properties, nature of bonding, size of atom, optical/magnetic/electrical properties.
- Electrons and protons are negative and positive charges of the same magnitude being 1.60×10^{-19} coulombs.
- Neutrons are electrically neutral.
- Protons and neutrons have approximately the mass, 1.67×10^{-27} kg, which is larger than that of an electron, 9.11×10^{-31} kg.

Atomic structure (contd...)

- Atomic number (Z) - is the number of protons per atoms.
- Atomic mass (A) - is the sum of the masses of protons and neutrons within the nucleus.
- Atomic mass is measured in atomic mass unit (amu) where $1\text{amu} = \frac{1}{12}$ the mass of most common isotope of carbon atom, measured in grams.
- $A \cong Z + N$, where N is number of neutrons.
- **Isotopes** - atoms with same atomic number but different atomic masses.
- A mole is the amount of matter that has a mass in grams equal to the atomic mass in amu of the atoms. Thus a mole of carbon has a mass of 12 grams.

Atomic structure (contd...)

- The number of atoms or molecules in a mole of substance is called the Avogadro's number, N_{ay} . $N_{ay} = 1 \text{ gram} / 1 \text{ amu} = 6.023 \times 10^{23}$.

E.g.: Calculating the number of atoms per cm^3 , n , in a piece of material of density δ (g/cm^3)

$$n = N_{av} \delta / M, \quad \text{where } M \text{ is the atomic mass in } amu.$$

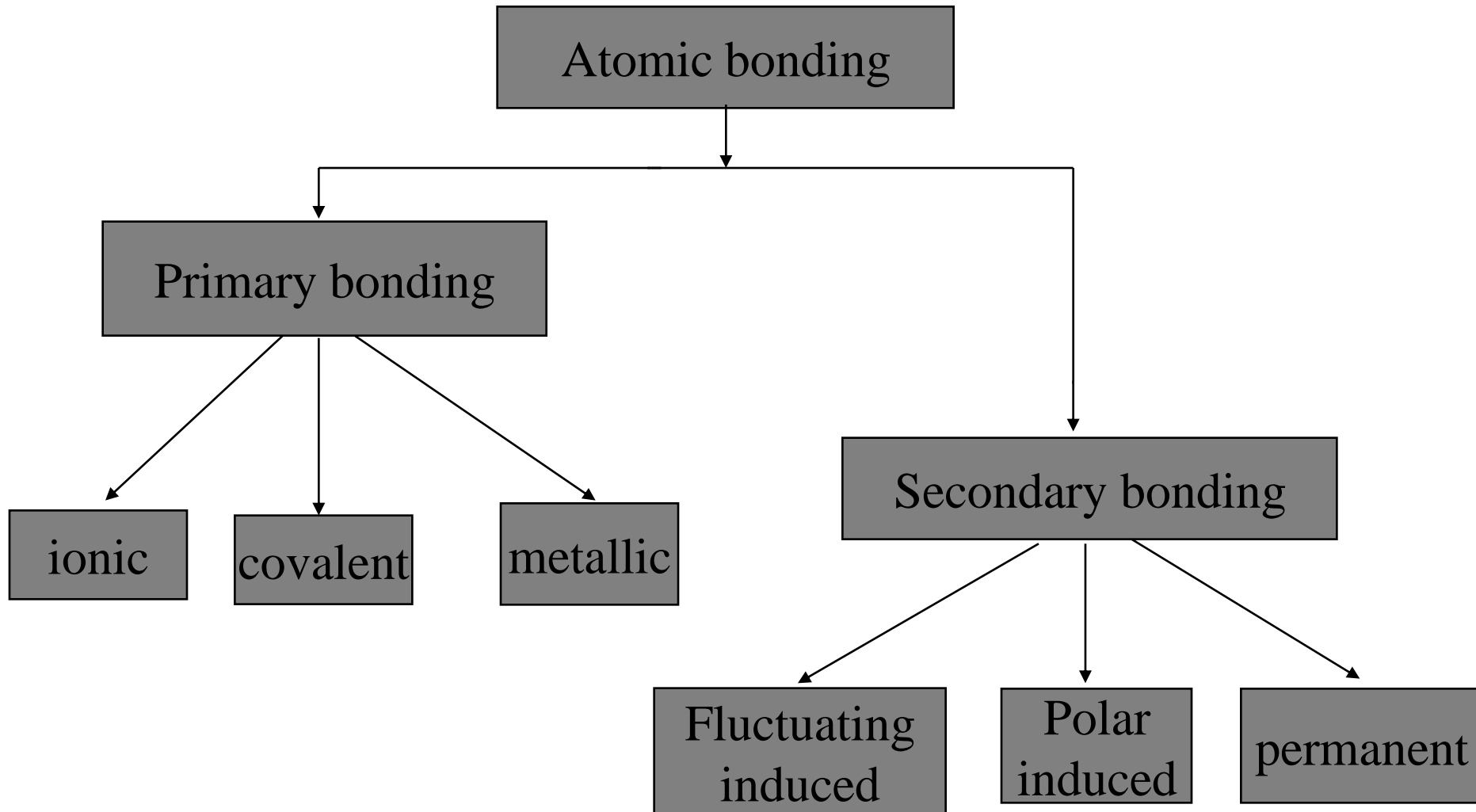
Thus, for graphite (carbon) with a density $\delta = 1.8 \text{ g}/\text{cm}^3$ and $M = 12$, $n = 6.023 \times 10^{23} \text{ atoms/mol} \times (1.8 \text{ g}/\text{cm}^3 / 12 \text{ g/mol}) = 9 \times 10^{22} \text{ atoms}/\text{cm}^3$.

