Material Science

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Chapter 2. Atomic Structure, Interatomic Bonding and Structure of Crystalline Solids

2.1 Atomic Structure and Atomic Bonding in Solids

2.1.1 Atomic Structure

Atoms are composed of electrons, protons, and neutrons. Electrons and protons are negative and positive charged particles respectively. The magnitude of each charged particle in an atom is 1.6×10^{-19} Coulombs.

The mass of the electron is negligible with respect to those of the proton and the neutron, which form the *nucleus* of the atom. The unit of mass is an atomic mass unit (*amu*) = 1.66×10^{-27} kg, and equals 1/12 the mass of a carbon atom. The Carbon nucleus has $Z=6$, and $A=6$, where Z is the number of protons, and A the number of neutrons. Neutrons and protons have very similar masses, roughly equal to 1 *amu* each. A neutral atom has the same number of electrons and protons, Z.

A *mol* 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*. The number of atoms in a mole is called the Avogadro number, $N_{av} = 6.023 \times 10^{23}$. Note that $N_{av} = 1$ *gram*/1 *amu*.

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

$$n = N_{av} \frac{\delta}{M}$$

where M is the atomic mass in *amu* (*grams* per *mol*). Thus, for graphite (carbon) with a density $\delta = 1.8$ g/cm^3, $M = 12$, we get 6×10^{23} atoms/mol $\times$ 1.8 g/cm^3 / 12 g/mol) = 9×10^{22} C atoms/cm^3.

For a molecular solid like ice, one uses the molecular mass, $M_{(H2O)}$ = 18. With a density of 1 g/cm^3, one obtains n = 3.3 × 10^{22} H$_2$O molecules/cm^3. Note that since the water molecule contains 3 atoms, this is equivalent to 9.9 × 10^{22} atoms/cm^3.

Most solids have atomic densities around 6 × 10^{22} atoms/cm^3. The cube root of that number gives the number of atoms per centimeter, about 39 million. The mean distance between atoms is the inverse of that, *or* 0.25 nm. This is an important number that gives the scale of atomic structures in solids.

2.1.2 Atomic bonding in solids

In order to understand the why materials behave like they do and why they differ in properties, it is necessary that one should look at atomic level. The study primarily concentrates on two issues: what made the atoms to cluster together, and how atoms are arranged. As mentioned in earlier chapter, atoms are bound to each other by number of bonds. These inter-atomic bonds are primarily of two kinds: Primary bonds and Secondary bonds. Ionic, Covalent and Metallic bonds are relatively very strong, and grouped as primary bonds, whereas van der Waals and hydrogen bonds are relatively weak, and termed as secondary bonds. Metals and Ceramics are entirely held together by primary bonds - the ionic and covalent bonds in ceramics, and the metallic and covalent bonds in metals. Although much weaker than primary bonds, secondary bonds are still very important. They provide the links between polymer molecules in polyethylene (and other polymers) which make them solids. Without them, water would boil at -80˚C, and life as we know it on earth would not exist.

Ionic Bonding: This bond exists between two atoms when one of the atoms is negative (has an extra electron) and another is positive (has lost an electron). Then there is a strong, direct Coulomb attraction. Basically ionic bonds are non-directional in nature. An example is NaCl. In the molecule, there are more electrons around Cl, forming Cl$^-$ and fewer electrons around Na, forming Na$^+$. Ionic bonds are the strongest bonds. In real solids, ionic bonding is usually exists along with covalent bonding.
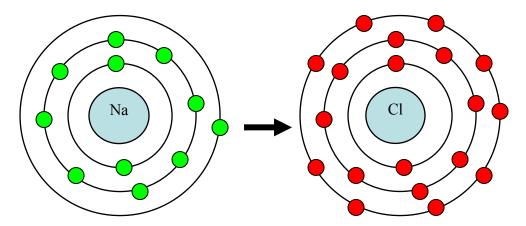

Fig.1 Schematic representation of ioning bonding. Here, Na is giving an electron to Cl to have stable structure

