Chapter-I

INTRODUCTION

Glass is perhaps the oldest synthetic thermoplastic material known to man Scientific study of glass began in the early part of this century (Zachariasen (1932, 1935), Warren and Loring (1935), Hagg (1935)) Glasses of a wide variety of compositions and properties have been prepared over the years Various techniques have been used to obtain glassy materials Renewed interest in the study of glasses has improved our understanding of these materials Their technological applications have multiplied manifold during the past decade or two (Hilton and Jones (1966), Ovshinsky (1979)

Solids in general, can be classified into two groups-crystalline solids and non–crystalline solids Non-crystalline or amorphous solids possess only short range order without any long range order A glass may be defined as an amorphous solid which exhibits a glass transition (Elliot 1990)

Due to the absence of a periodic lattice, for an amorphous solid, no reciprocal lattice exists Consequently, the phonon or electronic states cannot be described in terms of dispersion curves However, we can define 'density of states' of phonons and electrons

1.1 METHODS OF PREPARING GLASS

For a long time, it was thought that only a relatively restricted number of materials could form amorphous solids, on solidification from melt Those special

materials were called glass forming solids Turnbull and Cohen (1958, 1960) argued that all liquids could form glass on solidification if crystalline nucleation is suppressed In olden days, rapid quenching of melt was the only method of preparing glass However, several methods are now available to prepare glassy substances Some of these methods are discussed, in brief, below

1.1.1 Melt-quenching Method

In this method, the material is heated to liquid state and then cooled to undergo liquid-solid transition The rate of cooling is critical in the glass formation Materials which can be prepared in amorphous form fall into three groups There are materials which readily form glass on solidification In such cases, slow cooling (cooling rate 10^{-4} to 10^{-1}K/sec) is adequate for the melt to form a glassy solid SiO_2, As_2S_3 etc are the typical examples Some materials such as selenium require a more rapid cooling (moderate cooling rate $\sim 10^1$ to 10^2K/sec) for the melt to solidify into the glassy state However, a large percentage of materials generally form crystalline solids when the melt is cooled through liquid-solid transition temperature To get them in the glassy state, it is essential to develop rapid cooling techniques (10^5-10^8K/sec) Using these techniques, many liquid metals have been quenched into metallic glasses Roller quenching falls into this category In this technique a fine filament of the melt is allowed to fall on a rotating copper disc/roller Glass is obtained in the form of ribbons A modification of this method used two copper

rollers with a small gap between them, rotating in opposite directions (Lakshmikumar 1980)

1.1.2 Sol-gel Method

This is a non-melting method for the preparation of glasses It is also a recent method (Dislich (1971)) In this method, a viscous solution is formed using the required material and a suitable liquid The sol is allowed to form a semi-solid material called 'gel' by a process of continuing polymerization Finally, this homogeneous and amorphous gel is converted into glass by sintering This method is discussed in detail in Chapter-II

1.1.3 Thermal Evaporation

This method is widely used to produce amorphous thin films The method involves the vaporization of the starting material either by heating or by bombardment with high energy electrons and the vaporised material is collected on a cold substrate, under high vacuum conditions The atoms on reaching the cold substrate get 'frozen' in random positions due to their low mobility The problem of differential evaporation encountered in this technique (when multicomponent material is used) is overcome to some extent by allowing the powdered sample to fall on a heated ribbon so that instantaneous evaporation takes place The properties of the film thus obtained, may vary depending on (a) the substrate temperature (b) the separation and the relative orientation of source and substrate (c) gas pressure in the chamber

(d) impurities from the filament/boat and desorbed gases from the walls of the chamber and (e) the temperature of the filament/boat Films of amorphous Ge, Si, chalcogenide materials etc can be prepared by this method

1.1.4 Sputtering

The principle of this method is to bombard a target material with high energy ions from a low pressure plasma, so that the atoms from the surface of the target are ejected These atoms are allowed to be deposited on a cold substrate to form an amorphous film of the material of the target

This method is particularly suitable to get a multicomponent amorphous film because the sputtering rates for different elements (contained in the multicomponent target) do not appreciably vary A further advantage of this method is to introduce a sputtering gas which chemically reacts with the target Using this modification, chosen additives can be incorporated into the amorphous film The properties of the amorphous film depend on factors like sputtering gas pressure, RF power applied to the target and the bias voltage of the target of the substrate Films of amorphous Si, Ge, chalcogenide glasses and amorphous metals can be produced by this method

1.1.5 Glow Discharge Decomposition

Doped thin films of amorphous materials are produced by this method In this method, a reactant gas or its mixture with a carrier gas is introduced into the chamber The plasma is produced by an RF field Depending on the prevailing conditions such as the pressure of gas, temperature of substrate etc , the gas may undergo either glow discharge polymerization or glow discharge decomposition The amorphous film is deposited on a substrate placed in the plasma For example, using a mixture of SiH_4 and H_2O at low pressure as the reactant gas, a film of amorphous SiO_2 can be obtained

In general, the characteristics of the film depend on the gas pressure and temperature, the ratio of reactant gas to the carrier gas, gas flow rate, geometry of the chamber, substrate position, RF power, coupling method of RF power to plasma, substrate bias and temperature

1.1.6 Chemical Vapour Deposition

This method also involves decomposition of vapour as in glow discharge decomposition process A substrate is heated to high temperature (~1000K) by an RF field The vapour decomposes on the substrate and an amorphous or polycrystalline film is deposited It is the thermal energy which decomposes the vapour Film of hydrogenated silica have been deposited by this technique using SiH_4 vapour

1.1.7 Other Methods

Using solutions of the desired material, amorphous films can be deposited on the cathode by the process of electrolysis For example, electrolysis of $GeCl_4$ in glycol gives amorphous Ge films deposited on the cathode However, contamination from the solution and reaction products is difficult to avoid It is found that the precipitate formed during chemical reactions is amorphous in some cases For example, on passing H_2S gas through a solution of As_2O_3 in dilute HCl comes out as precipitate Films of amorphous SiO_2 can also be obtained by the anodic oxidation of Si Amorphous SiO_2 can also be produced by the oxidation of Si with dry oxygen or steam Using this method, films of silicate systems can also be formed by making use of appropriate electrolytes

