
UNIT 15 SPECIAL MATERIALS

Structure

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15.1 INTRODUCTION

So far you have learnt about metals and semiconductors. As you know, there is another class of solids, called insulators, which are characterised by very low electrical conductivity. Some familiar examples of insulators are mica, glass, porcelain, alumina. These are used in electrical appliances and installations. From PHE-07 course you may recall that oxide based insulators exhibiting electrical polarizing properties (dipoles) are called *dielectrics*. These are used in capacitors. The insulating materials possess some very interesting properties like electrical dipole moment, optical activity, mechanical deformation etc., which can be controlled externally by electric field, voltage, temperature etc. With advances in the field of materials science, many novel materials with interesting properties have been developed in recent years. You will learn about some such special materials in this unit.

The materials, which generate electrical signals when external pressure is applied on them are called **piezoelectrics**. Application of electrical signals to these materials induces a change in their physical dimensions. The materials showing change in the electrical properties with change in temperature are called **pyroelectrics**. You will learn the properties of piezoelectric and pyroelectric materials in Sec. 15.2. Some materials are known to exhibit spontaneous electrical polarization. These are called **ferroelectrics** and you will learn about these in Sec. 15.3. The most commonly used man-made materials are the plastics. These belong to a class of carbon containing materials made of chains of organic compounds called **polymers**. You will learn about them in Sec. 15.4.

Sec. 15.5 is devoted to **liquid crystals** which exhibit the property of electrical polarisation and as the name suggests, they occur in fluid form. In recent years, a new branch of materials called **nano-structures** has come into existence. These are made of a cluster of tens to hundreds of atoms. These materials are characterised by completely new properties. A detailed discussion on these is given in Sec. 15.6. The oxide based hard insulating materials used as heat and electrical resistants are called **ceramics**. Other commonly used silicon oxide based material for manufacturing optical components of various physics devices as well as for every day household items is **glass**. A glass is a supercooled liquid and has no definite crystal structure. Pre-stressed glasses have peculiar properties, which lend their use in wind screens in vehicles. You will learn the characteristics of these materials in Sec. 15.7.

Objectives

After studying this unit, you should be able to:

- list important properties of piezoelectric, pyroelectric, ferroelectric materials, polymers, liquid crystals, nano-structures, ceramics and glasses;
- state distinguishing characteristics of special materials;
- explain the physics governing the properties of special materials; and
- describe the applications of special materials.

15.2 PIEZOELECTRICS AND PYROELECTRICS

A crystal whose response to external impulse depends on direction is said to be *anisotropic*.

The piezoelectric crystals are also referred to as *piezo-crystals*.

Naturally occurring large single crystals of quartz are found in Brazil. Now, quartz crystals of large size and high purity are grown artificially.

We all know that insulators do not conduct electricity. However, when a potential difference is applied across some insulating materials, they show change in their physical dimensions. On the other hand, while working with anisotropic crystals of quartz, tourmaline and rochelle salt, P. Curie and J. Curie observed that electric charges developed across them when pressure was applied. This is called **piezoelectric effect**.

The most commonly used piezoelectric material is quartz. Chemically, quartz is silicon dioxide (SiO_2) crystallized in the trigonal trapezohedral form (Fig. 15.1a). Note that z-axis is the axis of three fold rotational symmetry. This crystal structure of quartz is known as the α -phase and is very stable at room temperature.

A quartz crystal can be cut into slabs with different orientations which are identified by the axis perpendicular to the face of the slab. Fig. 15.1b shows a *x*-cut quartz slab, which develops mechanical deformation in *x*-direction when voltage is applied along the *x*-axis.

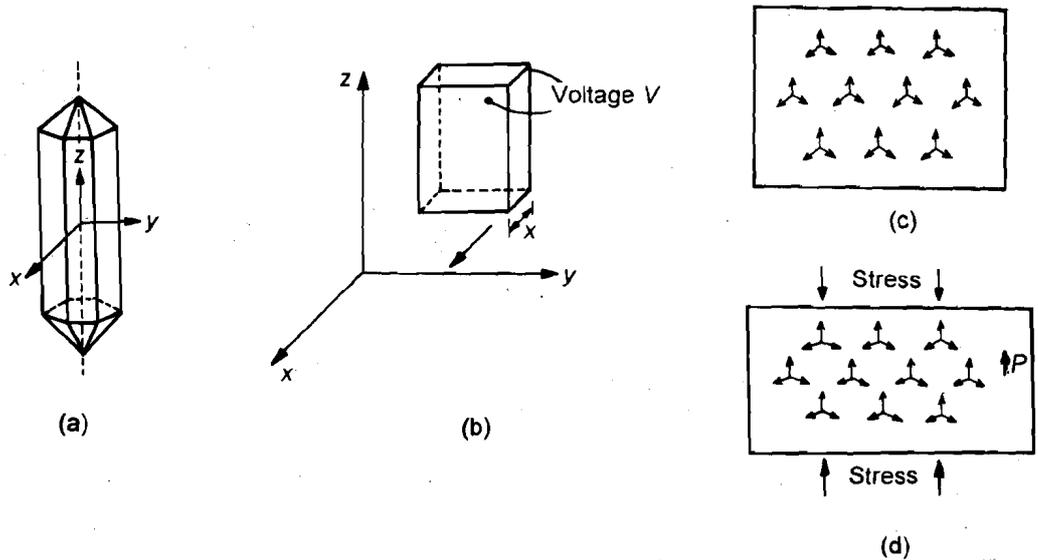


Fig.15.1: a) Crystal of quartz; b) *x*-cut slab of quartz; c) no dipole is evident when there is no stress in SiO_2 molecule; and d) electric dipole across SiO_2 molecule under mechanical pressure

If a quartz crystal is mechanically stressed, it become electrically polarized and charges appear at its opposite faces. The genesis of piezoelectric effect lies in the polar nature of molecules, i.e. the molecules of piezo-crystals have electric dipole property. The bonding in SiO_2 molecule is a mix of covalent and ionic bonds. It means that the electron shared by Si and O tends to be more attached to O atom and shifts the negative charge towards O. Now refer to Fig. 15.1c. When there is no stress, the SiO_2 molecules do not show any dipole moment since all 4 Si-O bonds are symmetrically

placed. But when this molecule is stretched (or compressed), as shown in Fig. 15.1d, there is a resultant dipole moment due to displacement of Si atom with respect to O atoms.

To understand this process better, let us take one more example. Barium Titanate (BaTiO_3) is a piezo-crystal and possesses electrical dipole even under no stress condition. The unit cell of BaTiO_3 has one Ba^{2+} , one Ti^{4+} and three O^{2-} ions. They are arranged in the *perovskite* structure (Fig. 15.2).