- Most solid materials will have atomic density in the order of 6×10^{22} , that's about 39 million atoms per centimeter.
- Mean distance between atoms is in the range of 0.25 nm. It gives an idea about scale of atomic structures in solids.

Atomic Bonding in Solids

- Two questions need to be answered: why the atoms are clustered together?, and how they are arranged?
- Bonds are two kinds – Primary, and Secondary
- Primary bonds – relatively stronger. Exists in almost all solid materials.
E.g.: Ionic, Covalent, and Metallic bonds.
- Secondary bonds – relatively weaker bonds. Exists in many substances like water along with primary bonds.
E.g.: Hydrogen, and van der Waals forces.

Atomic Bond in Solids



Primary inter-atomic bonds

- These bonds invariably involves valence electrons.
- Nature of bond depends on electron arrangement in respective atoms.
- Atoms tend to acquire stable electron arrangement in their valence orbitals by transferring (ionic), sharing (covalent, and metallic) valence electrons. This leads to formation of bonds.
- Bond energies are in order of 1000 kJ/mol.

Ionic bond

- This primary bond exists between two atoms when transfer of electron(s) results in one of the atoms to become negative (has an extra electron) and another positive (has lost an electron).
- This bond is a direct consequence of strong Coulomb attraction between charged atoms.
- Basically ionic bonds are non-directional in nature.
- In real solids, ionic bonding is usually exists along with covalent bonding.

E.g.: NaCl. In the molecule, there are more electrons around Cl, forming Cl^- and fewer electrons around Na, forming Na^+ .

Covalent bond

- This bond comes into existence if valence electrons are shared between a pair of atoms, thus acquire stability by saturating the valence configuration.
- Covalent bonds are stereospecific i.e. each bond is between a specific pair of atoms, which share a pair of electrons (of opposite magnetic spins).
- Typically, covalent bonds are very strong, and directional in nature.

E.g.: H₂ molecule, where an electron from each of the atom shared by the other atom, thus producing the covalent bond.

Metallic bond

- This bond comes into existence if valence electrons are shared between number of atoms, i.e. arranged positive nucleuses are surrounded by electron pool.
- Shared electrons are not specific to a pair of atoms, in contrast to Covalent bond, i.e. electrons are delocalized.
- As shared electrons are delocalized, metallic bonds are non-directional.
- Very characteristic properties of metals like high thermal and electrical conductivities are result of presence of delocalized electron pool.

Secondary inter-atomic bonds

- These bonds involves atomic *or* molecular dipoles.
- Bonds can exists between induced and permanent dipoles (polar molecules).
- Bond comes into existence because of Columbic attraction between positive end of one dipole and negative end of another dipole.
- Bond energies are in order of 10 kJ/mol

Secondary inter-atomic bonds (contd...)

- Existence of these depends on three kinds of dipoles – fluctuating dipoles, Polar-molecule dipoles and Permanent dipoles.
- Permanent dipole bonds are also called Hydrogen bonds as covalently bonded hydrogen atoms – for example C-H, O-H, F-H – share single electron becomes positively charged proton that is capable of strong attractive force with the negative end of an adjacent molecule.
- Hydrogen bonds is responsible for water t exist in liquid state at room temperature.