Bombardment of crystalline solids by neutrons, high energy ions and electrons produces crystal defects When the concentration of defects becomes large, crystal-amorphous transition takes place This transition can also take place if a crystal is exposed to shock waves (which produce intense pressure and temperature rise)

1.2 GLASS FORMERS AND MODIFIERS

Zachariasen's (1932) work on oxide glasses was the first to throw light on the structure of glass According to him, only those materials whose internal energy in the amorphous state is slightly larger than that in the crystalline state, readily form glasses Since the internal energy is related to the structure, it suggests

that structures of crystalline and amorphous states are similar This means, an irregular network of atoms could be constructed by incorporating variations in bond angles, dihedral angles and bond lengths Zachariasen's conclusions are summarised in the form of Zachariasen's rules These rules were later modified so that they could be applied to oxide glasses containing non-glass forming oxides also

The modified rules are as follows (Elliott 1990)

1   A high proportion of cations are surrounded by oxygen tetrahedra or triangles

2   The oxygen polyhedra only share corners with each other

3   Some oxygen atoms are linked to only two cations, and do not form additional bonds with any other cations

These rules however are not applicable to non-oxide glasses

It was pointed out by Goodman (1975) and Wang and Merz (1976) that the likely candidates for glass formers are those which exhibit polymorphic modification in the crystalline state

Philips (1979) argued that the glass forming tendency is maximum when the number of mechanical constraints, due to interatomic forces, experienced by each atom is equal to the number of degrees of freedom possessed by it Thus, a system with higher co-ordination number (larger number of constraints) do not easily form glass Using the valence force field model, he could predict the expected co-ordination number for binary alloys, to form glass

It was found that for a two-component system, compositions around the eutectic favours glass formation

1.3 GLASS TRANSITION

During a liquid to solid transition, crystallization involves substantial atomic re-arrangement and rupture of bonds Sun (1947) suggested that materials in which atoms are connected by strong bonds are less likely to form crystals on solidification Rawson (1967) pointed out the ease of glass formation is determined by bond strengths and thermal energy at the melting point T_m Thus, at the eutectic composition where T_m shows a sharp dip, the thermal energy is not able to break the bonds As a result, glass formation is favoured These simple criteria however were found to be applicable to materials where only one type of bonding exists

The volume-temperature curve of the liquid-solid transition is shown in the (fig 1 1) The crystallization is accompanied by an abrupt change in the volume at T_m, the melting point, whereas the liquid-glass transition occurs by a gradual change in volume in a narrow temperature range The liquid-glass curve shows that the liquid supercools before solidifying The curve shows no discontinuity but there exists a change in the slope at the transition However, the change of slope is gradual and takes place over a range of temperature The average of this range is termed as glass transition temperature T_g Furthermore, T_g is not unique for a given material but depends on the rate of cooling Slower the cooling, lower is T_g The transition temperature can be lowered by tens of degrees in
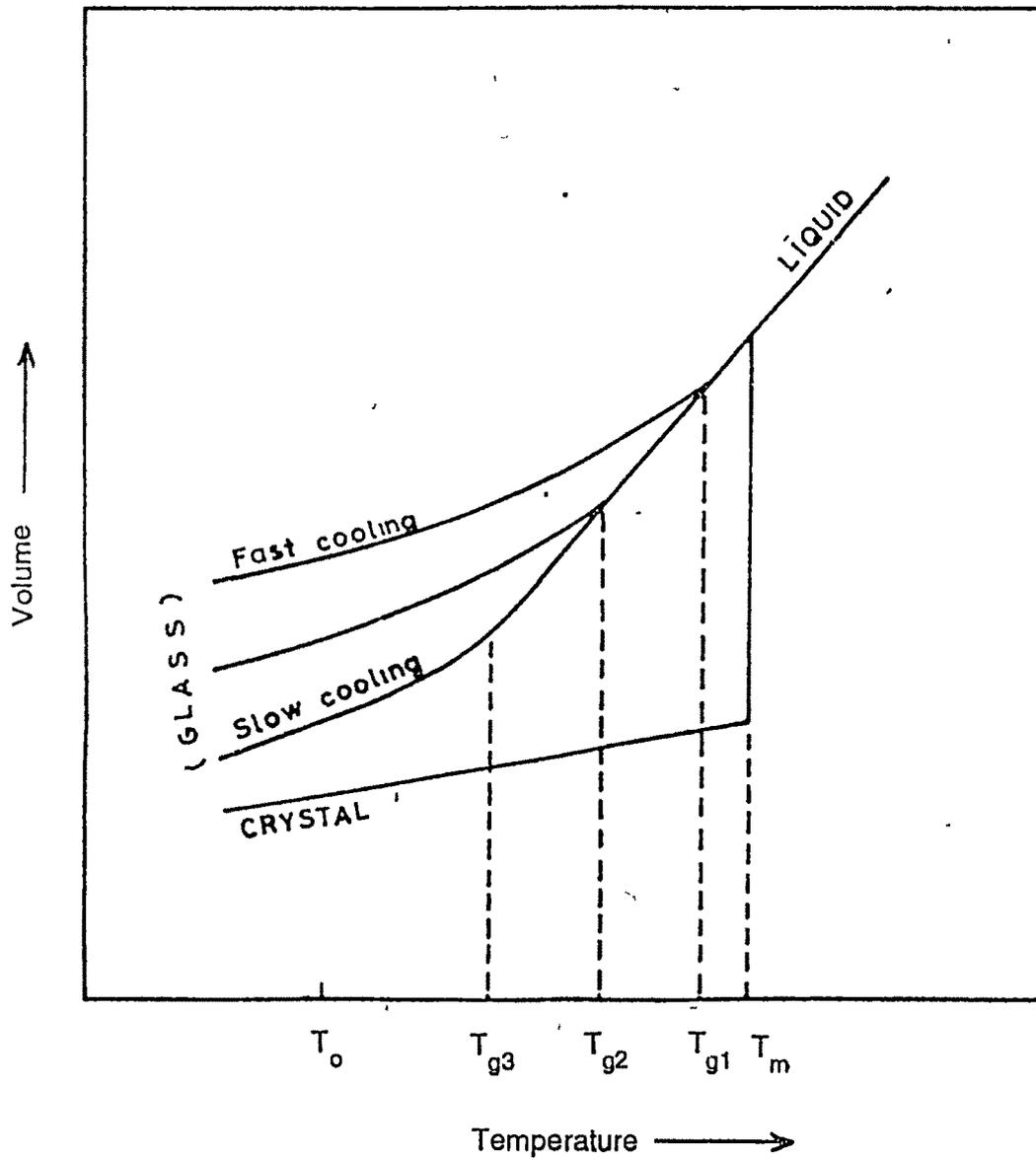
Fig. 1.1. Schematic diagram of the variation of volume with temperature when a liquid is cooled through liquid- crystal and liquid-glass transition temperatures.

