A general introduction on glassy materials and their methods of preparation has been presented. The physical processes are discussed in a more general way with special emphasis on glass formation from melt and sol-gel processing. The structure and topology of the glassy matrices are described in detail with various networking models. Structural change during gel to glass transition is briefly discussed. The advantages and merits of glasses as hosts for various rare earth ions and luminescent species are detailed. Spectroscopic properties and optical features of porphyrines and phthalocyanines and rare earth ions in glasses, which are instrumental in arriving at qualitative and quantitative results, are described. The importance of the Judd-Ofelt theoretical analysis of rare earth ions in condensed media and its limitations are touched up on. A brief account of radiative and non-radiative processes in glassy materials has been incorporated.
1.1 General background and technological properties

Photonics has issued new challenges to device technology and in doing so has attracted a rather formidable number of putative solutions. The best of these solutions is likely to emerge by considering how three disciplinary levels – systems, devices, materials (including process technology) – are interrelated. Thus one can expect to benefit from good system performance only for those solutions which involve interdisciplinary activities. In some sense, materials can be viewed as the playground for photonics [1]. During the emergence of quantum electronics spectroscopic studies of activated media, such as crystals, glasses etc. suggested their possible use in laser systems. Later experience accumulated in the studies of stimulated emission parameters allowed in many cases, a much deeper and more complete analysis of the characteristics of these materials. This also helped to uncover their properties, adding to the information from such conventional spectroscopic methods as luminescence and absorption analysis. Thus a new trend of spectroscopy namely stimulated emission spectroscopy of activated glassy and crystalline media, which is currently being rapidly developed.

Inorganic glasses have been used as optical materials for a long time due to their isotropy and high transparency over a wide spectral range from ultraviolet to infrared. Different doped inorganic glasses exhibit differing spectral absorption and have been used as coloured glasses or optical filter materials, where knowledge of the optical and spectroscopic properties is essential. In the last few decades a series of new glass forming systems have been developed to meet the demands of expanding field of optics and optoelectronics. In oxide glass systems besides traditional silicate glasses, phosphate, germanate, tellurite, borate etc. have emerged and new glass forming systems have also been expanded to non-oxide glasses such as halide and chalcogenide glasses. Since the advent of lasers, transition element doped
glasses (rare earth ions and transition metal ions) have become some of the most important laser materials. In addition to the absorption spectra, the emission and relaxation were investigated in detail. Newly developed laser spectroscopic techniques are the most powerful tools for characterizing the properties of the doped glasses.

The advantages of glass lasers over crystal can be summarized as follows. The laser glass can be made in a variety of sizes and shapes, with excellent homogeneity and low birefringence; it is less expensive than crystals and it has good coupling to broad band pump sources such as flash lamps and is thus capable of high stored energy density. Glass by its nature has a variety of sites that differ from each other in the number and position of the surrounding anions thus transitions in glass are inhomogeneous and relatively broad. The broader emission lines and generally lower cross sections of glass are compensated by its broader absorption bands, which allow glass to couple more efficiently to broad band pump sources than do crystals. Laser glass can store large amounts of energy because it can be produced in large sizes and because of its low cross section. Laser glass has an additional advantage over laser crystals in lasers operating in the picosecond and femtosecond regime. The broad fluorescence line width of glass allows for shorter transform limited pulses. In addition to rare earth and transition metal ions, the glass serves as a host for numerous other luminescent species such as porphyrins and phthalocyanines.

1.2 Definition of a glass

Glass is essentially a noncrystalline solid obtained by freezing supercooled liquids. However, there are many different methods by which we can produce amorphous solids, which we cannot classify as glass. On defining the glassy state two different approaches were taken by glass scientists. One definition is based on the concept of disorder. By disorder we mean mainly that the spatial
arrangement of atoms, ions and molecules do not exhibit three-dimensional periodicity (translational symmetry) and the long range order of the crystalline state is destroyed. Like liquids, glasses thus possess a disordered structure lacking long range order. There is only evidence of a short range order, which corresponds to the mutual arrangement of nearest neighbours to a given atom and varies according to the atomic site considered [2]. Some atoms are different from even the nearest neighbouring atoms in the bond angle, bond length and coordination number. Results of modern analysis of glass structure reveals that the structure of glassy materials is in order in the short range within 1nm [3]. In the region greater than 1nm, the structure tends to be topologically in disorder. Thus we can define the glassy state as a state with short range order and long range disorder.