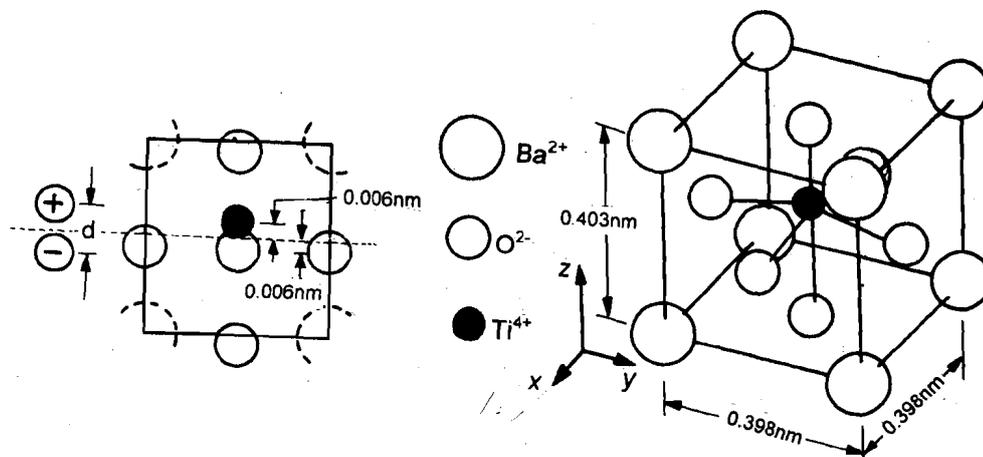


Fig. 15.2: BaTiO_3 crystal structure

This structure is basically an fcc lattice in which barium ions occupy eight corners, oxygen ions occupy the centre of the six faces and the body centre is occupied by titanium ion. This structure is tetragonal at room temperature and changes into a cubic structure above 393 K.

In the cubic state, the central Ti^{4+} ion is slightly (by 0.006 nm) shifted with respect to the centre determined by the O^{2-} ions in the face centre positions. That is to say that centre of positive charges (determined by Ti^{4+} and Ba^{2+} ions) and the negative charge centre (determined by O^{2-} ions) do not coincide. The displacement of Ti^{4+} gives rise to an electric dipole in the crystal. Note that the displacement can be in any direction; here we have shown it in positive z -direction. When we apply a potential difference along the direction of displacement (z -in this case), the dipole length as well as the crystal dimension in z -direction change. However, applying p.d. along x and y direction produces no significant change in crystal dimensions. This reveals the anisotropic nature of piezo-electric crystals. The axis along which piezoelectric effect is observed is called *piezo-active axis*.

Conversely, when some pressure is applied on the crystal along the dipole direction, the dipole length changes due to physical movement. Since the electric dipole moment is proportional to dipole length d , change in d results in change in the dipole moment and potential difference develops across the crystal.

Note that BaTiO_3 crystal has dipole moment even under normal conditions but in crystals like quartz, dipoles appear only under stressed condition. So we can say that *the only condition for piezoelectricity is that the crystal should possess anisotropic charge distribution*.

You may now like to answer an SAQ.

SAQ 1

Does BaTiO_3 crystal possess inversion symmetry? Justify your answer.

Electric dipole moment $p = Qd$, where Q is the charge and, d is the dipole length

Spend
2 min.

Materials and Devices

Resonance occurs when the frequency of the applied signal is equal to the natural frequency of the piezo-crystal. The mechanical vibrations then have maximum amplitude.

So far we have seen that application of p.d. across a piezoelectric crystal leads to generation of dipoles. What will happen if we apply an alternating emf across the faces of a piezoelectric bar? The answer to this question is: It may vibrate selectively at its (characteristic) resonant frequency determined by its structure. Since resonance occurs at a well defined frequency, such crystals are used as reliable frequency sources in digital watches or computer clock cycle generators. Piezo-crystals are also used as transducers to convert mechanical energy into electrical energy in appliances such as microphones, gramophone pick-ups, etc.

You will appreciate that piezoelectric effect can be used for controlling the dimensions of a solid. Does that mean that by applying variable voltage, it is possible to vary the length of a solid specimen? The answer to this question is affirmative but you must note that the changes are only a few microns. However, in advanced applications like robotics, where control of movement at micron level is needed, piezoelectric devices are very useful.

You now know that in piezoelectric materials electric charges develop when mechanical pressure is applied; and you may ask whether or not there are some solids which show the same effect under the influence of any other physical quantity? This question is quite logical. Crystals like lithium niobate and barium titanate develop charges across their faces when they are subjected to heating or cooling. These are known as *pyroelectric* materials. (Lithium niobate (LiNbO_3) shows pyroelectricity at room temperature.) The pyroelectric crystals inherently possess non-zero dipole moment. Addition of thermal energy induces thermal expansion in these crystals. As a result, inherent dipole moment becomes prominent and charges appear across the crystal. These crystals have very limited symmetry elements. You can convince yourself by referring to the unit cell structure of BaTiO_3 shown in Fig. 15.2. Apart from absence of the centre of inversion, as in case of piezo-crystals, the rotational axis can be only along the direction parallel to the dipole direction. Also, there are no mirror planes perpendicular to this direction. A pyroelectric crystal can be used as a temperature transducer that generates voltage across it, depending upon its temperature.

In piezoelectrics and pyroelectrics, mechanical pressure and thermal energy (temperature) respectively induce polarization effects. Do you know that some crystals possess spontaneous dipole moment? Such materials are called *ferroelectrics*. You will learn about these materials in the following section.

15.3 FERROELECTRICS

The name *ferroelectrics* is not very appropriate as ferroelectrics very rarely contain iron ions.

In Unit 13 of this course, you have learnt that ferromagnets show spontaneous magnetisation. Similarly, there are several dielectric crystals which show spontaneous electric polarization. Such crystals are known as **ferroelectrics**. (In a sense, ferroelectric materials form a subgroup of pyroelectric materials.) In a ferroelectric material, the direction of the spontaneous polarization can be reversed by applying an electric field. To understand this phenomenon, refer to Fig. 15.3. It shows a crystal of BaTiO_3 subjected to an external electric field. The polarity of the field is indicated by an arrow. The Ti^{4+} ion is displaced in $+z$ direction (Fig. 15.3a). As polarity is reversed (Fig. 15.3b), Ti^{4+} ion shifts in the opposite direction, reversing the polarity of the dipole. The ferroelectric materials show electric hysteresis loops, similar to magnetic hysteresis in ferromagnets. This is depicted in Fig. 15.4. The hysteresis loop in ferroelectric materials arises due to electric domain structure. When electric field E is applied, the electrical polarization P increases (path $O-A$). When E is reduced, the polarization follows the path $A-B-C$ instead of retracing the path $A-O$. So to take the specimen to zero dipole moment condition, additional electric field E_0 has to be applied. (This is analogous to the coercive field in ferromagnets.) By reducing the field further, negative polarization can be achieved. The area under $P-E$ curve signifies ferroelectric hysteresis loss.

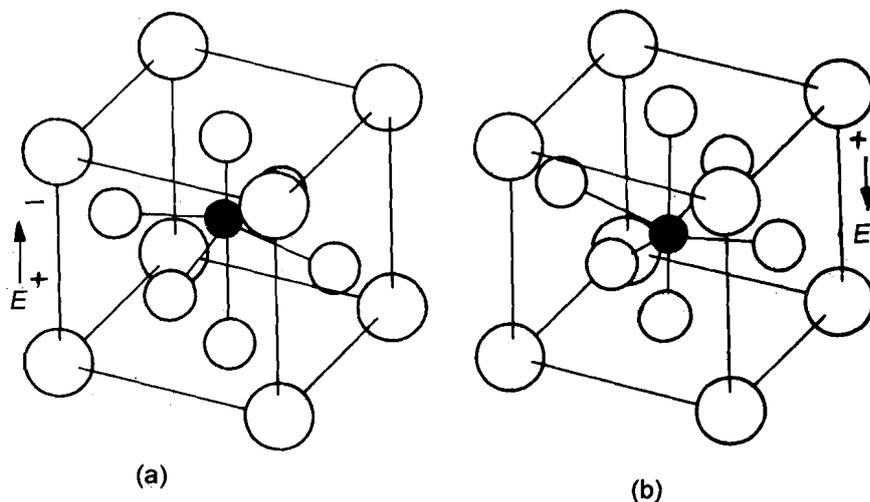


Fig.15.3: Ferroelectric effect in BaTiO_3 : a) with forward polarity; and b) with reversed polarity

The ferroelectric materials have a transition temperature called *ferroelectric Curie temperature* (T_c) above which spontaneous dipole moment is lost. Materials in such a state are called *paraelectric*. Can you correlate the term? It is analogous to paramagnets.