Covalent Bonding: In covalent bonding, electrons are shared between the atoms, to saturate the valency. The simplest example is the H_2 molecule, where the electrons spend more time in between the nuclei of two atoms than outside, thus producing bonding. Covalent bonds are stereo-specific 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. The hardness of diamond is a result of the fact that each carbon atom is covalently bonded with four neighboring atoms, and each neighbor is bonded with an equal number of atoms to form a rigid three-dimensional structure.
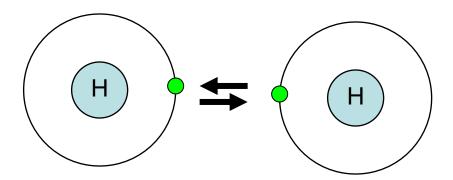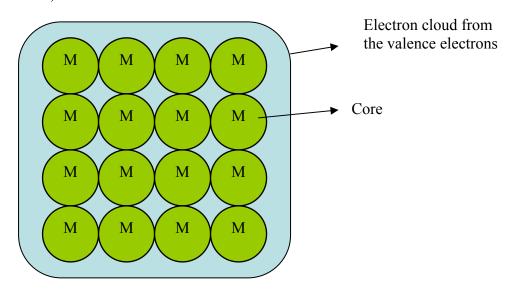

Figure 2. Schematic representation of covalent bond in Hydrogen molecule (sharing of electrons)

Metallic Bonding: Metals are characterized by high thermal and electrical conductivities. Thus, neither covalent nor ionic bondings are realized because both types of bonding localize the valence electrons and preclude conduction. However, strong bonding does occur in metals. The valence electrons of metals also are delocalized. Thus metallic bonding can be viewed as metal containing a periodic structure of positive ions surrounded by a sea of delocalized electrons. The attraction between the two provides the bond, which is non-directional.

Figure 3. Metallic bonding

Fluctuating Induced Dipole Bonds: Since the electrons may be on one side of the atom or the other, a dipole is formed: the + nucleus at the center, and the electron outside. Since the electron moves, the dipole fluctuates. This fluctuation in atom A produces a fluctuating electric field that is felt by the electrons of an adjacent atom, B. Atom B then polarizes so that its outer electrons are on the side of the atom closest to the + side (or opposite to the – side) of the dipole in A.

Polar Molecule-Induced Dipole Bonds: Another type of secondary bond exists with asymmetric molecules, also called polar molecules because of positively and negatively charged regions. A permanent dipole moment arises from net positive and negative charges that are respectively associated with the hydrogen and chlorine ends of the HCl molecule, leading to bonding. The magnitude of this bond will be greater than for fluctuating induced dipoles.
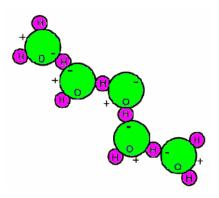
Figure 4. Dipole bond in water

These two kinds of bonds are also called van der Waals bonds. Third type of secondary bond is the hydrogen bond. It is categorized separately because it produces the strongest forces of attraction in this category.

Permanent Dipole Bonds / Hydrogen bonding: It occurs between molecules as covalently bonded hydrogen atoms – for example C-H, O-H, F-H – share single electron with other atom essentially resulting in positively charged proton that is not shielded any electrons. This highly positively charged end of the molecule is capable of strong attractive force with the negative end of an adjacent molecule. The properties of water are influenced significantly by the hydrogen bonds/bridges. The bridges are of sufficient strength, and as a consequence water has the highest melting point of any molecule of its size. Likewise, its heat of vaporization is very high.

2.2 Crystal Structures, Crystalline and Non-Crystalline materials

2.2.1 Crystal structures

All metals, a major fraction of ceramics, and certain polymers acquire crystalline form when solidify, i.e. in solid state atoms self-organize to form *crystals*. Crystals possess a long-range order of atomic arrangement through repeated periodicity at regular intervals in three dimensions of space. When the solid is not crystalline, it is called amorphous. Examples of crystalline solids are metals, diamond and other precious stones, ice, graphite. Examples of amorphous solids are glass, amorphous carbon (a-C), amorphous Si, most plastics.