Crystal Structures

- All solid materials are made of atoms/molecules, which are arranged in specific order in some materials, called *crystalline solids*. Otherwise *non-crystalline* or *amorphous solids*.
- Groups of atoms/molecules specifically arranged – crystal.
- *Lattice* is used to represent a three-dimensional periodic array of points coinciding with atom positions.
- *Unit cell* is smallest repeatable entity that can be used to completely represent a crystal structure. It is the building block of crystal structure.

Unit cell

It is characterized by:

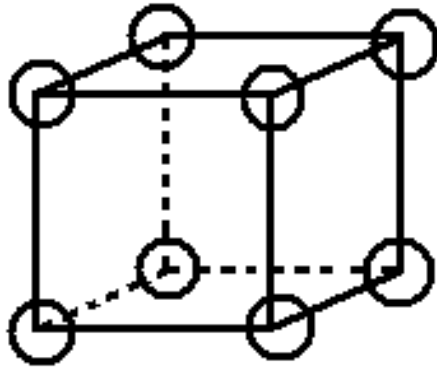
- Type of atom and their radii, R
- Cell dimensions, a and c (for hexagonal structures)
- Number of atoms per unit cell, n
- Coordination number (CN)– closest neighbors to an atom
- Atomic packing factor, APF

Most common unit cells – Face-centered cubic, Body-centered cubic and Hexagonal.

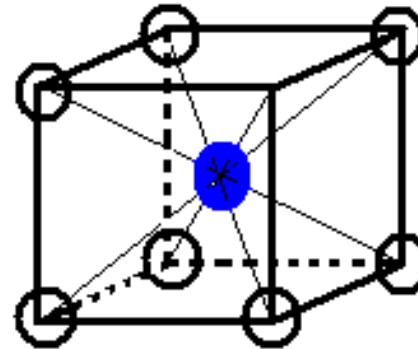
Common Crystal Structures

Unit Cell	n	CN	a/R	APF
Simple Cubic	1	6	$4/\sqrt{4}$	0.52
Body-Centered Cubic	2	8	$4/\sqrt{3}$	0.68
Face-Centered Cubic	4	12	$4/\sqrt{2}$	0.74
Hexagonal Close Packed	6	12		0.74

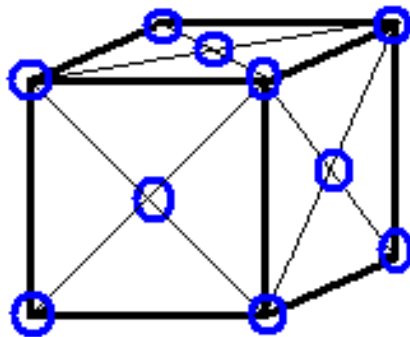
Schematic Unit Cells



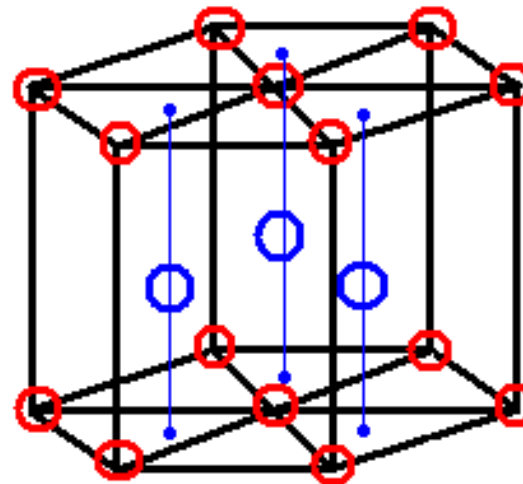
Simple Cubic



Body Centered Cubic



Face Centered Cubic



Hexagonal Close Packed

Miller indices

- A system of notation is required to identify particular direction(s) or plane(s) to characterize the arrangement of atoms in a unit cell
- Formulas involving Miller indices are very similar to related formulas from analytical geometry – simple to use
- Use of reciprocals avoids the complication of infinite intercepts
- Specifying dimensions in unit cell terms means that the same label can be applied to any plane with a similar stacking pattern, regardless of the crystal class of the crystal. Plane (111) always steps the same way regardless of crystal system