The ferroelectric interaction is thought to be due to interaction amongst neighbouring dipoles. This dipole interaction falls off relatively slowly with distance (as $1/r$) and is independent of the angle between the axes of the dipoles. Some of the important ferroelectric substances are the ionic crystal barium titanate (BaTiO_3) and lead titanate (PbTiO_3). The Curie temperatures for BaTiO_3 and PbTiO_3 are 393 K and 763 K,

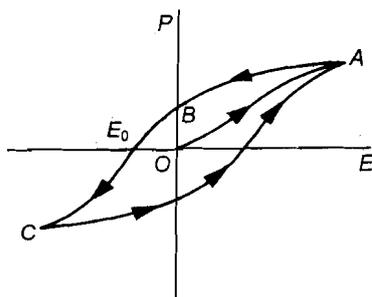


Fig.15.4: Ferroelectric hysteresis loop

respectively. Above the Curie temperature, the crystal structure of BaTiO_3 is cubic. Below 393 K, in the ferroelectric state, it converts into tetragonal structure by slight lengthening of the c -axis i.e. $a = b \neq c$. When the temperature is lowered to 273 K, the tetragonal structure deforms to become orthorhombic and at 183 K another phase transformation from orthorhombic to rhombohedral takes place. But in these phases, the material remains ferroelectric in nature.

Ferroelectric domains

In ferroelectric materials, a domain structure develops so as to attain minimum free energy state of the crystal. This is shown in Fig. 15.5. The ferroelectric domains, also called *Weiss domains*, are areas of local dipole alignment with an associated net dipole moment and net polarization.

Domains are separated from one another by domain walls. These domain boundaries are usually described through the angle between the domains that they separate. In Fig. 15.5, the domain structure is shown with dark lines representing 90° domain walls. In the presence of electric field, the domains align themselves along the direction of the field, increasing the dipole moment in this direction.



Fig. 15.5: Ferroelectric domains

The physical basis of ferroelectricity can be understood on the basis of *Curie-Weiss law*. According to this law, we can mathematically express the dielectric constant of an isotropic dielectric material above Curie temperature by the relation

$$\epsilon = \alpha + \frac{\beta}{T - T_c}, \quad (15.1)$$

where α and β are temperature independent constants. T is the temperature of the specimen and T_c is Curie temperature. From Eq. (15.1) it is clear that as temperature of the specimen approaches T_c (from the higher side), $\epsilon \rightarrow \infty$. This causes a sudden structural transition at $T = T_c$. Below T_c , the new structure persists with spontaneous polarization.

Note that all ferroelectric materials are piezoelectric but all piezoelectrics are not necessarily ferroelectric. For example, BaTiO_3 can be easily reoriented by reversing field polarity but due to covalent nature of bonding, the dipole moment of quartz can not be reversed by electric field reversal. Since these materials can be polarized by external electric field and retain the dipole moment, they are useful as dielectrics in capacitors. You may recall that in a capacitor, charges accumulate across the capacitor depending on the direction of electric field (voltage) applied to it.

Before we introduce you to *polymers*, we would like you to answer an SAQ.

Spend
2 min.

SAQ 2

What distinguishes piezoelectrics from ferroelectrics?

15.4 POLYMERS

Polymers are made of long chain structured organic molecules. We are familiar with plastics and textile fibres, which find so varied applications in our everyday life. These materials consist of natural (e.g. cellulose) or synthetic (e.g. nylon) polymeric substances. The word polymer is made of two words: *poly*+*mer*. In Greek *poly* means many and *mer* means a unit. So a polymer stands for several units joined together. A polymer is a macromolecule, which is generally described in terms of its *monomer* structural unit. Fig. 15.6a shows a typical monomer unit which joins together to form a polymer (Fig. 15.6b).

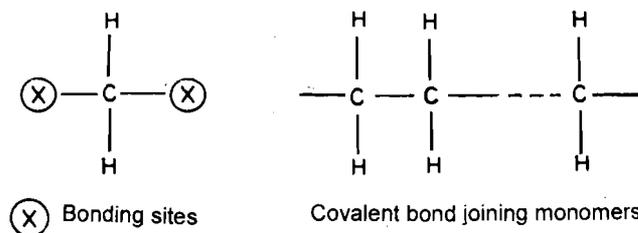


Fig. 15.6: a) A monomer structural unit; and b) a polymer molecule

The structural units in a polymer molecule are groups having two or more bonding sites and linked to one another through covalent bonds. These units may be joined in a variety of ways; from simple to very complicated. The most straightforward type of polymer is linear with units connected to one another in a chain-like arrangement such as $X-M-M-M-Y$. In general, the simplest polymer can be denoted as $X-(M)_n-Y$, where M is a *structural unit* or *monomer*; and X and Y are *terminating structures* called *end groups*. Here, n denotes the *degree of polymerization* (D.P.), which specifies the number of repeating monomers in a chain. The molecular weight of a chain molecule is obtained by multiplying D.P. with the molecular weight of the monomer. Molecular weights of chains typically range from 10^4 to 10^5 u. Since the

chain of structural units is terminated on either end by terminating structures, the structural units must be at least bivalent (two bonding sites) and the end groups X and Y monovalent (one bonding site). The end groups may be identical or different.

Note that the structural unit in a polymer can even be trivalent or polyvalent. Such polymers have non-linear or branched structures. Fig 15.7 shows a typical branched polymer. Polymer molecules can be interconnected to have a network structure in planer form or in a three-dimensional space.

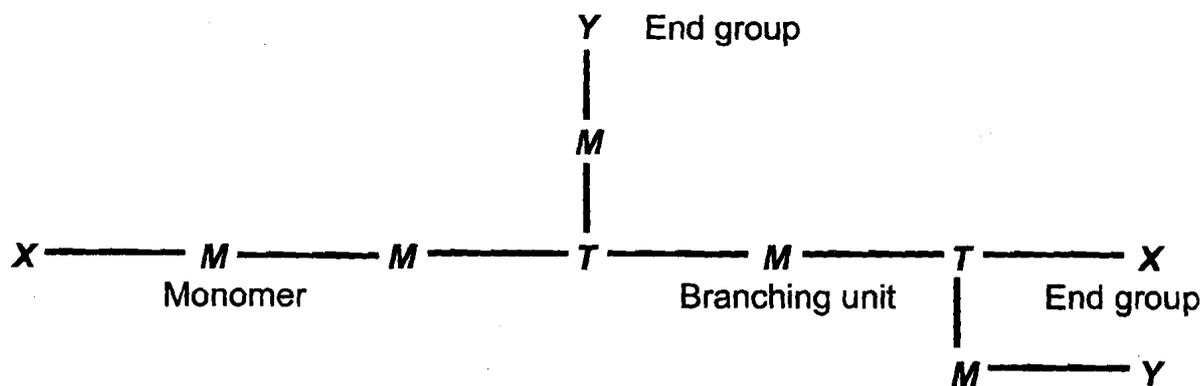


Fig.15.7: Schematics of a typical branched polymer

Due to covalent bonding in structural units, normally polymers act as insulators. However, doping of polymers with some metallic atoms in the structural units can allow us to achieve desired electrical conductivity. This offers possibilities of developing polymer based devices, just like semiconductor devices.