this manner Such a large variation in T_g suggests that the glass transition is not a genuine thermodynamic phase transition Kauzmann (1948) had argued that T_g cannot be reduced indefinitely and it has a lower limit called the ideal glass transition temperature Thus, glass samples of the same material but of different thermal history (different methods of glass preparation, rates of cooling etc) may exhibit properties which differ from one sample to another

The thermodynamic variables like volume, entropy, enthalpy etc are continuous through T_g but their derivatives such as thermal expansion coefficient, compressibility and heat capacity are found to be discontinuous Thus, the liquid-glass transition resembles a second order thermodynamic transition

The glass transition is closely related to the relaxation processes as the temperature of the supercooled liquid decreased The configurational changes that cause the relaxation of the supercooled liquid becomes slower as the temperature decreases If the time of observation t_o is long compared to the relaxation time τ_r, the material behaves like a liquid and if $t_o << \tau_r$ it behaves like a solid The transition is said to occur if liquid-like parameters differ significantly from solid-like parameters Thus transition occurs when $t_o \sim \tau_r$

An alternative definition of T_g is that, the transition occurs at a temperature when the liquid attains a viscosity $\sim 10^{13} P$. Viscosity does not show any discontinuity at T_g

1.4 STRUCTURE OF AMORPHOUS SOLIDS

In amorphous solids, the atomic arrangement is irregular However, in a length scale of a few interatomic distances, the atomic distribution is non-random Thus, the short range order in amorphous solids is not zero Of the many probes used to study the structure, X-rays occupy a dominate place

1.4.1 X-ray Diffraction

The powder photograph of a crystalline solid contains sharp circles whereas that of an amorphous solid has diffused haloes The atomic distribution in a non-crystalline solid can be represented by a distribution function The simplest is the pair distribution function $g(r)$ It corresponds to the probability of finding another atom at a distance r from the centre of an atom (chosen as origin atom) The relationship between $g(r)$ and atomic distribution is shown in fig (1 2) As the atoms come closer than the core atomic diameter, $\lim_{r \to 0} g(r) = 0$ At larger distances atomic correlation vanishes so that

$$\lim_{r \to 0} g(r) = 1$$

Another function which is frequently used in the structural study of amorphous solids is the radial distribution function (RDF)

$$J(r) = 4\pi r^2 \rho_0 \, g(r) \qquad\qquad \longrightarrow (1\ 1)$$

where ρ_0 is the average number-density of atoms (fig 1 3) This function corresponds to the number of atoms in a spherical shell of radius r For large values of r, RDF approaches the average density parabola $4\pi r^2 \rho_0$
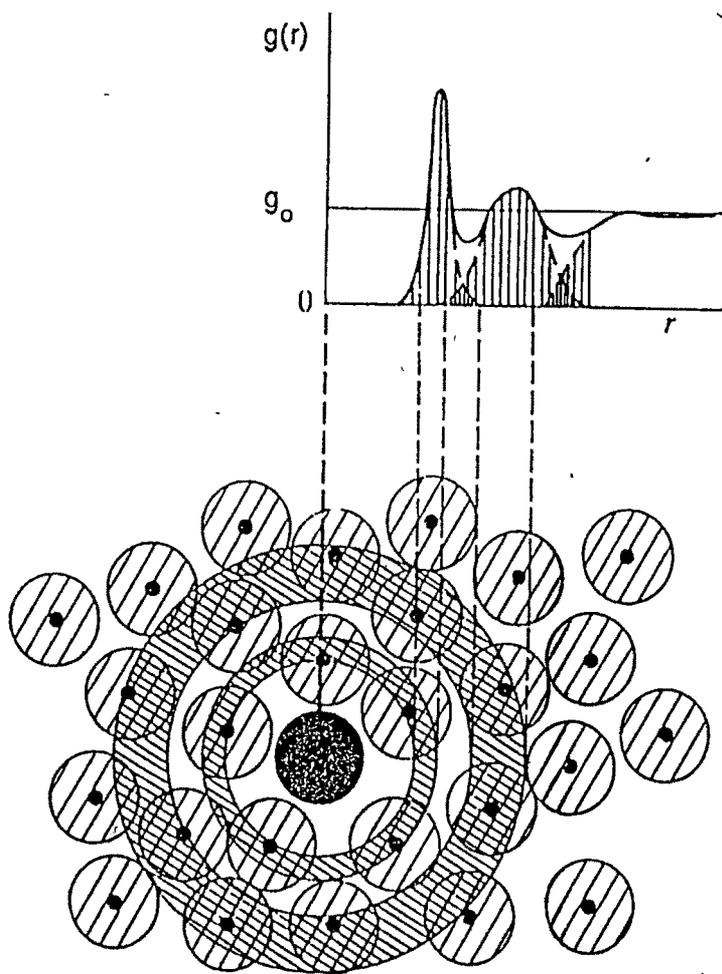
Fig. 1 2   Schematic diagram showing relationship between the pair distribution function g(r) and the distribution of atoms around an arbitrarily chosen atom.
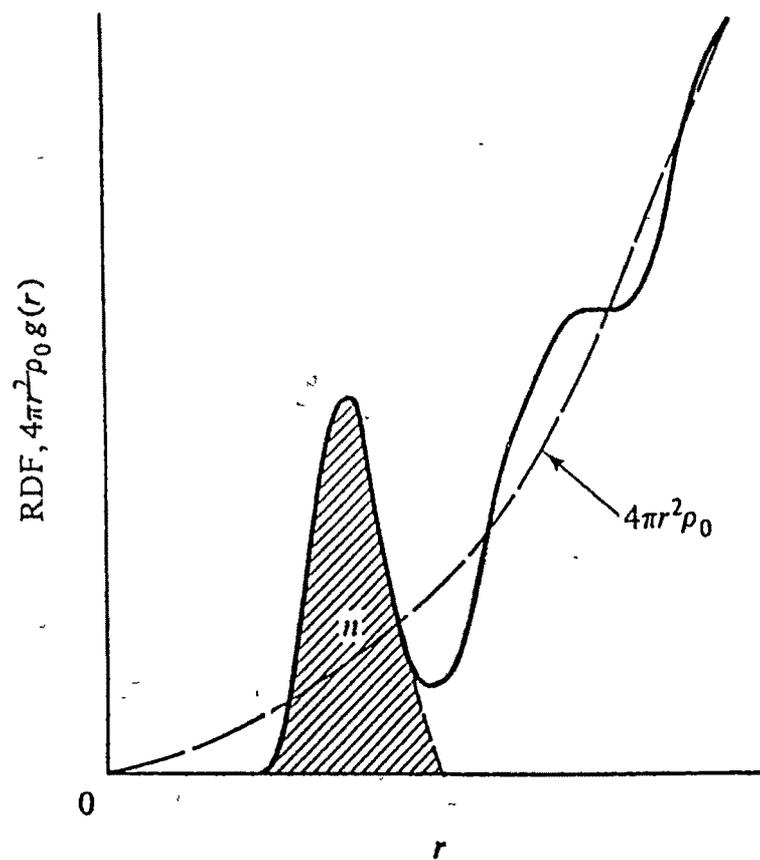
Fig. 1.3: Schematic diagram of radial distribution function.