There is very large number of different crystal structures all having long-range atomic order; these vary from relatively simple structures for metals to exceedingly complex structures for ceramics and some polymers. To discuss crystalline structures it is useful to consider atoms as being hard spheres, with well-defined radii. In this scheme, the shortest distance between two like atoms is one diameter. In this context, use of terms *lattice* and *unit cell* will be handy. *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. Thus it can be considered that a unit cell is the building block of the crystal structure and defines the crystal structure by virtue of its geometry and the atom positions within.
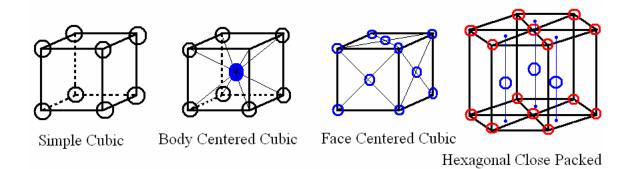
Important properties of the unit cells are

- The type of atoms and their radii R.
- Cell dimensions (Lattice spacing a, b and c) in terms of R and
- Angle between the axis α, β, γ
- a*, b*, c* - lattice distances in reciprocal lattice , α*, β*, γ* - angle in reciprocal lattice
- n, number of atoms per unit cell. For an atom that is shared with m adjacent unit cells, we only count a fraction of the atom, $1/m$.
- CN, the coordination number, which is the number of closest neighbors to which an atom is bonded.
- APF, the atomic packing factor, which is the fraction of the volume of the cell actually occupied by the hard spheres. APF = Sum of atomic volumes/Volume of cell.

Some very common crystal structures and relevant properties are listed in table 2.1.

Table 2.1: Common crystal structures and their properties.

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

Simple Cubic   Body Centered Cubic   Face Centered Cubic

Hexagonal Close Packed

Figure 2.1: *Common metallic crystal structures.*

2.2.2 Crystalline and Non-crystalline materials

Single Crystals: Crystals can be *single crystals* where the whole solid is one crystal. Then it has a regular geometric structure with flat faces.

Polycrystalline Materials: A solid can be composed of many crystalline grains, not aligned with each other. It is called *polycrystalline*. The grains can be more or less aligned with respect to each other. Where they meet is called a *grain boundary*.

Non-Crystalline Solids: In amorphous solids, there is no long-range order. But amorphous does not mean random, since the distance between atoms cannot be smaller than the size of the hard spheres. Also, in many cases there is some form of short-range order. For instance, the tetragonal order of crystalline SiO_2 (quartz) is still apparent in amorphous SiO_2 (silica glass).

2.3 Miller Indices, Anisotropy, and Elastic behavior of composites

2.3.1 Miller indices:

It is understood that properties of materials depend on their crystal structure, and many of these properties are directional in nature. For example: elastic modulus of BCC iron is greater parallel to the body diagonal than it is to the cube edge. Thus it is necessary to characterize the crystal to identify specific directions and planes. Specific methods are employed to define crystal directions and crystal planes.

Methodology to define crystallographic directions in cubic crystal:

- 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 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 *<uvw>*.
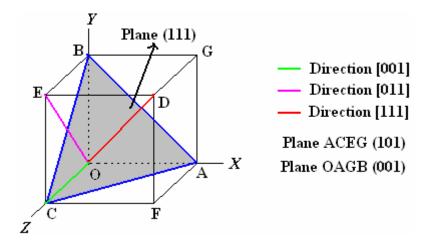
Methodology to define crystallographic planes in cubic crystal:

- 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}*.

For example, if the x-, y-, and z- intercepts of a plane are 2, 1, and 3. The Miller indices are calculated as:
- take reciprocals: 1/2, 1/1, 1/3.
- clear fractions (multiply by 6): 3, 6, 2.
- reduce to lowest terms (already there). => Miller indices of the plane are (362).

Figure 2.2 depicts Miller indices for number of directions and planes in a cubic crystal.

Figure 2.2: *Miller indices in a cubic crystal.*

Some useful conventions of Miller notation:

- If a plane is parallel to an axis, its intercept is at infinity and its Miller index will be zero.