15.4.1 Classification

Polymers are classified mainly on the basis of their structure, temperature dependent behavior and mechanism of polymerization. On the basis of structure, polymers are categorized as *plastics*, *fibres*, and *elastomers*.

In *plastics*, the branched polymer molecules are randomly oriented. So a plastic polymer has no directional property, unless it has been mechanically worked in such a way as to align the chains.

Fibres have a high degree of polymerization and form long chain molecules. Since all the chains are more or less aligned in the same direction, fibres have unique directional properties. Their strength and modulus of elasticity in the direction of the fibre length are an order of magnitude larger than those in the transverse direction. Fibres are used in synthetic textiles like nylon, rayon etc. Protein molecules, which form backbone of the living world, also have fibre structure.

Elastomers are non-crystalline polymers with three dimensional space network. They have high resistance to plastic deformation. These find wide use in motor car tyres, packaging materials, etc.

Based on the temperature dependent behaviour, polymers may be classified as *thermoplastics* and *thermosets*. *Thermoplastic* polymers are long chain molecules held together by weak cross-links, called secondary bonds. As temperature increases, secondary bonds begin to break. That is why thermo-plastics soften at higher temperatures and harden at lower temperatures and are easily mouldable. In fact, high plasticity is one of the technologically attractive properties of thermo-plastics since it allows shaping of the materials in any desired form. However, these are unsuitable for high temperature applications. Polystyrene and polyethylene are familiar examples of thermoplastics.

Thermosets have a three dimensional network of primary bonds and polymerization occurs in all directions. These are therefore relatively hard and rigid at room

temperature. On moderate heating, they may become harder due to completion of any left-over polymerization reaction. If heated to the melting temperature, they decompose owing to their reaction with atmospheric oxygen. Bakelite used for electrical appliances, epoxies used in adhesives are thermoset polymers.

Yet another criterion for classification of polymers is based on polymerization mechanism. The polymer forming processes are classified as *addition polymerization*, *condensation polymerization* and *co-polymerization*.

In *addition polymerization* process, the monomer units combine together to form a polymer with the same empirical formula but higher molecular weight. Polyethylene is the best known example of addition polymerization. We illustrate it in Fig. 15.8. Ethylene molecule has a double bond necessary for chain formation. During polymerization, the double bond opens up to form two single bonds as shown in Fig. 15.8a. The monomers are bonded together end-to-end in a polymerization reaction (Fig. 15.8b).

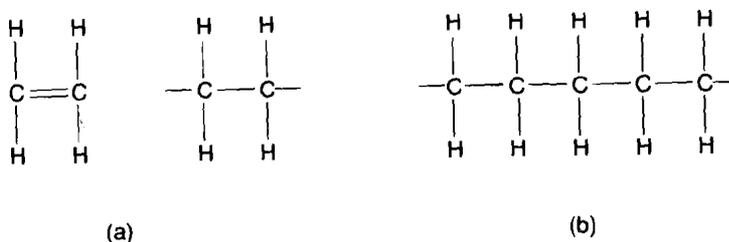
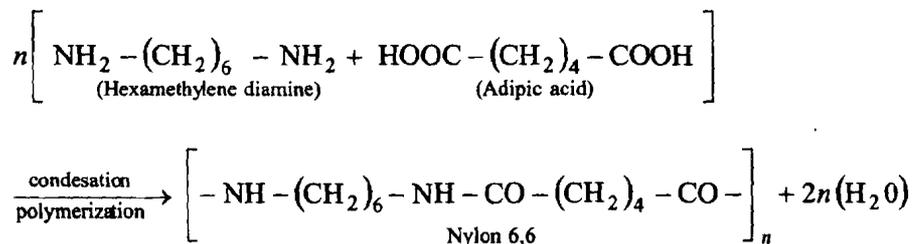
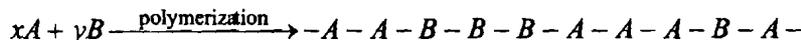


Fig.15.8: a) Ethylene double bond breaks during polymerization; and b) formation of polymer chain of ethylene

In *condensation polymerization*, the combination of monomer units is accompanied by generation of some small molecule. For example, nylon 6,6 is formed by combining the molecules of hexamethylene diamine and adipic acid with evolution of two water molecules:

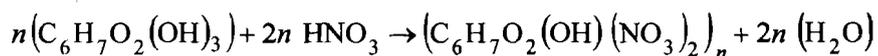


In *co-polymerization*, a long chain polymer consisting of at least two types of monomers is formed. The sequence of the monomers in this case may be regular (alternate) or irregular as shown in the following reaction:

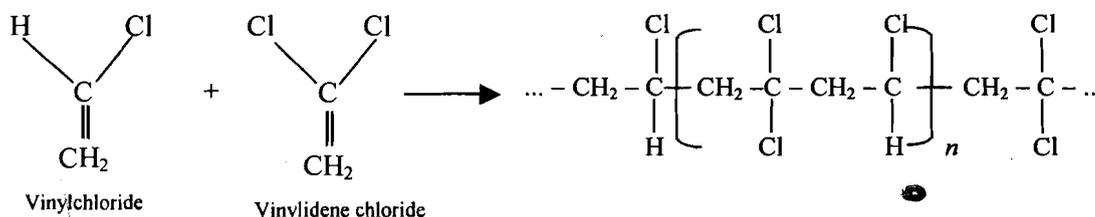


Before proceeding further, you may like to answer an SAQ.

(i) The formation of cellulose dinitrate polymer follows the reaction given below:



(ii) *Saran* used in food wrapping materials is formed in the following reaction:



Classify these reactions.

We hope that you now understand how a long chain polymer is formed starting from a monomer. Now we consider the structure of polymers.

15.4.2 Structure, Crystallinity and Stability

Again refer to Fig. 15.8. You will note that in polyethylene, each carbon atom is *tetrahedrally bonded* to four neighbours in sp^3 hybridized bonding with bond angle $109^\circ 28'$. Polyvinyl chloride or PVC plastic used for pipes, sheets etc. and polystyrene used for synthetic fabric are very commonly used polymers in daily life. Fig. 15.9a and c show monomers of PVC and polystyrene and Fig. 15.9b and d show schematics of PVC polymer chain and polystyrene, respectively.