If a shell of radius between r_1 and r_2 is chosen the average number of atoms within it gives the co-ordination number (fig 1 3)

$$n = \int_{r_1}^{r_2} 4\pi r^2 \, \rho_o \, g(r) \, dr \qquad \longrightarrow (1\ 2)$$

'n' is estimated from the area under the peak The position of the first peak gives the average distance R_1 of the nearest neighbours The second peak corresponds to the average distance R_2 of second neighbours and so on The average bond angle,

$$\theta = 2\sin^{-1} \frac{R_2}{2R_1} \qquad \longrightarrow (1\ 3)$$

There are other methods which help us in the structural study of glass These are briefly discussed below

1.4.2 Nuclear Magnetic Resonance (NMR) Technique

NMR is observed in systems having non-zero nuclear spins The NMR spectra exhibit sharp peaks in them From the peak positions and relative intensities of the peaks it is possible to obtain information about which atoms are bonded together, co-ordination numbers, nearest neighbours and so on

1.4.3 Visible and UV Spectroscopy

Information on the local structure of amorphous materials can be obtained by UV and visible spectroscopy Spectroscopically active materials like transition metal compounds or heavy metal cations

like Tl^+ Pb^{2+} etc have been added to the raw material and their spectra are recorded From the nature of the spectrum, the co-ordination numbers can be deduced and hence, the presence of such sites in the glass structure can be detected The spectra of *species* such as Pb^{2+} are sensitive to the degree of covalent character in the bonds between a Pb^{2+} ion and the neighbouring anions

1.4.4 IR and Raman Spectroscopy

IR and Raman spectroscopy provide useful information about the structure of amorphous solids The various bands present in the IR and Raman spectra correspond to covalently bonded linkages such as hydroxyl groups, trapped water, SiO_2 etc and these bands throw light on the different types of structural linkages such as linear, square, planar or octahedral

It was found that IR and Raman spectroscopy are very useful tools in the study of chemical and structural changes occurring during the gel to glass transformation (see for example Bertoluzza et al (1982) Kusabiraki (1987))

1.4.5 Neutron Diffraction

The structure determination using this technique is similar to X-ray diffraction technique, but it has some advantages Neutron diffraction technique can be used to study magnetic structure of matter A recent neutron diffraction technique called the pulsed method gives

much more rapid data collection and it can be used to study the short time relaxation phenomena when the samples are subjected to pulsed magnetic fields In the study of matter containing light atoms like hydrogen, scattered intensity of X-rays is weak whereas hydrogen scatters neutrons strongly Thus, neutron diffraction can be used to locate light atoms, especially hydrogen in hydrides, hydrates and organic structures The study of inelastic scattering of neutrons gives information about phonons and interatomic forces However, the main difficulty is that the neutron sources are available only at nuclear installations For this reason, both X-ray and neutron diffraction results can be used to get the maximum information about the structure of solids

1.5. GLASS MODELS

The structural information of glasses obtained from the diffraction techniques is limited because of the random network of atoms in glasses It gives information upto two co-ordination shells i e , the bond lengths and bond angles for nearest neighbours of basic structural unit (For example SiO_4 tetrahedra in silica glass) can be determined For multicomponent systems, structural information obtained from diffraction experiments is more complicated So attempts have been made to explain the structure of glasses in terms of models Some of these models are discussed below