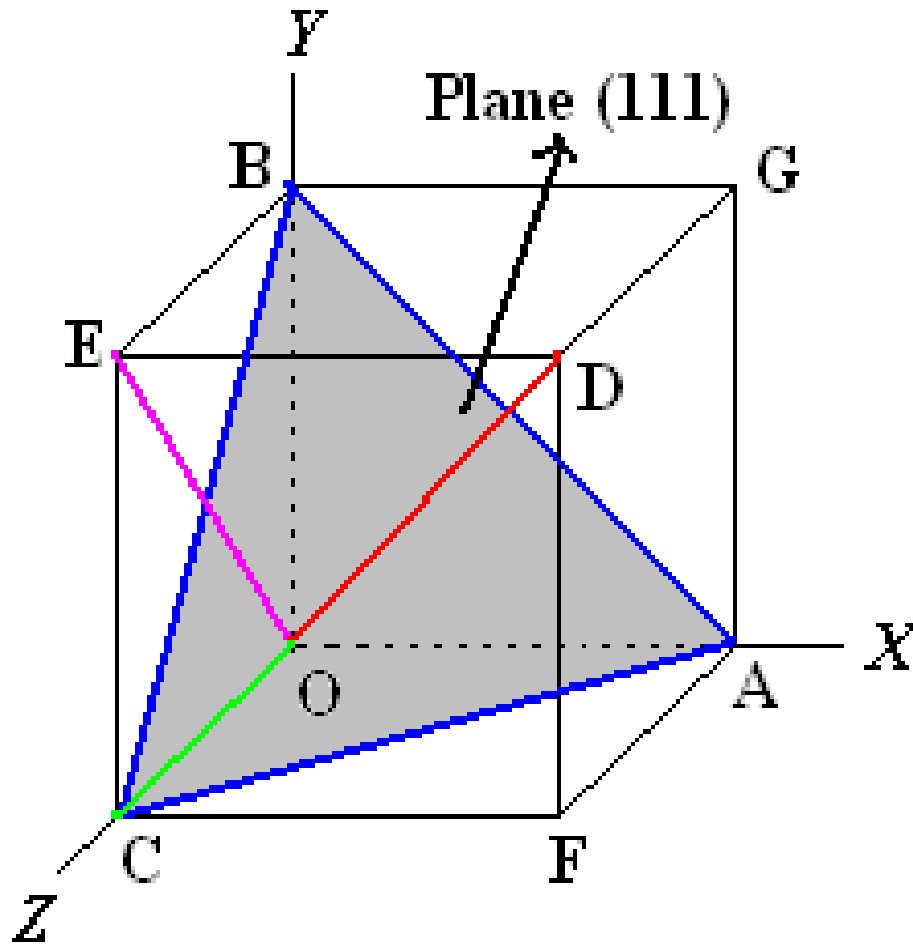
Miller indices - Direction

- A vector of convenient length is placed parallel to the required direction
- The length of the vector projection on each of three axes are measured *in terms of unit cell dimensions*
- These three numbers are made to smallest integer values, known as indices, by multiplying or dividing by a common factor
- The three indices are enclosed in square brackets, $[uvw]$.
- A family of directions is represented by $\langle uvw \rangle$

Miller indices - Plane

- Determine the intercepts of the plane along the crystallographic axes, *in terms of unit cell dimensions*. If plane is passing through origin, there is a need to construct a plane parallel to original plane
- Take the reciprocals of these intercept numbers
- Clear fractions
- Reduce to set of smallest integers
- The three indices are enclosed in parenthesis, (hkl).
- A family of planes is represented by {hkl}

Miller indices - Examples



— Direction $[001]$

— Direction $[011]$

— Direction $[111]$

Plane ACEG (101)

Plane OAGB (001)

Miller indices – Useful Conventions

- If a plane is parallel to an axis, its intercept is at infinity and its Miller index will be zero
- *Never alter negative numbers.* This implies symmetry that the crystal may not have! Use bar over the number to represent negative numbers.
- A plane or direction of family is not necessarily parallel to other planes or directions in the same family
- The smaller the Miller index, more nearly parallel the plane to that axis, and vice versa
- Multiplying or dividing a Miller index by constant has no effect on the orientation of the plane
- When the integers used in the Miller indices contain more than one digit, the indices must be separated by commas. **E.g.:**
(3,10,13)