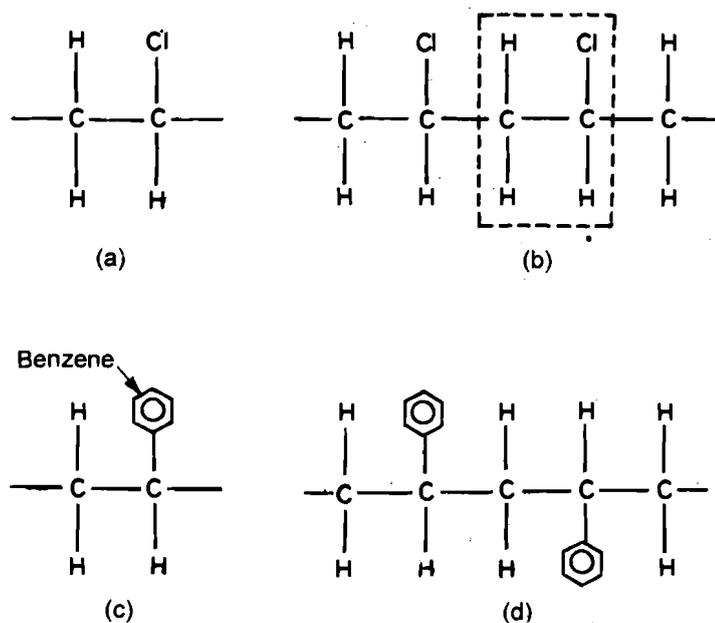


Fig.15.9: a) Vinyl chloride monomer; b) polyvinyl chloride chain; c) styrene group; and d) polystyrene

Polymers are in amorphous or semicrystalline form. That is, the chains in the polymer are either randomly oriented (Fig. 15.10a) or some chains are oriented parallel to each other and embedded in an otherwise amorphous polymer lattice, as shown in Fig. 15.10b. It is also possible to grow single crystals of a polymer. In the non-crystalline form, the long chains are randomly entangled with one another. In the semicrystalline form, parts of the polymer volume have parallel chain arrangement, while other parts are randomly oriented. The single crystals have a folded chain

structure, where the same chain folds back and forth many times into a parallel arrangement as shown in Fig. 15.10c.

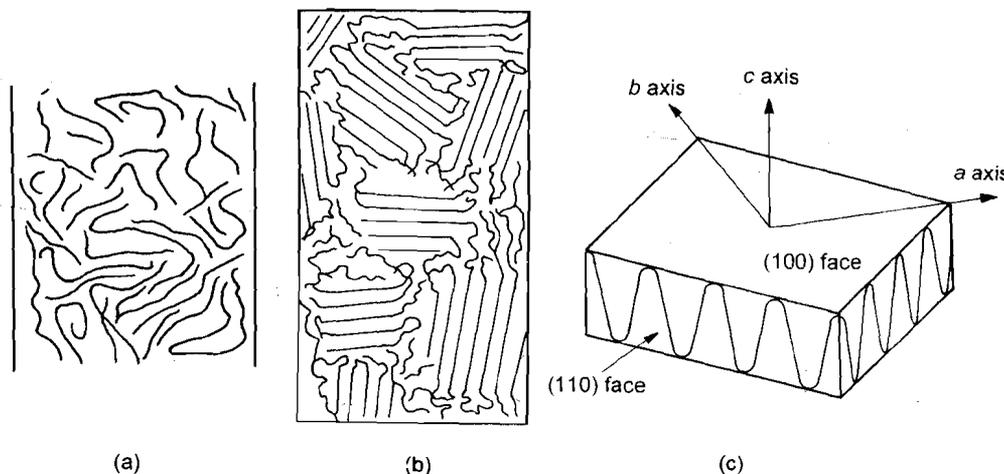


Fig.15.10: a) Amorphous polymer; b) semicrystalline polymer; and c) crystalline polymer

In all polymers, the long chains can be aligned to some extent by mechanical working. Such an alignment promotes crystallinity. As the chains are more closely packed in the crystalline form, the density increases with increasing alignment of the chains.

The polymers are prone to losing long chain structure due to temperature. To appreciate the significance of this statement fully, let us reconsider how polymers are synthesized. To synthesize a polymer, we need *monomers*, *initiator* (which starts the polymerization reaction) and *stabilizer* (which stabilizes the polymeric product). Organic polymers, both natural and synthetic, dissociate due to the ageing process which mostly involves oxidation. To counter balance this process, an agent that prevents or slows down oxidation is added. It means that most stabilizers are *antioxidants*.

Having learnt the generic characteristics of polymers, we now study *liquid crystals*, a class of polymers that shows very interesting ordering behaviour under applied voltage.

15.5 LIQUID CRYSTALS

The term liquid crystal is used to describe materials which exhibit a crystal-like ordered structure but are fluid in nature. These consist of rod shaped molecules of organic materials which have permanent dipole moment and can orient themselves parallel to each other. The elongated nature of molecules gives them anisotropic optical properties, i.e. refractive index and optical polarizability of liquid crystals are direction dependent. The orientation of liquid crystal molecules can be altered by external parameters like temperature, electric field, magnetic field etc. Hence by changing one of these parameters, it is possible to alter the orientation of the molecules and have different optical behaviour.

Liquid crystals are used for display devices in calculators, digital meters, lap-top computer screens, flat television screens etc. The peculiar behaviour of liquid crystals was first discovered by Reinitzer in 1888 when he observed that solid cholesteryl benzoate melts into a turbid liquid at 418.5 K and turns into a clear liquid when heated to 451.5 K. The ordered clear phase of such materials is called *mesophase*.

The structure of a liquid crystal can be considered to be made of various layers; each layer corresponding to a plane of molecules. In any one plane, all the molecules are aligned parallel to each other but the inter-molecular distance may not be same over

the whole area. Also, in any two adjacent planes, molecules may or may not be aligned parallel to each other. These features are schematically shown in Fig. 15.11.

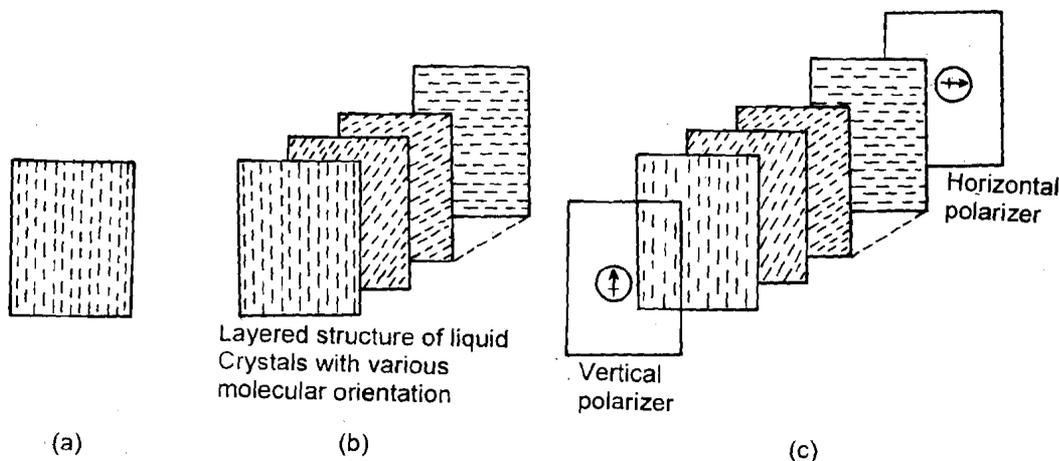


Fig.15.11: a) A typical plane in a liquid crystal; b) molecules in different planes of a liquid crystal are differently aligned; and c) a liquid crystal display

When light polarized parallel to the first layer orientation is incident on a liquid crystal, its plane of polarization rotates each time it passes through a different plane because of different molecular orientations. If you refer to Fig. 15.11b and consider that light polarized in vertical direction enters the crystal, it will emerge out with polarization in the horizontal direction. If two polarizers – vertical in front and horizontal at the back – are placed around the liquid crystal, as shown in Fig. 15.11c, the light passing through the first vertical polarizer will emerge from the horizontal polarizer. But if the orientation of molecules in the liquid crystal changes, the plane of polarization of emerging light will not be horizontal and the second polarizer will not allow this light to pass with the result that we get a dark display.