- If a plane has negative intercept, the negative number is denoted by a bar above the number. *Never alter negative numbers.* For example, do not divide -1, -1, -1 by -1 to get 1,1,1. This implies symmetry that the crystal may not have!
- The crystal directions of a family are not necessarily parallel to each other. Similarly, not all planes of a family are parallel to each other.
- By changing signs of all indices of a direction, we obtain opposite direction. Similarly, by changing all signs of a plane, a plane at same distance in other side of the origin can be obtained.
- Multiplying or dividing a Miller index by constant has no effect on the orientation of the plane.
- The smaller the Miller index, more nearly parallel the plane to that axis, and vice versa.
- 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)
- By changing the signs of all the indices of (a) a direction, we obtain opposite direction, and (b) a plane, we obtain a plane located at the same distance on the other side of the origin.

More conventions applicable to cubic crystals only:

- $[uvw]$ is normal to (hkl) if $u = h$, $v = k$, and $w = l$. E.g.: $(111) \perp [111]$.
- Inter-planar distance between family of planes $\{hkl\}$ is given by:

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

- $[uvw]$ 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 $u_1u_2 + v_1v_2 + w_1w_2 = 0$
- Angle between two planes is given by:

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

The same equation applies for two directions.

Why Miller indices are calculated in that way?
- Using reciprocals spares us the complication of infinite intercepts.
- Formulas involving Miller indices are very similar to related formulas from analytical geometry.
- 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.

2.3.2 Miller-Bravis indices

Though Miller indices can describe all possible planes through any crystal, Miller-Bravis indices are used in hexagonal crystal systems. This is because they reveal hexagonal symmetry more clearly. Although partially redundant, they are used exclusively for hexagonal systems.

Direction indices are obtained as above where first three indices are representative of projections of the direction over three co-planar axes in the plane called basal plane while the last index denotes the projection over the axis perpendicular to the basal plane. Miller-Bravis indices for a plane are denoted as *[uvtw]*, where $t = -(u+v)$

In the same procedure, planes in a hexagonal crystal are denoted by *(hkil)*, where $i = -(h+k)$.

2.3.3 Anisotropy

It's been agreed that many of the materials properties depend on the crystal structure. However, crystals are not symmetric in all directions, or not the crystal planes same with respect to atomic density/packing. Different directions in the crystal have different packing. For instance, atoms along the edge of FCC crystals are more separated than along its face diagonal. This causes properties to be different in different directions. This directionality of properties is termed as *Anisotropy*.

Substances in which measured properties are independent of direction in which they are measured are called *isotropic*. Though, in polycrystalline materials, the crystallographic orientations of individual grains are random, specimen may behave isotropically.

2.3.4 Elastic Behavior of Composites

The idea is that by combining two or more distinct materials one can engineer a new material with the desired combination of properties (e.g., light, strong, corrosion resistant). The idea that a better combination of properties can be achieved is called the *principle of combined action*.

For example, Pearlitic steel that combines hard and brittle Cementite with soft and ductile ferrite to get a superior material.

A composite is defined as a artificially made muti-phase material, where constituent phases are chemically dissimilar and separated by a distinct interface. Thus, composites shall have at least two or more constituent phases. Many of the composites are made of two phases – one is termed as *matrix*, which is continuous and surrounds the other phase, called *dispersed phase*. Dispersed phase can exist in many forms like particulates, short-/long- fibers.

Properties of composites depend on

- Properties of the constituent phases.
- Geometry of dispersed phase (particle size, size distribution, orientation).
- Amount of each constituent phase.

Classification of composites based on geometry of dispersed phase:
- Particle-reinforced (large-particle and dispersion-strengthened)
- Fiber-reinforced (continuous (aligned) and short fibers (aligned or random)
- Structural (laminates and sandwich panels)

Classification of composites based on matrix phase:
- Metal Matrix Composites.
- Polymer Matrix Composites.
- Ceramic Matrix Composites.

Composite properties can be calculated using *rule of mixtures*. For example, elastic modulus of a particle reinforced composite bound by the limits given by

$$E_c(u) = E_m V_m + E_p V_p$$

$$E_c(l) = \frac{E_m E_p}{E_m V_p + E_p V_m}$$

where E and V denote the elastic modulus and volume fraction respectively; c, m, and p represent composite, matrix, and particulate phases.