The second definition is based on the internal stability of the materials. The non-crystalline solids obtained by different methods will contain an excess energy incorporated by quenching, mechanical action, radiation or chemical potential. This is a metastable or nonequilibrium state of matter. Heating of amorphous deposits generally leads to their rapid crystallization or their decomposition before the melting point is reached. In contrast, classic glasses are characterized not only by the absence of crystallinity but above all by their ability to pass progressively and reversibly to a more and more fluid state as the temperature is increased. In the course of this change there is modification of properties at a point called the glass transition. Gradual softening with increasing temperature is moreover, extremely important in technical applications and constitutes one of the fundamental properties of a glass material. Based on these conditions Zarzyki [2] adopted the definition “A glass is a noncrystalline solid exhibiting the phenomenon of glass transition.” He named the corresponding physical state as vitreous state. Glass scientists introduced more definitions [4]. Elliot defined glass as an amorphous solid, which exhibits glass transition [5] Varshneya [6] adopted the definition of
glass as a 'solid with liquid like structure', 'a noncrystalline solid' or 'simply an amorphous solid'. However Doremus [7] did not make any distinction between the words glassy and amorphous.

1.3 Formation of glass

A noncrystalline solid can be obtained by three different routes: by retaining (locking in) the structural disorder of a liquid phase, by taking advantage of the disordered character of a gaseous phase, or by disrupting the order of a crystalline phase. Hypotheses were proposed based the atomistic viewpoint correlating the nature of the chemical bond, and the geometrical shape of the groups involved [8]. For a simple oxide of general formula $A_mO_n$, there is a correlation between the ability to form glass and the relative sizes of the oxygen and $A$ atoms [9]. Glass-forming oxides are those for which the ratio of ionic radii $R_A/R_O$ lies in the range 0.2 to 0.4. Zachariasen [10] postulated that, as in crystals, the atoms in glass must form extended three dimensional networks. However Hagg [11] pointed out that an infinite three dimensional network may not be a necessary condition for glass formation. He concluded: 'it seems as if a melt contains atomic groups which are kept together with strong forces, and if these groups are so large and irregular that their direct addition to the crystal lattice is difficult, such a melt will show a tendency to supercooling and glass formation'. According to Smekal [12] mixed chemical bonding in a material is necessary for glass formation. Sun [13] showed that bond strengths in glass forming oxides are particularly high. Turnbull [14] pointed out that bond type, cooling rate, density of nuclei and various material properties like crystal liquid surface tension, and entropy of fusion are significant factors which affect tendency of different liquids to form glasses. Uhlmann [15] developing Turnbull's idea has provided some useful guidelines for glass formation by using theoretical time-temperature-transformation (T-T-T) curves to specify critical cooling rates in terms of material constants. A few other hypotheses were proposed after these,
however none of these are really capable of explaining to a more satisfactorily extent

1.3.1 Glasses from Melts

On melting vast majority of elements and mineral compounds form liquids with relatively low viscosities of the order of a few centipoise. On cooling, such liquids crystallize rapidly at their freezing point even if the cooling rate is high. It is possible to supercool fine droplets of liquids but this state cannot be maintained and crystallization inevitably occurs in the cooling process.

![Diagram](image)

**Figure 1.1** Variation of the specific volume (or the enthalpy) with temperature

There are however substances which melt to give liquids with high viscosities of the order of $10^5$-10$^7$ dPa s. On cooling such materials starting from a temperature well above the freezing point it may or may not crystallize depending on the rate of cooling. However crystallization can be avoided if the cooling rate is sufficiently rapid. To study this process with more precision it is convenient to follow the thermodynamic variable, the specific volume $V$ as a function of temperature (Figure 1.1). Starting with a liquid at an elevated temperature, the lowering of temperature first causes a contraction. When the point of solidification or freezing point $T_f$ is reached two phenomena may occur—either the liquid crystallizes and a discontinuity $\Delta V_f$ is introduced in the
curve or crystallization is avoided and the liquid passes to a supercooled state. In the latter case, the representative points follow an extension of the liquid curve, which passes the temperature \( T_f \) without discontinuity. In the first case, on completion of crystallization, as the temperature decreases the crystalline solid contracts again, the slope of the curve now being less than that of the initial liquid. In the second case the decrease in temperature at first causes a contraction of the supercooled liquid with a coefficient identical to that of the original liquid. Then starting at a certain temperature \( T_g \), the slope of the curve decreases to become close to that of the crystalline solid. This break in the cooling curve marks the passage from a supercooled liquid to a glass. The temperature \( T_g \) is called the transition temperature or glass transformation temperature. The viscosity of the liquid increases continuously as the temperature increases, and the passage through \( T_g \) corresponds to a viscosity in the neighbourhood of \( 10^{13} \) dPa s. The coefficient of expansion \( \alpha \) shows a rapid change on passing through \( T_g \) (Figure 1.2). At constant pressure, the position of the transition point \( T_g \) is not fixed as in the case of \( T_f \) but varies slightly with the rate at which the liquid is cooled. Rapid cooling has the effect of shifting the break defining \( T_g \) towards higher temperatures while