1.5.1 The Continuous Random Network Theory

Zacharıasen (1932) proposed this theory to explain the structure of covalent amorphous solids According to him, in an

amorphous material there exists structural units (co-ordination polyhedra), similar to those in the corresponding crystalline material, which are linked together randomly to form a continuous 3-d network Thus, covalently bonded amorphous solids generally have well defined bond lengths, bond angles and nearest neighbour co-ordination similar to those found in the corresponding crystalline solids The basic structural units formed by the nearest neighbours; for example, SiO_4 tetrahedra in silica glass, are connected together to form a continuous network and their relative orientation is characterized by the dihedral angle

This model is formulated to explain the structure of amorphous materials prepared by conventional method of melt-quenching at relatively slow cooling rates The relationship between the structural units found in the crystal and glass are not necessarily applicable to the amorphous solids prepared from the non-equilibrium processes such as vapour deposition or glow discharge deposition For example, the tetrahedral bonding in evaporated amorphous Si and Ge are found to be more distorted than that in their bulk counterparts

1.5.2 Random Packing Model

This model was put forward to describe the structure of amorphous metals They do not have well-defined directional bonding and therefore their structure was considered as being that of a frozen liquid The model is constructed either by the dense random packing

of spheres or trigonal prisms The former is suitable to explain the structure of pure amorphous metals like Bi, Ga etc and the latter is applicable only for amorphous transition metal-metalloid alloys where there exists chemical ordering compared to other amorphous metals

(i) **Dense Random Packing of Spheres:** The physical models were constructed from the aggregates of equal-sized ball bearings held in flexible bags On squeezing the bag the balls get glued into position attaining the non-crystalline packing

(ii) **Random Packing of Trigonal Prisms:** Gaskell (1979), suggested that in transition metal-metalloid glasses, the basic structural unit is trigonal prismatic polyhedra A physical model was constructed using 434 spheres which represent T-atoms These formed regular trigonal prisms, connected randomly through their edges in a cementite-like fashion Metalloid atom was fitted in the central hole of the regular trigonal prism

1.5.3 Random Coil Model

This model was used to describe the structure of organic glasses It was assumed that organic glasses were composed of long-chain organic molecules or polymers Each individual chain adopted random coil configuration These random coils were substantially intermeshed

1.5.4 Monte Carlo Simulations

The structure of amorphous $As_x Se_{1-x}$ system was described using monte carlo approach In this model, the atoms were chosen at random and were moved in an arbitrary direction If the radial

distribution function (RDF) calculated using this structure fits with the experimental curve, the structure generated from this move was found to be correct

1.5.5 Molecular Dynamical Simulations

In this model, classical Newtonian equations were solved for a small collection of interacting atoms or molecules in a cube The atoms were given a random Boltzmann distribution of velocities corresponding to a temperature of several thousand kelvin The Newtonian equations of motion were then solved for a series of time steps followed by a step-wise reduction in the temperature The structure of the system was evaluated in terms of RDF at the end of each temperature decrement

1.6 ELECTRICAL CONDUCTIVITY IN GLASSES

Electrical conduction in solids occurs by the transport of either electrons or ions Usually conduction by one of the carriers predominates, but in some inorganic materials both electrons and ions contribute to the conduction Ionic conduction is well understood in the crystalline solids (see for example Salamon 1979, Chandra 1981) Cations as well as anions can carry the current in certain cases

Point defects such as Frenkel defects Schottky defects and impurity atoms in the lattice play an important part in the ionic conduction In each case, an anion has to overcome a potential barrier to move from one interstial to another

or from its site to a vacancy Since these defects can be thermally generated, the ionic conductivity follows the Arrhenius equation with regard to its temperature dependence Further, dislocation lines and grain boundaries provide easy paths for the migration of ions In short, the conductivity of an ionic crystal depends on the thermal history of the sample Recently, materials called superionic conductors (Hu et al (1977)) with conductivities comparable with those of electrolytes ($\sim 10^{-1}$-10^{-4}ohm^{-1}.cm^{-1}) have become prominent due to their potential applications

In amorphous solids too, current carriers may be ions as well as electrons In those containing alkali elements the conduction is predominantly ionic The ionic conductivity in glasses was established a century ago by Warburg (1884) Ionic conductivity in different oxide glasses have been reported by many workers (For example Morey (1954), Hughes and Isard (1972), Tuller et al (1980)) The conductivity of these glasses is cationic and is found to be largest for alkali and silver cations ($\sim 10^{-8}$ohm^{-1} cm^{-1} at room temperature) Superionic conduction has also been observed in certain glassy systems Examples for these highly conducting ionic glasses are the mixed silver halide-silver oxysalt system AgI-Ag_2XO_4 (where X= As, Cr) (Ingram and Vincent 1977) Lithium based niobate, tantalate and $LiCl$-Li_2O-B_2O_3 system (Levasseur et al 1977) They have room temperature conductivities in the range 10^{-2}-10^{-1}ohm^{-1} cm^{-1}

The ionic conductivity in glasses has certain special features compared to that in crystalline solids In the former, ionic conductivity is isotropic and does

not involve any grain boundary effects like that in polycrystalline materials The electronic contribution to the total conductivity is very small due to the aperiodic potential fluctuations imposed by the disordered structure of glass Thus, the metal impurities are unable to appreciably enhance the electronic conductivity This fact has been used in electrochemical devices where a glass membrane is used as an ionic separator without the possibility of electron leakage

The different models for ionic conduction in glasses are discussed in detail in Chapter - III

1.7 LUMINESCENCE IN SOLIDS

There are substances which absorb energy and reemit a fraction of this energy in the form of electromagnetic radiation in the visible, infrared or ultraviolet region of the spectrum The phenomenon is called luminescence The materials which exhibit luminescence are called phosphors