However, in case of continuous fiber reinforced composites upper bound is applicable to condition of longitudinal loading, while the lower bound is applicable to transverse loading condition. The above equations can be simplified using the following relations:

$$V_m + V_p = 1$$

When fiber orientation is random, or short and discontinuous fibers are used, rule of mixtures will be modified as follows to take care of the randomness of fibers:

$$E_{cd} = E_m V_m + K E_f V_f$$

where K – is fiber efficiency parameter that depends on V_f and E_f/E_m ratio. K's values are less than unity, usually attains a value in the range of 0.1 to 0.6.

Many applications, like in aircraft parts, there is a need for high strength per unit weight (specific strength). This can be achieved by composites consisting of a low-density (and soft) matrix reinforced with stiff fibers.

2.4 Structure and properties of polymers

Polymers are common in nature, in the form of wood, rubber, cotton, leather, wood, silk, proteins, enzymes, starches, cellulose. Artificial polymers are made mostly from oil. Their use has grown exponentially, especially after WW2 (World War-2). The key factor is the very low production cost and useful properties (e.g., combination of transparency and flexibility, long elongation, etc.).

Most polymers are organic, and formed from hydrocarbon molecules. These molecules can have single, double, or triple carbon bonds. A *saturated hydrocarbon* is one where all bonds are single, i.e. the number of atoms is maximum (or saturated). Among this type are the paraffin compounds, C_nH_{2n+2}. In contrast, non-saturated hydrocarbons contain some double and triple bonds.

Isomers are molecules that contain the same molecules but in a different arrangement. An example is butane and iso-butane. Some physical properties of hydrocarbons depend on the isomeric state.

2.4.1 Polymer molecules

Polymer molecules are huge, macromolecules that have internal covalent bonds. For most polymers, these molecules form very long chains. The backbone is a string of carbon atoms, often single bonded. Polymers are composed of basic structures called **mer** units. A molecule with just one mer is a monomer. Within each molecule / mer atoms are bonding together by strong covalent bonds. When many mers are together, they form polymer. Bi-functional monomers may bond with two other units in forming 2-D chain-like structures; while Tri-functional monomers can form three active bonds, and thus 3-D molecular network. Examples of polymers are polyvinyl chloride (PVC), poly-tetra-fluoro-ethylene (PTFE or Teflon), polypropylene, nylon and polystyrene. When all the mers are the same, the molecule is called a *homopolymer*. When there is more than one type of mer present, the molecule is a *copolymer*.

The mass of a polymer is not fixed, but is distributed around a mean value, since not all polymer chains will grow same extent. The average molecular weight can be obtained by averaging the masses with the fraction of times they appear (*number-average*) or with the weight fraction of the molecules (*weight-average*). Another representation of average chain size is *degree of polymerization* (*n*) – average number of mer units in a chain. It is obtained by dividing the average mass of the polymer by the mass of a mer unit. Numbers of polymer characteristics are affected by the magnitude of the molecular weight. Short chain polymers usually exist in form of gases or liquids at room temperature; where as medium range polymers are waxy solids and soft resins. Solid polymers are commonly having weights ranging between 10K and several million g/mol.

2.4.2 Polymer structures

Polymers consist of large number of molecular chains which are usually not linear; bending and rotations can occur around single C-C bonds (double and triple bonds are very rigid). Random kinks and coils in chains along with bending of chains lead to

intertwining and entanglement of neighboring chains, situation like in the spaghetti structure. These characteristic entanglements are responsible for a number of properties specific to polymers, e.g.: large elastic extension. However, physical properties of polymers depend not only on molecular weight and shape, but also on differences in structure of the chains. It should be remembered that polymers are not usually of only one distinctive structural type, though they are classified into different groups. Typical polymer chain structures are: (a) *linear*, where mer units are joined together end to end in single chains. E.g.: PVC, nylon. (b) *branched*, where side-branch chains are connected to main ones. Branching of polymers lowers polymer density because of lower packing efficiency. (c) *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. (d) *network*, trifunctional mer units with 3-D networks comes under this category. E.g.: epoxies, phenol-formaldehyde.
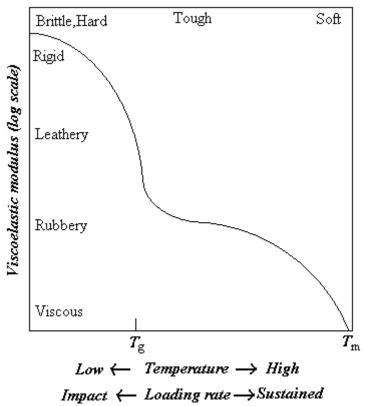
2.4.3 Polymer crystallinity