Useful Conventions for cubic crystals

- $[uvw]$ is normal to (hkl) if $u = h$, $v = k$, and $w = l$. E.g.: $(111) \perp [111]$
- $[uvw]$ is parallel to (hkl) if $hu + kv + lw = 0$
- Two planes $(h_1k_1l_1)$ and $(h_2k_2l_2)$ are normal if $h_1h_2 + k_1k_2 + l_1l_2 = 0$
- Two directions $(u_1v_1w_1)$ and $(u_2v_2w_2)$ are normal if $u_1u_2 + v_1v_2 + w_1w_2 = 0$
- Inter-planar distance between family of planes $\{hkl\}$ is given by:

$$d_{\{hkl\}} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

- Angle between two planes is given by:

$$\cos\theta = \frac{h_1h_2 + k_1k_2 + l_1l_2}{\sqrt{h_1^2 + k_1^2 + l_1^2} \sqrt{h_2^2 + k_2^2 + l_2^2}}$$

Miller-Bravis indices

- Miller indices can describe all possible planes/directions in any crystal.
- However, Miller-Bravis indices are used in hexagonal systems as they can reveal hexagonal symmetry more clearly
- Indices are based on four axes – three are coplanar on basal plane at 120° apart, fourth axis is perpendicular to basal plane
- Both for planes/directions, extra index is given by

$$t = -(u+v), i = -(h+k)$$

where plane is represented as $[uv tw]$, and a direction is represented by $(hkil)$

E.g.: Basal plane – (0001), Prismatic plane – (10 10)

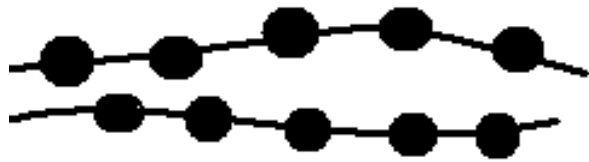
Polymers - definition

- Polymers are made of basic units called *mers*
- These are usually Hydrocarbons – where major constituent atoms are Hydrogen and Carbon
- When structure consists of only one *mer*, it is monomer. If it contains more than one *mer*, it is called polymer
- *Isomers* are molecules those contain same number of similar *mers* but arrangement will be different
E.g.: Butene and Isobutene
- When a polymer has ONE kind of *mers* in its structure, it is called *homopolymer*
- Polymer made with more than one kind of *mers* is called *copolymer*

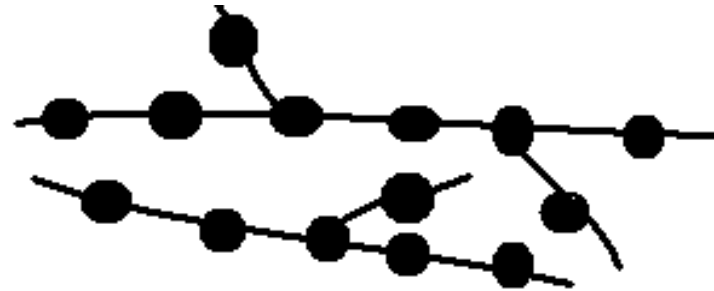
Polymer structures

- Linear, where mer units are joined together end to end in single chains. E.g.: PVC, nylon.
- Branched, where side-branch chains are connected to main ones. Branching of polymers lowers polymer density because of lower packing efficiency
- Cross-linked, where chains are joined one to another at various positions by covalent bonds. This cross-linking is usually achieved at elevated temperatures by additive atoms. E.g.: vulcanization of rubber
- Network, trifunctional mer units with 3-D networks comes under this category. E.g.: epoxies, phenol-formaldehyde.