Since liquid crystal molecules have dipole moment, they orient themselves parallel to the applied field direction. That is to say, their natural orientations are disturbed when an electric field is applied. As soon as electric field is removed, the molecules reorient themselves along their original direction. This fact is used in liquid crystal displays. The transparent electrodes of varied shapes are used in these displays. In Fig. 15.12, a 7-segment display used for depicting numbers is shown. Depending on the number to be displayed, appropriate electrode segments are powered, and we can see a number displayed as black on clear background. For example, to display number 2, the segments *a*, *f*, *g*, *c* and *d* need to be powered. In watches and calculators, we use a reflector below the plane of displays as ambient light falling on them from top has to be reflected. In a car radio display, the reflector is replaced by a light source on the back side, so that the segments of the display appear black on the lighted background.

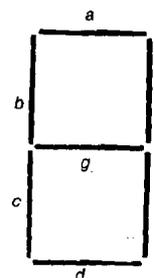


Fig.15.12: 7-segment display

You must have noted here that by applying an emf to the liquid crystal display, we can reorient their molecular orientation. Since no significant current flows through the circuit, there is very little power consumption. So liquid crystal displays can be used where limited power is available, as in case of battery powered equipments.

You may now like to answer an SAQ.

SAQ 4

The liquid crystal displays cannot be seen in a dark room. Why?

Having learnt about technologically applicable form of organic molecules, we now get into the world of ultra small entities called *nano-structures*. A lot of interest has been generated by these materials in recent years because of their immense high-tech applications. You will now discover the reasons.

Spend
2 min.

15.6 NANO-STRUCTURES

Nano-structures have dimensions of the order of 10^{-9} m.

Nano-structures are clusters of a few (10 to 1000) atoms of a material. Though their structure within the cluster matches the crystal structure of the bulk material, they are devoid of long range ordering in their arrangement. Because of this, the electronic band structure, optical absorption and magnetic behaviour of nano-structures are completely different from those of the bulk. Moreover, since dimensions of nano-structures are comparable to atomic dimensions, many of the quantum mechanical phenomena are observed easily in these. For example, the electronic structure of nano-structures shows discrete nature confirming quantum well model. Electrons migrate via tunneling action, as predicted by quantum mechanics. For this reason, nano-structures are also termed as *quantum structures*. A nano-structure with nano-scale lengths in all three dimensions is called *quantum dot*. If the structure is such that its diameter is of nano-scale dimensions while the length is in microns, it constitutes what is called *quantum wire*.

Since it is very difficult to keep a cluster of such small number of atoms together in a stable state, and once formed these materials are expected to be immune to undesired reaction with atmospheric constituents, production of nano-structures is a technologically challenging task. However, because of their significant applications, this is one of the latest and most fertile area of research and many industries are interested in it. One of the most obvious applications of nano-structures is in compactness of circuit dimensions. The integrated circuit components which so far had dimensions of a few microns can now be built at nano-scale. Even a single molecule can be used as an electronic switch so that the number of devices per unit volume of the integrated circuit chip can be enormously increased. Another major application of nano-structures is in medicine. A very selective drug delivery can be achieved by encapsulating the drugs in small quantities in nano-structure form. Such small drug capsules can be delivered at the precise position, like the site of a tumor. This avoids undesired effects (of the drug) on other parts of the body. Since the drug can be administered in the appropriate area, the amount of drug required is also very small. The nano-structures can also be used in the form of tiny machines or robots (called nanobots) to perform mechanical jobs at molecular level. This has promising applications in genetic engineering.

Various methods have been developed to obtain nano-structures. A detailed discussion is beyond the scope of this course. However, for brevity, we now discuss some of these in brief.

- In **bottom up method**, carefully controlled chemical reactions are used to assemble atoms and molecules into quantum dots with dimensions between 2 to 10 nm. If necessary, these dots are capped by organic molecules to avoid reaction with atmospheric constituents. Fig. 15.13 shows a typical quantum dot

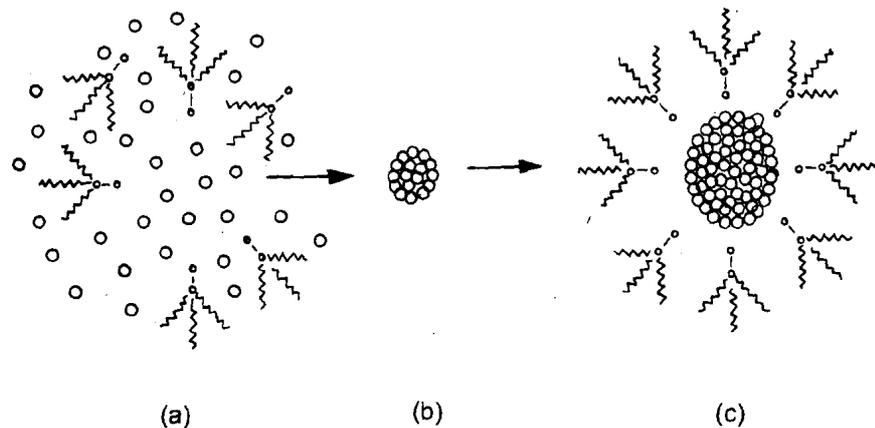


Fig.15.13: A typical quantum dot assembly: a) metal ions and organic molecules are brought together by chemical reaction; b) metal ions assemble together to form a nucleus which grows into a quantum dot; and c) when nano-structure reaches its optimum size, its surface is coated with organic molecules in a stable packing

assembly where controlled chemical reactions bring together metal ions and organic molecules and bind them to form a nano-structure.

The chemical route is fairly cost-effective since sophisticated instruments are not required. However, this method cannot lead to designed, interconnected patterns of quantum dots. These structures are normally in a powder form and are useful in biological/medical applications; however these are of little help in designing electronic devices and microchips.

- **Scanning probe method** of nano-structure fabrication employs special *atomic forceps* to pick individual atoms and place them together in required pattern. However, to sustain such a structure, a rigid support is necessary. Also, this method is very time consuming since every atom is individually picked and placed. Moreover, this method is very expensive, since atomic forceps require very sophisticated instrumentation.
- **Photolithography** is commonly used to manufacture microelectronic circuits. A little modification makes it useful for production of nano-structures. In this