Crystallinity in polymers is more complex than in metals. Polymer molecules are often partially crystalline (*semicrystalline*), with crystalline regions dispersed within amorphous material. The degree of crystallinity may range from completely amorphous to almost entirely crystalline; on the other hand metals are almost always crystalline whereas ceramics are either completely crystalline or noncrystalline. The degree of crystallinity of a polymer depends on cooling path, and also on chain configuration. For copolymers, the more irregular and random the mer arrangement, the greater is probability for noncrystalline nature. Crystalline polymers are denser than amorphous polymers, so the degree of crystallinity can be obtained from the measurement of density.

Different models have been proposed to describe the arrangement of molecules in semicrytalline polymers. In the fringed-micelle model, the crystallites (micelles) are embedded in an amorphous matrix. Polymer single crystals grown are shaped in regular platelets (lamellae). Spherulites are chain-folded crystallites in an amorphous matrix that grow radially in spherical shape "grains". These are considered to be the polymer analogue of grains in polycrystalline metals and ceramics. Many semicrystalline polymers form spherulites; each spherulite consists of a collection of ribbonlike chain-folded lamellar crystallites that radiate outward from its center. E.g.: polyethelene, PVC.

A polymer's response to mechanical forces under elevated temperatures is related to its molecular structure. Based on this response, polymers are classified as: *thermoplasts* (soften when heated and harden when cooled), and *thermosets* (become permanently hard when heat is applied and do not soften upon subsequent heating). Thermosets are generally harder and stronger than thermoplasts, and have better dimensional stability. Most of the cross-linked and network polymers are thermosets; whereas linear and some branched polymers are thermoplasts.

2.4.4 Properties of polymers

Fluids and amorphous solids undergo viscous flow when external forces are applied. It is well known that polymers exhibit very high viscosity in order of 10^{12} Pa.s at room temperature. Polymers are non-Newtonian in nature, and formed into plastic products at a temperature above their glass-transition temperature. It is evident that temperature has very strong influence on mechanical behavior of polymers. Elastic strain occurs simultaneously with viscous flow, resulting in visco-elastic deformation of polymers under externally applied loads. Below the glass transition temperature elastic deformation dominates and the material behaves rigid. In the range of glass temperature, the materials is leathery; in the rubber plateau, polymers deform readily but quickly regain their previous shape if the stress in removed. At still higher temperatures, under sustained loads, the polymer deforms extensively by viscous flow. Figure below depicts temperature effect on deformation behavior of polymers.

Figure 2.3: *Dependence of polymer viscosity on temperature and/or loading rate.*

2.5 Structure and properties of ceramics

Ceramics are inorganic and non-metallic materials that are commonly electrical and thermal insulators, brittle and composed of more than one element (e.g., two in Al_2O_3). As ceramics are composed of two or more elements, their crystal structures are generally more complex than those of metals. Ceramic bonds are mixed, ionic and covalent, with a proportion that depends on the particular ceramics. The ionic character is given by the difference of electronegativity between the cations (+) and anions (-). Covalent bonds involve sharing of valence electrons. Very ionic crystals usually involve cations which

are alkalis or alkaline-earths (first two columns of the periodic table) and oxygen or halogens as anions.