Luminescence can occur in polymers, organic or inorganic crystals, amorphous substances etc under appropriate conditions The phenomenon involves transitions between electron levels of impurity atoms present in the glass lattice It may also be connected with electronically active defect states in the material In short, the ability of a material to luminesce depends on the presence of these 'activators' Activators may be traces of impurity atoms in the host material or a stoichiometric excess of one of the constituents of the materials For example, Cu, Bi etc are added as activators to the phosphorescent sulphides like ZnS, CdS etc In the case of alkali halides, stoichiometric excess of alkali metals play

the role of activators In some cases, crystal lattice defects behave like activators Materials like Uranyl salts $(NO_3)_2UO_2$ nH_2O exhibit luminescence in the pure state Here $(UO_2)^{2+}$ group, having incomplete shell of electrons, is well screened from its surroundings and it functions like a foreign molecule Luminescence disappears on heating and reappears by the introduction of water Rare earth salts of Eu, Gd, Sm, Tb, Dy etc exhibit luminescence due to the transition of 4f electrons The incorporation of certain types of impurities may destroy the luminescence of other centres They are referred to as 'killers' For example, Fe, Ni, Co etc destroy luminescence of ZnS

Luminescence involves two steps (i) the excitation of electrons in a solid (ii) the subsequent emission of photons Depending on the mode of excitation, luminescence can be classified as shown in Table 1 1

Table – 1.1

	Type of Luminescence	Excitation through
(i)	Photoluminescence	photons
(ii)	Cathodoluminescence	electrons
(iii)	Radioluminescence	high energy particle radiations
(iv)	Electroluminescence	application of electric field
(v)	Triboluminescence	mechanical forces
(vi)	Chemiluminescence	chemical reaction
(vii)	Bioluminescence	biological process

1.7.1. Fluorescence and Phosphorescence

If the emission of light occurs during the excitation or within 10^{-8}sec of excitation, the process is called 'fluorescence' and if the emission occurs after the excitation has ceased, the process is called phosphorescence or after glow

The mechanism of fluorescence and phosphorescence can be explained using a typical energy level scheme (fig 1 4a) An electron is excited from the ground state G to the excited state A (step 1) If it returns to ground state (step 2) by spontaneous emission of light, the process is termed as fluorescence The phenomenon of phosphorescence can be explained on the basis of metastable state M (trap or trapping state) The electron on excitation, goes to the excited state A (step a) It can undergo transition to the metastable state M (below the excited state) (step b) The direct transition from the M state to the G state is forbidden The electron remains in the M state until it gets enough energy E (called as trap depth) to reach the excited state again (step c) Then electron from the state A undergoes direct transition to the ground state (step d) with the emission of light Thus the emission is delayed in time by an amount equal to the time spent in the M state This phenomenon is referred to as phosphorescence However, the transition from M to G can also take place through the interaction with phonons This is a non-radiative transition
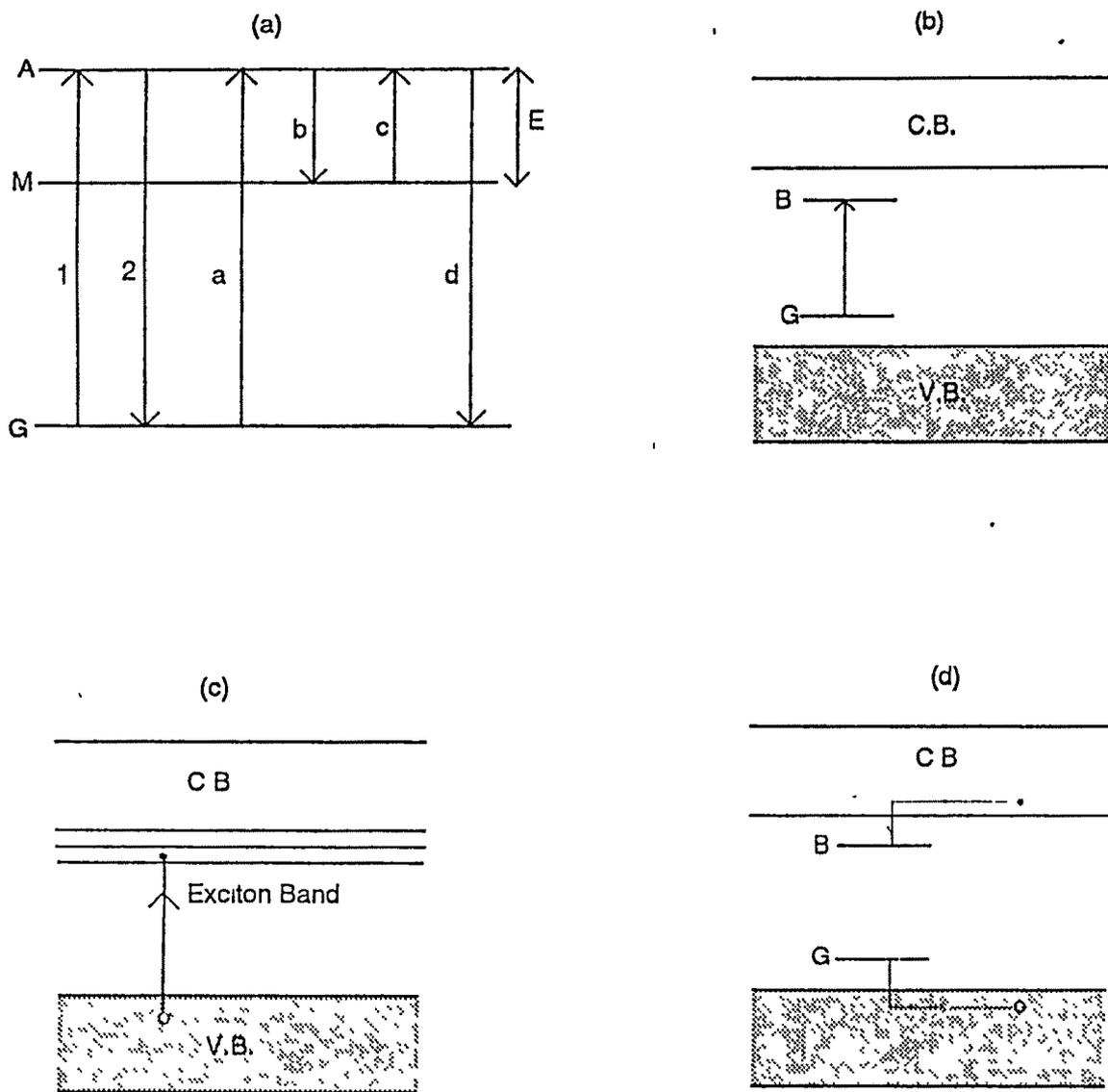
(a)

A

b c E

M

1 2 a d

G

(b)

C.B.