![Diagram](image-url)
slow cooling displaces $T_g$ towards lower temperature as shown in Figure 1.3. Hence it is preferable to substitute for $T_g$ the concept of a transition interval or a transformation interval $[T_g]$ where the upper and lower limits were defined respectively by the highest and the lowest cooling rates used to determine $T_g$.

Another phenomenon, which can be observed, is the stabilization. If the system is cooled at a rate $U_2$ into the transformation interval and subjected to an isothermal treatment at a temperature $T'$, it is found that the glass contracts to a point on the curve represented by a linear extrapolation of the supercooled liquid.

![Figure 1.3 Influence of cooling rate on temperature](image)

There are certain classes of materials, which can form glasses of their melt. Depending on the function of the components added the basic glass forming constituents can be classified as glass formers or network formers, intermediates or marginal glass formers and network modifiers or modifiers.

Glass formers are those materials, which can form glass by their own. Some of the inorganic glass formers are listed below.

- **Elements**: S, Se, Te, P
- **Oxides**: SiO$_2$, GeO$_2$, B$_2$O$_3$, As$_2$O$_3$, Sb$_2$O$_3$, P$_2$O$_5$ etc.
Chalcogenides: As-S, As-Se, P-Se, Ge-Se etc.

Halides: BeF₂, ZnCl₂, AlF₃ etc.

Certain molten salts, aqueous solutions of salts, acids and bases, inorganic compounds, organic polymers and metals can also form glass. Intermediates are those materials which do not form glasses on their own, but help in the formation of glass. These can be present in large proportions in glass if there is one glass former present in the material. The cations of the intermediates are capable of entering the glass network and occupying positions of the glass former. Some of the cations which act as intermediates in glass formation are Ti, Zn, Pb, Al, Th, Be, Z, Cd etc. Modifiers form glasses only when mixed in suitable proportions with the glass formers. The modifier ions are capable of building up continuous network and they affect the glass structure. By the addition of modifiers, the continuous glass network is disrupted and there are now two ligands of oxygen ions: one that bridge two tetrahedrons and those that do not or are non bridging. Some of the commonly used modifier cations are Li, Na, K, Ba, Sr, Hg, Cs, In, Nd, Pr, Sm, Tm, Er and Eu.

1.3.2 Sol-Gel processing

The sol-gel process is the name given to the process involving a solution or sol that undergoes a sol-gel transition. A solution is a single phase liquid while a sol is a stable suspension of colloidal particles. At the transition the solution or sol becomes a rigid porous mass by destabilization, precipitation or super saturation. Sol-gel processing has already been commercialized for high volume production of coatings, fibers, composites, refractories and semiconductor doping. Passive, active and non-linear optical materials for photonic devices are accessible by sol-gel methods that offer extra ordinary design flexibility through materials definition at the molecular level [16].
Sol-gel process [17,18] is based on the mixing of liquid reactants on molecular scale and subsequent solidification of the solution into a porous amorphous oxide gel. This is then subjected to suitable environments to produce different forms of materials such as thin films, glasses, fibres etc. A schematic diagram of the process which leads to different final products is shown in Figure 1.4. In 1846, Ebelmen [19] reported the formation of a transparent solid by slow hydrolysis of silica esters. As early as 1864, Thomas Graham [20] had prepared Gels of Silica. Multicomponent oxide glasses can now be produced not only by melting methods but also by hydrolysis and condensation of alkoxide complexes with several metals [21]. The word 'sol'
implies a dispersion of colloidal particles in a liquid. Colloids are in turn described as solid particles with dimensions in the range of 10 to 1000 Å, each containing 10^3 to 10^9 atoms. When the viscosity of the sol increases sufficiently, usually throughout the practical loss of its liquid phase and/or polymerization of the solid particles, it becomes a porous solid body; it is now termed 'Gel'. For approximately hundred years, the potentials of the sol-gel process were not well appreciated. Around 1980, the sol-gel process was 'rediscovered' [22]. A great deal of scientific knowledge has been generated at this time and many new materials were prepared. The most important reagent in sol-gel process is a metal alkoxide, M(OR)_x, where OR is an alkoxyl group. Tetraethyl orthosilicate (TEOS) is an alkoxide precursor commonly used for preparing silica sol-gel materials. The basic chemical reactions are as shown below. First step is hydrolysis of the alkoxide precursor.