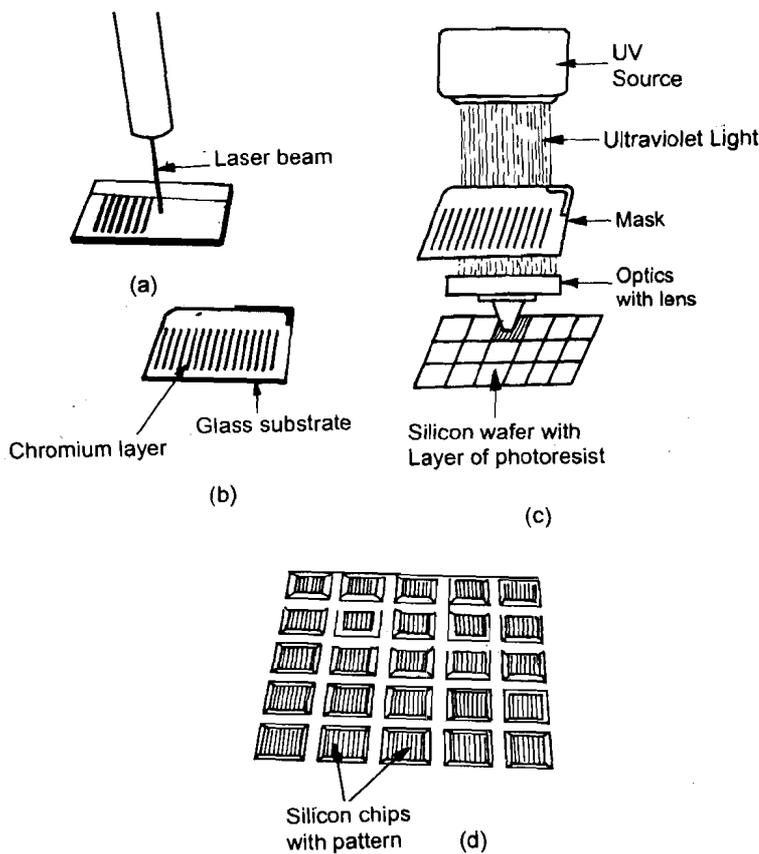


Fig.15.14: Photolithography process for nano-structure fabrication

process, a beam of light *writes* the circuit pattern on a glass plate covered with chromium and a light-sensitive polymer is on top (see Fig. 15.14a). The polymer is removed from the regions where light falls, exposing chromium, which is removed by etching process. The remaining polymer is then removed by chemical dissolving. The result is a mask of the pattern written on the glass plate by the light beam (Fig. 15.14b). Now this mask is placed over a silicon wafer covered with photo resist. When ultraviolet light (with wavelength 100 nm) is concentrated through this assembly, the light passes through the pattern etched on chromium coated glass plate and reacts with the photoresist on silicon wafer (Fig. 15.14c). The exposed parts of photoresist are then removed and replication of pattern in miniature form is obtained on the silicon wafer (Fig. 15.14d).

Note that the patterns obtained using this technique cannot be smaller than the wavelength of ultraviolet light used. If X-rays or electrons with wavelengths 0.1 nm to 10 nm are used, the nano-structures can be fabricated. This method has the obvious advantage that we can generate desired patterns of nano-structures by using appropriate masks.

We hope that you have enjoyed studying about the fascinating world of nano-structures. Now you will learn about various oxides with high electrical resistivity. Depending on their constituents and structure, they are either termed as *ceramics* or *glasses*.

15.7 CERAMICS AND GLASSES

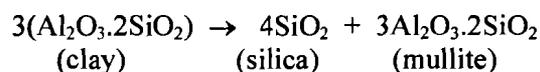
You may be familiar with porcelain ceramics used as electrical insulators between high voltage points in domestic power distribution, power transmission, etc. Ceramics do not conduct heat and are also used in furnaces and ovens, crockery, etc. Ceramics are dielectric materials with silica (SiO_2), alumina (Al_2O_3) and magnesia (MgO) as basic components. The ceramics are either grown from the melt or by mixing powdered constituent materials. In powder method, the mixture of constituent compounds in proper proportion is first compressed into a compact shape and then this piece is subjected to *sintering*. This thermal processing initiates a reaction between the constituent materials to form a strong ceramic piece. In some cases, the process of simultaneous compression and heating, called *hot-pressing*, is used. During the formation of a ceramic from the constituent materials, it is possible that some chemicals are released in gaseous form and thrown out. The escaping gas gives rise to porosity in some ceramics. Porcelain ceramics contain appreciable amount of potash (feldspar: $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$).

Sintering is heating of a mixture of chemicals to form bonds and result into a single complex compound.

The components of insulating porcelain are:

Feldspar ($\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$) ~ 35%
Dehydrated talc ($2\text{MgO} \cdot 4\text{SiO}_2$) ~2%
Dehydrated clay ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) ~38%
Raw silica ~25%.

During preparation, ceramics are subjected to heat treatment where clay decomposes into mullite and silica according to the reaction



and the final microstructure consists of silica particles embedded in glassy matrix that contains fine crystals of mullite.

There are different types of glasses, which find applications in optical components due to their specific optical properties like refractive index, wavelength dependent radiation absorption coefficients, etc. In everyday life, glass is used in windows, containers, lenses and filters which are rigid and transparent in the visible spectral region. They are based on silica (SiO_2) or various silicates.

Glass is a random three dimensional network of silica. It is a supercooled solidified form of silica based material without any crystal structure. The glasses do not have a fixed melting point but they soften at elevated temperatures.

The basic structural unit in silica based materials is a tetrahedron, as shown in Fig. 15.15a. Note the position of silicon. It is located at the centre with oxygen at the corners of the tetrahedron. This geometry is a natural result of four sp^3 hybrid orbitals of Si. Four oxygen atoms get bonded with four sp^3 hybrid bonds of Si. In this process, each oxygen atom shares one electron from Si per bond. Since oxygen is divalent, it needs one more electron to complete its outermost valence shell. For this purpose, each oxygen atom binds with one more Si atom, which in turn is bound to three other oxygen atoms. When each tetrahedron shares corner oxygens with other tetrahedra, they are arranged randomly, resulting in a network structure of silica glass or vitreous silica (Fig. 15.15b).

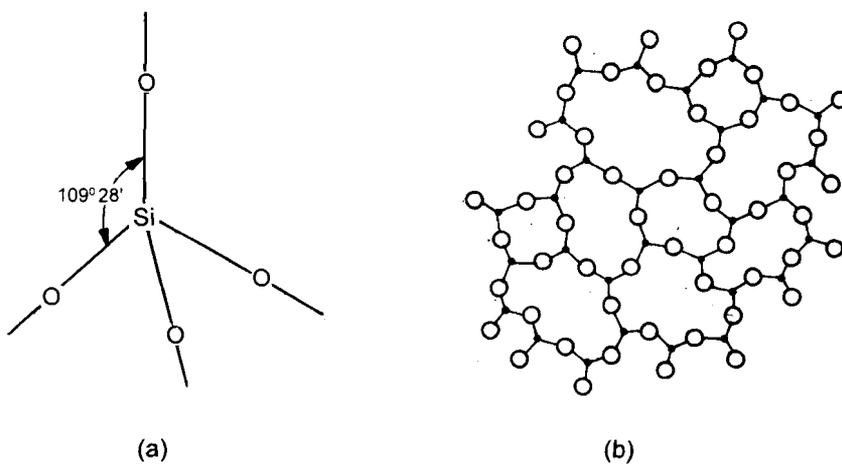


Fig.15.15: a) Basic unit in silica based materials; and b) amorphous net of SiO_2 glass in 2-D

The exact composition of glasses depends on their specific applications. In general, glasses contain oxygen, silicon, boron and aluminium. Table 15.1 lists some of the common glasses and their compositions.