B

G

V.B.

(c)

C B

Exciton Band

V.B.

(d)

C B

B

G

Fig. 1.4. Typical energy-level diagrams indicating the absorption and emission of radiation.

(a) The scheme of transition for fluorescence (Steps 1 & 2) and phosphorescence (Steps a to d).

(b) The absorption of energy involving electron transition from the activator ground state G and excited state B.

(c) The absorption of energy resulting in electron transition from V B to exciton band

(d) The motion of exciton with its eventual capture by activator levels

There are many mechanisms which give rise to luminescence
Some of these are discussed briefly in the following section

1.8 MECHANISM OF LUMINESCENCE PROCESSES

1.8.1 Photoluminescence

An activator atom in a solid (semi conductor/insulator) produces localised levels in the energy gaps of the crystal Let B be an excited state and G be the ground state of an activator atom (fig 1 4b) The excitation process can be any one of the following processes

(i) An electron can be transferred to the state B from the state G by the absorption of a photon of proper frequency (i e , direct transition) (Fig 1 4b)

(ii) An electron from the valence band (V B) can be raised to one of the levels below the conduction band (C B) (Fig 1 4c) This electron is bound to the hole due to coulomb attractive interaction This electron-hole bound pair is called exciton The exciton can move through the solid and it may transfer its energy to the lattice vibrations or imperfections resulting in the excitation of the electron Thus the energy is transferred to the activator atom through the host material (i e , indirect transition)

(iii) The absorption of a photon may also create mobile electron-hole pairs in the solid The state G can capture a hole from the valence band and the state B can trap an electron from the conduction band (Fig 1 4d) resulting in the excitation of the activator This type of excitation is associated with conductivity

The excited centre in the solid returns to the ground state with or without the emission of a photon The former process is called radiative recombination (luminescence) and latter non-radiative recombination The frequency of the emitted photon is not the same as that of the incident photon This can be explained using Frank-Condon principle and configurational co-ordinate diagram (Fig 1 5) According to Frank-Condon principle, when an electron is transferred from the ground state G to an excited state B by the absorption of a photon, the energy corresponding to the peak of the absorption band is equal to the magnitude G $\longrightarrow$ B This excited electron either goes back to the ground state by spontaneous emission of light or is transferred to the state B^l by giving up the energy as phonons The energy corresponding to the maximum of emission spectrum is equal to the magnitude of $B^l \longrightarrow G^l$

1.8.2 Electroluminescence

Luminescence by the application of electric field or by plasma is known as electroluminescence There are three types of electroluminescence

(i) **Pure or Intrinsic Electroluminescence:** The excitation process involves three steps (a) the emptying of electrons from the traps by the field (b) the acceleration of electrons by the field in the conduction band (c) these accelerated electrons hit the luminescent centres transferring their energy to the electrons of the centre, thereby releasing these electrons into the
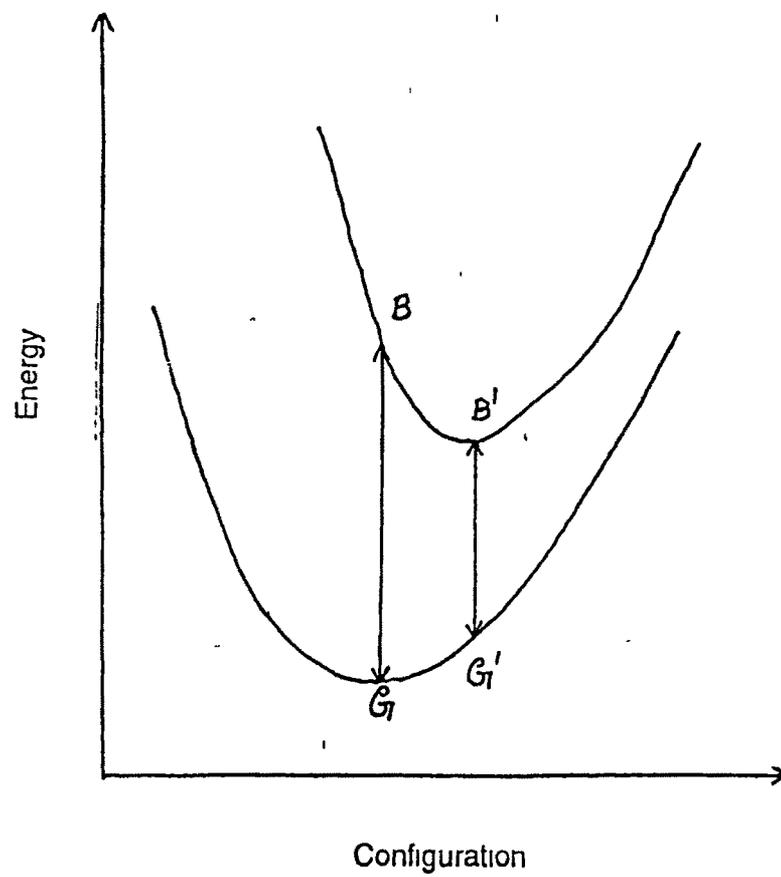
Fig. 1.5: Typical configuration co-ordinate diagram.

conduction band The emission of light occurs when these freed electrons recombine with empty centres

(ii) **Electroluminescence due to Charge Carrier Injection:** The luminescent emission occurs by the injection of carriers through a rectifying contact or p-n junction Carrier injection can be done in two ways

    (a)   electrons are injected from the electrode into the crystal Injected electrons are accelerated by the field and they excite luminescence centres as in the intrinsic case

    (b)   p-n junction is forward biased, the electrons from the n-region move into the p-region and the holes move from the p-region into the n-region They combine with their respective counterparts resulting in the emission of light