\[
\text{Si(OR)}_4 + \text{H}_2\text{O} \rightarrow \text{HO-Si(OR)}_3 + \text{R(OH)}
\]

R is an alkyl group and R(OH) is an alcohol. Depending on the amount of water and catalysts present hydrolysis may go to completion,

\[
\text{Si(OR)}_4 + 4\text{H}_2\text{O} \rightarrow \text{Si(OH)}_4 + 4\text{R(OH)}
\]

or stop while it is only partially hydrolysed, \(\text{Si(OR)}_{4-n}(\text{OH})_n\). Two partially hydrolysed molecules can link together in a condensation reaction such as,

\[
(\text{OR})_3-\text{Si-OH} + \text{OH-Si-(OR)}_3 \rightarrow (\text{OR})_3-\text{Si-O-Si-(OR)}_3 + \text{H}_2\text{O}
\]

or

\[
(\text{OR})_3-\text{Si-OR} + \text{OH-Si-(OR)}_3 \rightarrow (\text{OR})_3-\text{Si-O-Si-(OR)}_3 + \text{R-OH}
\]

This condensation reaction grows, and more and more Si-O-Si bonds are formed. As polymerisation continues, the viscosity of the solution increases until a solid gel is formed. Molecular and chemical variations of the solution depends on the following factors [23].

1. Structure and chemical reactivities and sequence adding reactants
2. Nature of solvents and solubility of reactants in the solvents
3. Concentration of water and sequence of addition
4. pH of the reaction medium or presence of catalysts
5. Time and temperature of reactions

The prime objective in all preparations of multicomponent oxide compositions is to obtain initially a solution of all components in the form of soluble precursor compounds. Mixing of these compounds at the molecular level can be considered and if this level can be retained in the subsequent conversion to oxides a very homogeneous product should result. There are a number of different types of precursor materials that can be used [24]. All should be soluble in organic solvents and easily converted to the relevant oxide preferably by hydrolysis but alternatively by chemical reaction or thermal or oxidative decomposition [25]. Several preparative methods are available depending on the nature of the starting materials. Conversion of gel to glass can be achieved either by the melting of non-crystalline homogeneous gels or by sintering [26] of non-crystalline homogenous gel monoliths around $T_g$. Usually two methods of drying are used for the removal of solvents from the gel monoliths [27].

1. Drying by slow rate of evaporation of solvents at normal atmospheric pressure.
2. Evaporation of solvents under supercritical conditions in a pressure vessel

The selection of drying technique for gel powders will depend on the technique, which will be used for the conversion of gel to glass. The residual organics, molecular water and structural hydroxyl groups should be removed before the densification or melting of gels. The removal of residual organics can be achieved by thermal treatment in an oxidising atmosphere in the temperature range $300^\circ$ to $500^\circ$C. However the removal of hydroxyl groups to a few ppm level requires special chemical treatments with reactive gases like $\text{CCl}_4$, $\text{Cl}_2$ etc.[28].
The advantages of sol-gel process are [29]

1. Lower processing temperature
2. High homogeneity and purity
3. Possibility of various forming process

From the fundamental standpoint it was expected to produce

4. Glasses with new composition
5. Materials with new properties.

From various experiments it was found that pure and homogeneous glass from gels can be prepared without contamination resulting from the longer melting times and from stirring the glass melts which are essential for preparing glass by the conventional method. The ability to dope sol-gel derived silica hosts with controlled amounts of a lasing species affords the possibility of developing a new generation of advanced tunable solid state lasers [30].