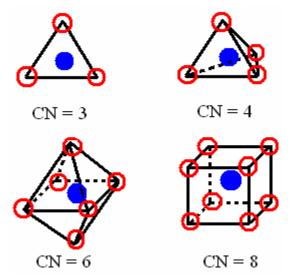The building criteria for the ceramic crystal structure are as follows:
- maintain neutrality (charge balance dictates chemical formula)
- achieve closest packing

The crystal stability condition i.e. condition of minimum energy implies maximum attraction and minimum repulsion. This leads to contact and configurations such that anions have the highest number of cation neighbors (coordination number) and vice versa. The coordination number is dependent on cation-anion radius ratio, which can be determined from geometric relations. Table 2.2 presents relevant coordination numbers and radius ratios.

Table 2.2. Co-ordination number dependency on cation-anion radius ratio.

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

Figure-2.4 presents schematic arrangement of cations and anions with respective coordinate positions for different radius ratios.

Figure 2.4: *Ion arrangements for different coordination numbers.*

2.5.1 Ceramic crystal structures

AX-type ceramic crystal structures: Most common ceramics are made of equal number of cations and anions, and are referred to as AX compounds (A-cation, and X-anion). These ceramics assume many different structures, named after a common material that possesses the particular structure.

Rock salt structure: here the coordination number is 6, i.e. r_c/r_a = 0.414-0.732. This structure can be viewed as an FCC of anions with cations occupying center of each edge and the center of the cell. Thus it can be said that lattice is made of two interpenetrating FCC lattices, one composed of cations, and the other of anions. E.g.: NaCl, MgO, FeO.

Cesium Chloride structure: here the coordination number is 8. Crystal structure consists of anions at corners of a cube while a cation occupies the center, and vice versa. E.g.: CsCl.

Zinc Blende structure: here the coordination number is 4. Unit cell is composed of one kind of ions occupying corners and face centers of a cube, while the other kind of ions occupies the interior tetrahedral positions. E.g.: ZnS, SiC.

A_mX_p- type structures: when the charges of cation and anions are not the same, to maintain the neutrality, ceramic structures with chemical formula would exist. For example – CaF_2 with r_c/r_a = 0.8, and thus coordination number of 8. It can be expected that crystal structure could be the same as that of CsCl. However cations are half many as anions, thus only half the center positions are occupied. One unit cell shall be made of eight cubes. E.g.: UO_2, ThO_2, PuO_2.

$A_mB_nX_p$-type structures: it is possible that ceramics do have more than one kind of cations. E.g.: $BaTiO_3$. unit cell is made of cube where Ba^{2+} ions occupies all eight corners, T^{4+} occupies cube center, while O^{2-} are at center of each face. This structure is called *perovskite crystal structure*.

It is worth to understand and know more about some common most common ceramic in nature. For example: silicates and carbon.

2.5.2 Silicates

Oxygen and Silicon are the most abundant elements in Earth's crust. Their combination (silicates) occurs in rocks, soils, clays and sand. The bond is weekly ionic, with Si^{4+} as the cation and O^{2-} as the anion. However the bonds in silicates are strongly of covalent character with strong directional Si-O bonds. Basic unit of silicates structures are thus is SiO_4^{4-} tetrahedron that consists of four oxygen atoms at corners of tetrahedron, and silicon atom at the center of it. Various silicate structures consists SiO_4^{4-} unit bonded in 1-, 2-, and 3- dimensions.

In silica (SiO_2) every oxygen atom is shared by adjacent tetrahedra. Silica can either be crystalline (e.g., quartz) or amorphous, as in glass. Crystalline forms of silica are known to be complicated and comparatively open, thus of low densities compared with amorphous glasses. Soda glasses melt at lower temperature than amorphous SiO_2 because the addition of Na_2O (soda) that act as *network modifier* breaks the tetrahedral network. Addition of *intermediates* such as Al_2O_3, TiO_2 substitute of silicon atoms and become part of stabilized network. Addition of network modifiers and intermediates lowers melting point, and thus it is easy to form glass, for instance, bottles.

In complicated silicate structure, corner oxygen atom of basic unit is shared by other tetrahedra, resulting in formulas such as SiO_4^{4-}, $Si_2O_7^{6-}$, $Si_3O_9^{6-}$, etc. The repeating unit of 2-D sheet or layered structure is represented as $Si_2O_5^{2-}$. Such layered structures are characteristics of clays and other minerals.