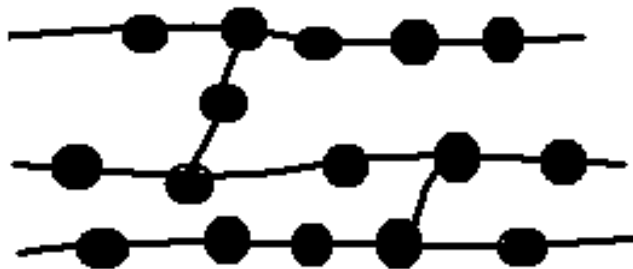
Polymer structures



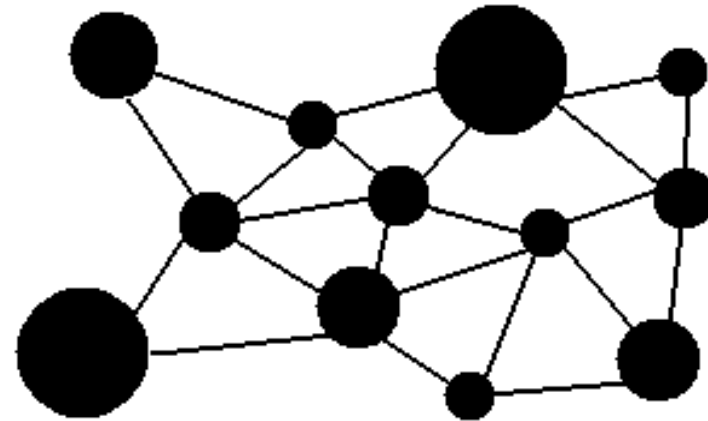
Linear



Branched



Cross-linked



Network

Schematic presentation of polymer structures.

Individual *mers* are represented by solid circles.

Thermo-sets – Thermo-plasts

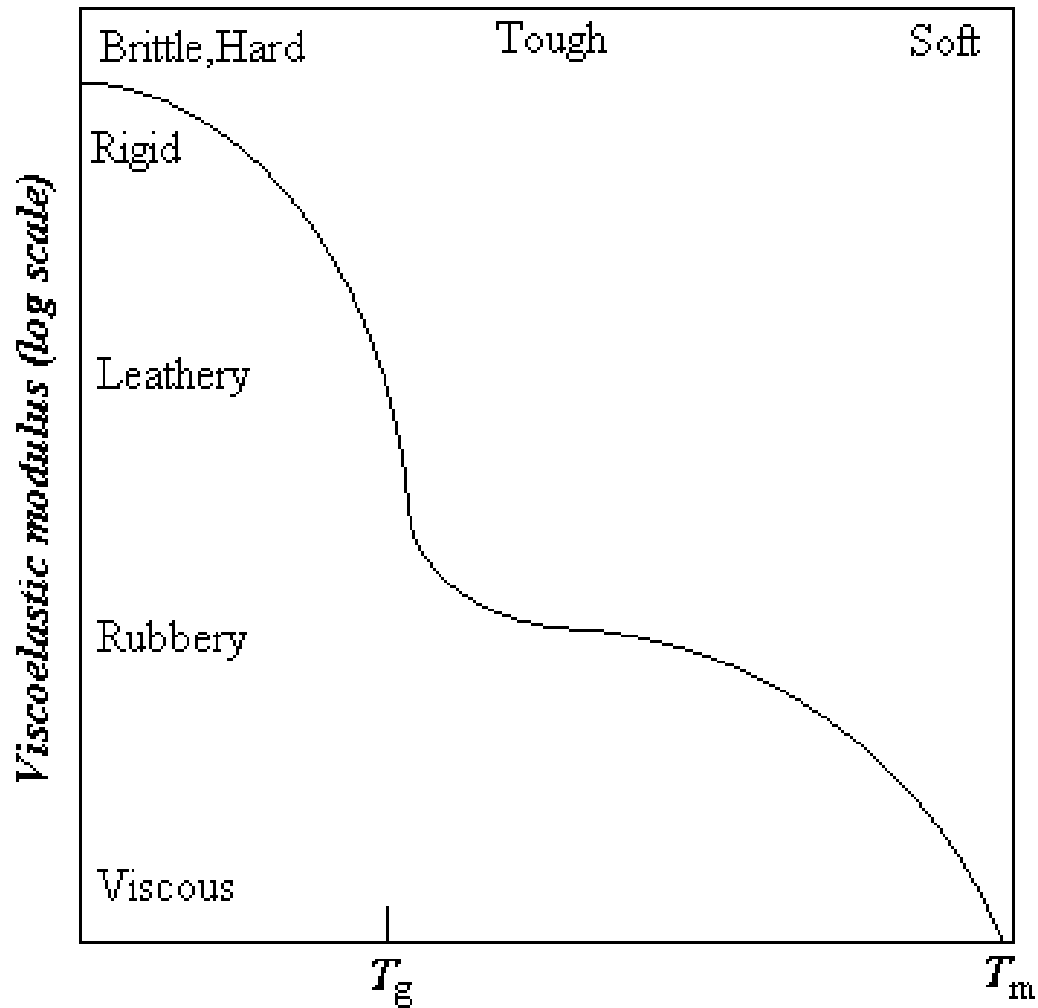
- Polymers mechanical response at elevated temperatures strongly depends their chain configuration
- Based on this response polymers are grouped in to two - thermo-sets and thermo-plasts
- Thermo-sets: become permanently hard when heated, and do not soften during next heat cycle. During first heating covalent bonds forms thus extensive cross-linking takes place. Stronger and harder than thermo-plasts.
E.g.: Vulcanized rubber, epoxies, some polyester resins
- Thermo-plasts: softens at high temperatures, and becomes hard at ambient temperatures. The process is reversible. Usually made of linear and branched structures.
E.g.: Polystyrene, Acrylics, Cellulosics, Vinyls