1.3.3 Structural evolution during gel to glass transition

For all types of gels, so called "polymeric" or "particulate" fibres, films, or the bulk the receding liquid during the final stages of drying exposes an interconnected porous network within the gel that completely surrounds the solid or skeletal phase. The average dimensions of the pores and the thickness of the skeleton depend upon the structure that exists at the gel point and the extent of collapse or distortion of this structure that results from drying. Dried gels either xerogels or aerogels are distinguished from other porous, ceramic green bodies by their enormous surface areas and correspondingly small sizes. Quite often the dimensions of the pores and the skeletal phase comprising the dried gels are sufficiently small (<1/10th wavelength of visible light) that despite very high volume percent porosities ($V_p$) xerogels and aerogels are transparent or translucent. For gels, the skeletal phase has evolved through continued condensation reactions without melting, so that the skeletal structure is rarely equivalent to that of melted glass. By comparison it is less highly condensed, may more or less homogeneous, and often contains excess
free volume (i.e., has a greater molar volume). Only as the gel is heated to higher temperatures does the skeletal structure approaches that of conventional glass made by melting. For example, in amorphous systems this requires heat treatment in the vicinity of the glass transition temperature ($T_g$) of the corresponding melted glass.

1.4 Structure and Topology

By the first quarter of this century, at least four models of glass had been developed: polymer, colloid and crystalline models and also the model of a supercooled liquid [31]. The colloidal model, which had been neglected for a long time, provided the development of sol-gel technology [32-33]. In 1932 Zachariasen [10] suggested the model of a continuous disordered network of related polyhedra of glass formers with voids being occupied by ion modifiers. This model was supported by Warren [34 -35] and became one of the main theories of glass formation. Hagg [36] withdrew the requirement of network continuity and indicated that all the glass forming oxides were in fact, anhydrides of polymer acids, whereas the oxide modifiers had an alkaline nature.

Zachariasen’s analysis was based on the following considerations.
1. The inter-atomic bonding forces in glasses and crystals must be similar given the similar mechanical properties of the two types of solids.

2. Like crystals, glasses consist of an extended three-dimensional network but there is no long range order.

The glass network may be compared with a unique molecule or a system with a giant unit cell. The disorder of the network introduces a distribution of bond forces; their progressive rupture on heating explains the gradual decrease of viscosity. The disorder would also explain the fact that the energy content is higher than that of a crystal. The structure can be analysed in terms of coordination polyhedra of cations surrounded by a variable number of oxygen ions (Figure 1.5). In crystalline oxides the polyhedra can have common corners, edges or faces.

Zachariasen described the manner in which the polyhedra could be joined to build a disordered network related to that of a crystal. In the case of the different crystalline forms of SiO₂ the glass network is built with SiO₄ tetrahedra joined at their corners but the mutual orientation of the consecutive tetrahedra is variable. Figure 1.6 represents a two-dimensional schematic representation of a hypothetical oxide structure A₂O₃ built from AO₃. Such a two-dimensional structure permits the introduction of some disorder without the cations approaching each other too closely which would cause a large increase in internal energy in the network. After systematic examination of the structures...
formed by different coordination polyhedra, Zachariasen showed that a glass forming oxide must satisfy the following rules.

1. The number of oxygens around a A atom must be small (3 or 4)
2. None of the oxygens may be shared by more than two A cations
3. The polyhedra must bond at corners but not on edges or faces
4. At least three corners each polyhedron must be shared with other polyhedra.

To form complex glasses by the addition of oxides of alkali metal, alkaline earth etc. It is necessary that the following conditions were to be satisfied.

1. The sample contains a sufficient percentage of cations surrounded by tetrahedra oxygen triangles
2. The tetrahedra or triangles have only corners in common.
3. Some oxygen atoms are only bonded to two of these cations and do not form new bonds with other cations.

When a non-glass forming oxide such as Na2O is added to SiO2 the additional oxygens participate in the network and cause the rupture of a specific number of bonds. An Si-O-Si bond is broken and the added oxygen saturates the unsatisfied bond of one Si and two Si-O- are formed. This leads to the formation of two types of oxygen. The one, which is bonded to two Si, is called bridging oxygen (BO) and the one, which is bonded to one Si, is called non-bridging oxygen (NBO). Zachariasen further suggested that modifying cations occupy the "holes" which form together with the glass network and that the cations are distributed at random. Warren and
his collaborators studied the structure of glass using X-ray diffraction methods and proved Zachariasen's idea [37]. The Zachariasen–Warren model of a continuous disordered network is shown schematically in Figure 1.7.