2.5.3 Carbon

Carbon is not really a ceramic, but one of its allotropic form, diamond may be considered as a ceramic. *Diamond* has very interesting and even unusual properties such as:
- possesses diamond-cubic structure (like Si, Ge)
- consists covalent C-C bonds
- having highest hardness of any material known
- very high thermal conductivity (unlike ceramics)
- transparent in the visible and infrared, with high index of refraction
- semiconductor (can be doped to make electronic devices)
- meta-stable (transforms to carbon when heated)

Synthetic diamonds are made by application of high temperatures and pressures or by chemical vapor deposition. Future applications of this latter, cheaper production method include hard coatings for metal tools, ultra-low friction coatings for space applications, and microelectronics.

Graphite, another allotropic form of carbon, has a layered structure with very strong hexagonal bonding within the planar layers (using 3 of the 3 bonding electrons) and weak, van der Waals bonding between layers using the fourth electron. This leads to easy inter-planar cleavage and applications as a lubricant and for writing (pencils). Graphite is a good electrical conductor and chemically stable even at high temperatures. Applications include furnaces, rocket nozzles, electrodes in batteries, etc.

Recently (1985) discovered allotropic form of carbon is the C_{60} molecule, also known as *fullerene* or *bucky-ball* (after the architect Buckminster Fuller who designed the geodesic structure that C_{60} resembles.). Structure of this form resembles a hallow spherical cluster of 60 atoms, and is found to consist of 20 hexagons and 12 pentagons where no two pentagons share a common edge. Fullerenes and related structures like nanotubes are exceptionally stiff, strong, and ductile. Future applications of fullerenes are as a structural material and possibly in microelectronics, due to the unusual properties that result when fullerenes are doped with other atoms.

2.5.4 Imperfections in ceramics

Imperfections in ceramics include point defects and impurities. Their formation is strongly affected by the condition of charge neutrality (creation of unbalanced charges requires the expenditure of a large amount of energy). Both vacancies and interstitials are possible in ceramics as in metals; however as ceramics have more then one element these defects can be associated with each of these elements. Neutral charge defects include the Frenkel and Schottky defects. A *Frenkel-defect* is a vacancy- interstitial pair of cations

(placing large anions in an interstitial position requires a lot of energy in lattice distortion). A *Schottky-defect* is a pair of nearby cation and anion vacancies.

Non-stoichiometry refers to a change in composition so that the elements in the ceramic are not in the proportion appropriate for the compound (condition known as stoichiometry). To minimize energy, the effect of non-stoichiometry is a redistribution of the atomic charges. Introduction of impurity atoms in the lattice is likely in conditions where the charge is maintained. This is the case of electronegative impurities that substitute lattice anions or electropositive substitutional impurities. This is more likely for similar ionic radii since this minimizes the energy required for lattice distortion. Defects will appear if the charge of the impurities is not balanced.

2.5.5 Mechanical response of ceramics

Brittle Fracture of Ceramics: The brittle fracture of ceramics limits their engineering applications. It occurs due to the unavoidable presence of microscopic flaws (micro-cracks, internal pores, and atmospheric contaminants) that result during cooling from the melt. The flaws need to crack initiation, and crack propagation (perpendicular to the applied stress) is usually trans-granular, along cleavage planes. The flaws cannot be closely controlled in manufacturing; this leads to a large scatter in the fracture strength of ceramic materials.

Under compressive stresses, however, flaws do not associate with amplification of stress. Hence, the compressive strength of ceramics is typically ten times to their tensile strength. This makes ceramics good structural materials under compression (e.g., bricks in houses, stone blocks in the pyramids), but not in conditions of tensile stress, such as under flexure.

Plastic deformation in crystalline ceramics is by slip, which is difficult due to the structure and the strong local (electrostatic) potentials. There is very little plastic deformation before fracture. Non-crystalline ceramics, like common glass, deform by viscous flow (like very high-density liquids) as deformation can not occur by slip because of absence of regular atomic structure, which occurs in metals. Characteristic property of viscous flow, viscosity, is a measure of non-crystalline material's resistance to deformation. It was found to decrease with increasing temperature. At room temperature, the viscosity of many non-crystalline ceramics is extremely high.

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