Polymer crystallinity

- Crystallinity in polymers is more complex than in metals
- Polymer crystallinity range from almost crystalline to amorphous in nature
- It depends on cooling path and on chain configuration
- Crystalline polymers are more denser than amorphous polymers
- Many semicrystalline polymers form *spherulites*. Each spherulite consists of collection of ribbon like chain folded lamellar crystallites.

E.g.: PVC (Poly Vinyl Chloride)

Polymer properties



Low ← Temperature → High

Impact ← Loading rate → Sustained

Ceramics

- Ceramics are inorganic and non-metallic materials
- Atomic bonds in ceramics are mixed – covalent + ionic
- Proportion of bonds is specific for a ceramic
- Ionic bonds exist between alkalis/alkaline-earth metals and oxygen/halogens.
- Mostly oxides, carbides, nitrides of metals are ceramics

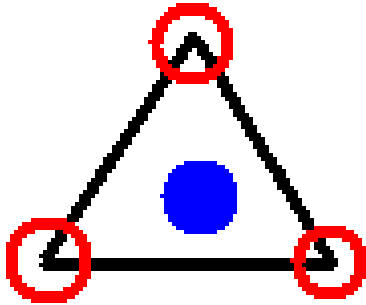
E.g.: Sand, Glass, Bricks, Marbles

Ceramic structures

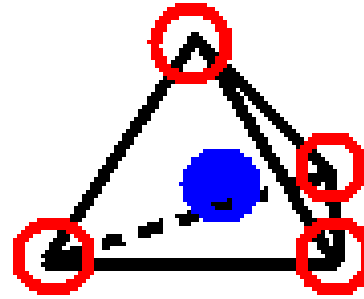
- Building criteria for ceramic structures:
 - maintain neutrality
 - closest packing
- Packing efficiency can be characterized by coordination number which depends on cation-anion radius ratio (r_c/r_a)

<i>Cation-anion radius ratio (r_c/r_a)</i>	< 0.155	0.155 – 0.225	0.225 – 0.414	0.414 – 0.732	0.732 – 1.000	> 1.000
<i>Coordination number</i>	2	3	4	6	8	12

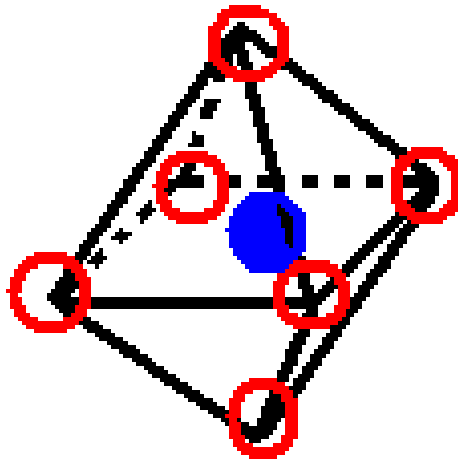
Ion arrangement – Coordination numbers



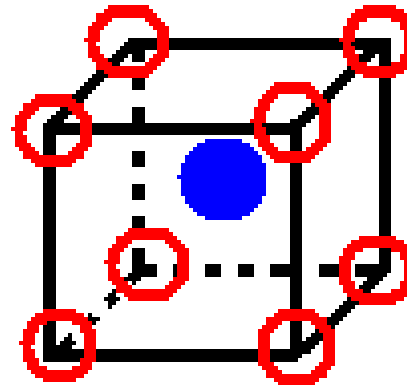
CN = 3



CN = 4



CN = 6



CN = 8

Ceramic crystal structures

- AX-type: most common in ceramics. They assume different structures of varying coordination number (CN).

Rock salt structure – CN=6.

E.g.: NaCl, FeO

Cesium Chloride structure – CN=8

E.g.: CsCl

Zinc Blende structure – CN=4

E.g.: ZnS, SiC

- A_mX_p-type: number of anions and cations are different (m≠p). One unit cell is made of eight cubes.