Table 15.1: Some technically important glasses

Type	Typical composition (wt.%)	Characteristics
Soda-lime-silica glasses		
(a) Window glass	72% SiO_2 –14% Na_2O –9% CaO –4% MgO –1% Al_2O_3	Relatively low melting temperature; relatively high coefficient of thermal expansion
(b) Container glass	73% SiO_2 –15% Na_2O –5% CaO –4% MgO –2% Al_2O_3 –1% K_2O	
High-silica glass		
(a) Vitreous silica	>99.5% SiO_2	Relatively high melting temperature; very low coefficient of thermal expansion; chemically resistant.
(b) Vycor	96% SiO_2 –4% B_2O_3	
Borosilicate glasses (Pyrex)	80.5% SiO_2 –13% B_2O_3 –3.8% Na_2O –2.2% Al_3O_3 –0.5% K_2O	Chemical and heat resistant; intermediate coefficient of thermal expansion
Lead glasses (Light flint optical glass)	54% SiO_2 –37% PbO –8% K_2O –1% Na_2O	Low softening temperature; high density; high refractive index.

You can see from this table that in addition to SiO_2 , different glasses contain varying amounts of other oxides. These help to change or modify the basic properties of the glass. These oxide additives are called *modifiers* because they interrupt the basic (Si-O in silica glass) network as illustrated in Fig.15.16.

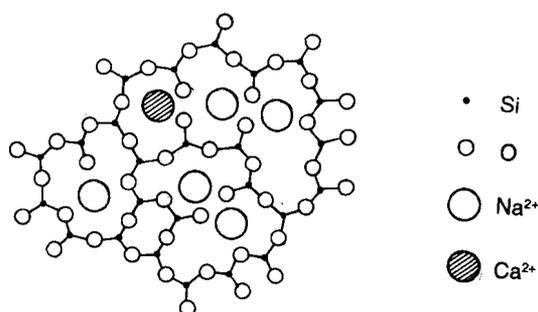


Fig.15.16: Soda-lime glass with interrupted silica networks

Addition of oxides such as Na_2O , K_2O or CaO in silica significantly lowers the softening temperature of glass. Common window and container glasses contain soda (Na_2O), lime (CaO) and silica. These are manufactured at a relatively lower temperature. Apart from SiO_2 , both B_2O_3 and GeO_2 have tetrahedral structural units and meet the conditions for being network formers. Borosilicate glasses are formed by heating silica with boric oxide.

When heated, glasses soften gradually and do not melt abruptly like crystals. In fact, glass is a liquid which has been cooled rapidly in a manner that the atoms do not get a chance to rearrange themselves before their motion is arrested. The viscosity of glass is very high. Upon cooling, the viscosity increases further. If sufficient time is allowed, the atoms may tend to adopt more symmetrical and more stable crystalline structure even in the highly viscous state. The process of crystallization from a solid glass is called *devitrification*. The crystalline SiO_2 network structure is shown in Fig. 15.17.

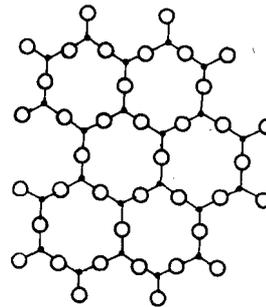


Fig.15.17: SiO_2 crystalline network of devitrified silica glass

Glasses behave like isotropic medium for visible light. This is due to randomness of their structural arrangement. The refractive index of glass also depends on its previous history. If a glass is stressed, preferred orientation occurs in the immediate vicinity of the induced strains resulting in local anisotropy. If a glass were pre-stressed (by heating followed by rapid cooling), the randomness of its structure allows it to absorb considerable amount of strain without breaking. Such pre-stressed glasses, developed recently, are remarkably strong. In addition, when such glasses are subjected to an abrupt impact, they break into a large number of tiny particles, instead of large pieces. This property of pre-stressed glasses makes them ideal for application in wind screens of vehicles, which are prone to receiving impact in accidents.

Let us now summarize the salient features of some special materials.

15.8 SUMMARY

- **Dielectrics** are oxide based insulating compounds.
- **Piezoelectric** materials undergo change in physical dimensions when voltage is applied across them. Charges appear across a piezoelectric crystal when it is subjected to pressure.
- **Pyroelectric** materials are used as temperature transducers.
- **Ferroelectric** materials show spontaneous electrical dipole moment.
- **Polymers** are organic chain compounds with large molecular weights. They are formed by combining many basic molecular units, called **monomers**.
- **Liquid crystals** exhibit a crystal like structure but are fluids. These are made of rod shaped organic molecules possessing dipole moment. These are used in the display devices due to their peculiar electro-optical properties.

- **Nano-structures** are clusters of a few atoms. They have very different properties than the bulk materials due to the small dimensions. Quantum phenomena are experimentally observed in these materials. Methods like chemical route, scanning probe and lithography are used to obtain nano-structures. These materials find wide applications in areas ranging from genetic engineering to electronic circuits.
- **Ceramics** are electrically and thermally insulating compounds essentially made of silica, alumina and magnesia.
- **Glasses are super cooled liquid structures** consisting of silica. They have very high viscosity, high electrical resistivity and optical transparency in the visible region.

15.9 TERMINAL QUESTIONS

Spend 20 min.

1. The CH_3Cl molecule exhibits dipole moment. If the displacement between its positive and negative charge centres is 0.1\AA , calculate the dipole moment per molecule.
2. What is polymer degradation?
3. The band structure is not observed in nano-structures. Discuss.
4. Soda lime glasses have low softening temperature. Comment.

15.10 SOLUTIONS AND ANSWERS

Self-Assessment Questions

1. The BaTiO_3 crystal is an anisotropic crystal. In case of inversion symmetry, there must exist a point in the crystal, around which we can symmetrically invert the structure i.e. for every point (x, y, z) there must exist an identical point at $(-x, -y, -z)$ so that interchange between these points does not alter the crystal structure. Now, since the positive and negative centres in BaTiO_3 unit cell do not coincide, there is no unique point around which inversion can result in an identical structure.
2. Piezoelectric materials generate dipole moment when mechanically stressed while ferroelectrics exhibit dipole moment by application of potential difference across them. Ferroelectrics are subset of piezoelectrics. Piezoelectrics are used as transducers whereas ferroelectrics are used as dielectrics in capacitors.
3. The reaction process to form (i) cellulose dinitrate is condensation polymerization and (ii) *saran* is copolymerization.
4. Liquid crystals are not light generating devices, but they just modify the light falling on them. Hence, in dark ambience, these displays are ineffective.

Terminal Questions

1. The dipole moment

$$p = Qd$$

In case of CH_3Cl molecule, there are 26 electrons. Hence total charge on the molecule, Q , is $26 \times (1.6 \times 10^{-19})\text{ C}$.

Since $d = 0.1\text{\AA}$, the polarization,

$$p = 26 \times (1.6 \times 10^{-19}) \times 0.1 \times 10^{-10}$$
$$= 42 \times 10^{-30} \text{ C m.}$$

2. The polymers are formed by bonding of monomers together. If due to certain conditions like temperature, pressure, chemical reactivity etc., the bonds in polymers break, the polymer does not retain its original properties. This is known as degradation of polymer.
3. Due to very small number of atoms and lack of long range ordering in the atomic arrangement of nano-structures, the collective contribution of atoms in forming energy bands is not possible. That is why electronic states are of discrete nature and not band like.
4. In soda-lime glass, the SiO_2 network is broken due to sodium and calcium ions embeded in the matrix. This weakens the glass structure and it can soften at low temperatures.