        This type of electroluminescence differs from the intrinsic one in that, the luminescence remains as long as the direct current flows The intensity of luminescence is proportional to the current

(iii) **Electro photoluminescence:** Gudden and Pohl discovered that when d c field is applied to a previously excited phosphor such as ZnS, a flash of light is observed The same effect is observed on removing the field When a field is applied, an internal field is set up in the solid due to polarization which counteracts the applied field When the field is removed the polarization field produces the flash and decays quickly to zero This type of luminescence, observed during or after photo excitation is called electrophotoluminescence

        The free electrons in the conduction band are accelerated by the field and they may empty the traps The effect is similar to thermoluminescence Here the electric field plays the part of thermal energy

1.8.3 Cathodoluminescence

Luminescence excited by cathode rays (or electrons) is called cathodoluminescence The incident electrons excite and ionize the luminescence centres The incident electrons also undergo scattering in the crystal lattice losing a fraction of their energy Finally, this energy is transferred to the luminescence centres Luminescence emission occurs due to the bimolecular recombination of conduction electrons with empty emission centres

Emission bands observed in cathodoluminescence are the same as in photoluminescence However, at high excitation densities, definite shifts in the position of these bands are observed The intensity of the colour of the emission band can be varied in the case of cathodoluminescence unlike in photoluminescence For example, in activated ZnS, the blue band is more intense than the green band under cathode ray excitation The phosphors which do not exhibit luminescence under ultraviolet radiation can be excited by cathode rays For example, pure calcium can be excited by cathode rays, but not by ultra-violet radiation

1.8.4 Radioluminescence

The emission of visible light from phosphors like ZnS and organic polymers when exposed to high energy radiations like X-rays, γ-rays, cosmic rays etc and particles like α and β is called radioluminescence These phosphors are used as detectors for

high energy nuclear radiations The constant stream of particles excite the luminescence centres and emission of light occurs during the recombination of free electrons with holes

1.8.5 Chemiluminescence

Chemiluminescence occurs as a result of chemical reactions like oxidation-reduction processes in which electronic charge is transferred from one species to another The light is emitted due to the release of energy from the reaction For example, when luminol is treated with a base and an oxidizing agent, nitrogen molecules are produced with the emission of light

1.8.6 Bioluminescence

Bioluminescence is the emission of light as a result of enzyme-catalized oxidation processes in biological systems For example, glow worm produces a molecule called luciferin and an enzyme, luciferace These molecules in the presence of oxygen and adenosine phosphate emit yellow light

1.8.7 Thermoluminescence

When a meta stable state (M state) exists below the excited state (Fig 1 4a) the excited electrons may fall into the M state If an electron is forbidden to return to the G state from the M state, the electron gets trapped in the M state The electron escapes from this trap when the required energy is obtained from the electron-phonon interaction

This leads to phosphorescence On the other hand, when the specimen is warmed up, the electrons are liberated at a faster rate The freed electrons reach the ground state with the emission of light Since the emission of light result from heating, the phenomenon is called thermoluminescence (TL)

As already pointed out in section (1 7) the excitation of electrons to a higher state can be achieved through radiations like UV, X-ray, γ-ray, etc The electrons eventually get captured by traps The TL studies have been used as an experimental method in the study of electron and hole traps, and their trapping and recombination processes in crystalline solids like pure alkali halides (Curle (1960)), alkali halide activated with thallium (Dekker (1957)) and conventional phosphors like ZnS and CdS (Curie (1960)) The radiation dosimeters utilising TL output of certain materials like LiF, Al_2O_3, MgO etc have been used in the detection of ionizing radiations (Gorbics et al (1967) Burch (1968))

The TL exhibited by solids may contain two different types of atomic or molecular defects or impurities One type functions as electron or hole traps and the other functions as electron or hole recombination centres

The mechanism of electron and hole traps and their recombinations can be explained as follows

When a solid is irradiated with ionizing radiations like X-ray, γ-ray etc free electron-hole pairs are produced Most of the free carriers recombine at recombination centres with the emission of light (fluorescence) However, a fraction of electrons and holes are captured by traps and electron-hole recombinations do not take place immediately They will contribute to TL On heating the crystal, an electron gets sufficient energy to come out of the trap, wanders through the crystal, encounters a trapped hole and recombines with it with the emission of light Such centres are called recombination luminescent centres Another mechanism for luminescence may involve ground state and one or more excited states of an impurity defect When a thermally released electron encounters such a centre it may be trapped at one of the excited states Since the life time of an excited state is very short, the trapped electron will undergo transition to the ground state with the emission of light At high temperatures, trapped electron recombines with thermally released hole with or without the emission of light Thus a single type of defect or impurity may act as an electron trap, a luminescence centre, a recombination centre or some combination of these

Another type of defects and impurities responsible for TL is colour centres and the substitutional atoms in the place of host atoms The valencies of the substitutional atoms are either more or less than the host atoms They trap electrons when they have deficiency of

electrons and capture holes (release electrons) when they have excess electrons When the substitutional impurity has the same valency as the host atom, the atom may function as an electron trap, hole trap or in both ways The colour centres function as electron traps or recombination centres under appropriate conditions

Phosphors of TL: Natural quartz, calcite ($CaCO_3$ Mn), thallium activated KCl (KCl Tl), Al_2O_3 Cr, ZnS Cu are some of the materials exhibiting the TL due to the presence of impurities Alkali halides like pure KCl exhibit TL due to the presence of defects and colour centres

The TL is also observed in glasses (see for example, Hensler (1959), Spurny and Novotny (1965)) It was found that the mechanism of TL in glasses is the same as that in crystals except that the impurity and defect states are distributed in the energy gap between valence band and conduction band

The TL is studied by obtaining a curve of luminescent intensity as a function of temperature called the 'glow curve' The glow curve may contain single or multiple peaks The detailed study of TL in glasses and the evaluation of kinetic parameters like trap depth and order of kinetics are discussed in detail in Chapter - IV