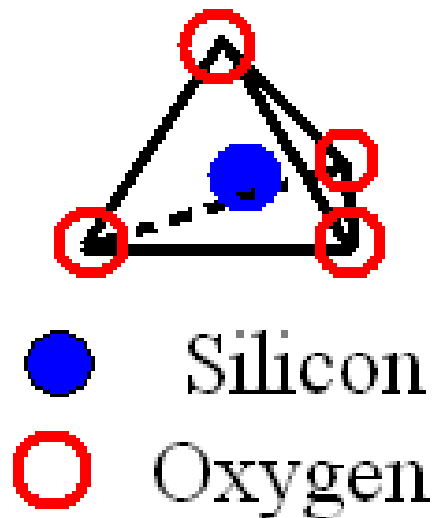
E.g.: CaF₂, ThO₂

- A_mB_nX_p-type: when ceramic contains more than one kind of cations. Also called *perovskite crystal structure*.

E.g.: BaTiO₃

Silicates

- Most common ceramic in nature – Silicates, as constituent elements – silicon and oxygen – are most abundant in earth's crust.
- Bond between Si^{4+} and O^{2-} is weak ionic and very strong covalent in nature. Thus, basic unit of silicates is SiO_4^{4-} tetrahedron.



Silicates (contd...)

- In Silica (SiO_2), every oxygen atom the corner of the tetrahedron is shared by the adjacent tetrahedron.
- Silica can be both crystalline (quartz) and amorphous (glass)
- Crystalline forms of silica are complicated, and comparatively open...thus low in density compared with amorphous glasses
- Addition of network modifiers (Na_2O) and intermediates (Al_2O_3 , TiO_2) lowers the melting point...thus it is easy to form. E.g.: Bottles.
- In complicated silicates, corner oxygen is shared by other tetrahedra....thus consists SiO_4^{4-} , $\text{Si}_2\text{O}_7^{6-}$, $\text{Si}_3\text{O}_9^{6-}$ groups
- Clays comprises 2-D sheet layered structures made of $\text{Si}_2\text{O}_5^{2-}$

Carbon

- Carbon is not a ceramic, but its allotropic form - Diamond - is
- Diamond:
 - C-C covalent bonds, highest known hardness,
 - Semiconductor, high thermal conductivity, meta-stable
- Graphite - another allotropic form of carbon
 - layered structure - hexagonal bonding within planar layers, good electrical conductor, solid lubricant
- Another allotropic form - C₆₀ - also called Fullerene / Bucky ball. Structure resembles hallow ball made of 20 hexagons and 12 pentagons where no two pentagons share a common edge.
- Fullerenes and related nanotubes are very strong, ductile - could be one of the important future engineering materials

Imperfections in ceramics

- Imperfections in ceramics – point defects, and impurities. Their formation is strongly affected by charge neutrality
- *Frenkel-defect* is a vacancy-interstitial pair of cations
- *Schottky-defect* is a pair of nearby cation and anion vacancies
- Impurities:
 - Introduction of impurity atoms in the lattice is likely in conditions where the charge is maintained.
 - E.g.: electronegative impurities that substitute lattice anions or electropositive substitutional impurities

Mechanical response of ceramics

- Engineering applications of ceramics are limited because of presence of microscopic flaws – generated during cooling stage of processing.
- However, as ceramics are high with hardness, ceramics are good structural materials under compressive loads.
- Plastic deformation of crystalline ceramics is limited by strong inter-atomic forces. Little plastic strain is accomplished by process of slip.
- Non-crystalline ceramics deform by viscous flow.
- Characteristic parameter of viscous flow – viscosity. Viscosity decreases with increasing temperature. However, at room temperature, viscosity of non-crystalline ceramics is very high.

Mechanical response of ceramics (contd...)

- Hardness – one best mechanical property of ceramics which is utilized in many application such as abrasives, grinding media
- Hardest materials known are ceramics
- Ceramics having Knoop hardness about 1000 or greater are used for their abrasive characteristics
- Creep – Ceramics experience creep deformation as a result of exposure to stresses at elevated temperatures.
- Modulus of elasticity, E , as a function of volume fraction of porosity, P : $E = E_0 (1 - 1.9 P + 0.9 P^2)$
- Porosity is deleterious to the flexural strength for two reasons:
 - reduces the cross-sectional area across where load is applied
 - act as stress concentrations