With the accumulation of new experimental facts and the development of new methods of glass research [38] such as Small Angle X-ray Scattering, EXAFS [39], electron microscopy and NMR [40] spectroscopies, computer simulation etc [41], it became possible to refine and modify the Zachariasen's theory. For glasses of tectosilicate composition where the charge of the modifier cation equals the number aluminium atoms (as in NaAlSi3O8) the conventional view of glass structure is that only BO's are present [42]. Stebbins and Xu [43] reported that a considerable amount of NBO's can be present in a tectosilicate glass obtained from melt.

1.5 Spectroscopy of porphyrins and phthalocyanines

Organic semiconductors play a very important role in today's high technology applications viz, optical imaging, optical switching, optical computing, data storage, photodynamic therapy, dynamic holography, frequency mixing, harmonic generation and optical communications. Among the organic semiconductors the phthalocyanines (Pc), naphthalocyanines (Nc) and porphyrins (PP) are of special significance because of their inexpensiveness, thermal and environmental stability, non-toxicity as well as excellent optical and electronic properties [44]. A combination of these features together with their chemical stability makes them an important class of photo-electronic materials for applications in various opto-electronic devices. These materials offer unique chemistry based on the properties of the stable hetero aromatic π-system. The less reactive and more thermally stable metal phthalocyanines (MPc) have a wide variety of industrial applications. Porphyrins and phthalocyanines have two major absorption bands namely the Q-band in the visible light region (600-800 nm) and the B- band or Soret band in the violet
Figure 1.8 (a) Schematic energy diagram of excited states of porphyrins Fl-fluorescence, Phosp-Phosphorescence T-T Triplet-Triplet absorption

Figure 1.8 (b) Schematic energy diagram of excited states of phthalocyanine Fl-fluorescence, Phosp-Phosphorescence T-T Triplet-Triplet absorption

or ultraviolet region(300-400 nm). In most photochemical reactions of these compounds, visible light is irradiated to excite the ground state of the molecules in the lowest singlet excited state \((S_1)\); the resulting excited state emits fluorescence or undergoes intersystem crossing to the lowest triplet state
(T₁), which often participates in reactions or radiationless deactivation (internal conversion) to the ground state (see Figure 1.8)[45].

In most photochemical reactions, once higher excited states are produced by excitation of the second or higher absorption bands, the generated excited states usually deactivate very rapidly to the lowest excited state, which deactivates to the ground state exhibiting emission via radiationless processes or undergoes reactions competing with deactivation. The above behavior of higher excited states is often said to obey Kasha's rule [46], the courses of most photochemical reactions do not depend on the wavelength of excitation, however under some conditions photochemical reactions show wavelength dependent feature [47].

A plethora of experimental as well as theoretical investigations have been carried out over the past several years about the physical, chemical and technological aspects of phophyrines and phthalocyanines. However most of these studies are concentrated on the optical properties of these molecules in various solvents or either in thin film or vapour forms. Studies on the optical properties of these molecules have been barely done in solid matrices except for some reports on the thermo plastic media viz. styron, tyril 767 and plexi glass [48]. Optical studies of these molecules in condensed media are of special significance because of the effectiveness of these systems as potential candidates in a variety of technological applications due to their added advantage such as compactness, inexpensiveness, manageability and lack of toxicity.

1.6 Glass as laser host

Many simple and multicomponent glass matrices have been shown to accommodate activator ions such as rare earths. When 4f ions are introduced into glasses they replace the network cation, which forms the glass, or they act as network modifiers. The precise manner in which the dopants enter in the
glass structure depends on the relative sizes, valency and bonding of the constituents involved [49]. Rare earth activated lasers were reported by Snitzer [50] as early as 1961. He demonstrated a Nd-doped glass laser using barium crown glass. Since then many host glasses were investigated and the features and merits of glass lasers were established. Glasses used for lasers include oxides, phosphates, fluorides and mixed anion glasses. Rare earth ions such as Yb, Ho, Er, Tm and Tb were also employed as dopants in glass lasers [3]. The material design aspect of rare earth laser glasses similar to the one presented by Tanabe [51], is schematically shown in Figure 1.9.

Sol-gel matrices were also found to be a good host of rare earth ions. Neodymium has been incorporated into sol-gel SiO₂ at concentrations up to 5-10wt% without crystallization [30,52]. Careful comparison of the spectra of sol-gel and melted silica containing 0.5% Nd₂O₃ shows that they are identical. At these concentrations the Nd fluorescence decay shows no very fast component due to the clustering. However lifetime may be shortened if the
water content is not reduced to very low concentrations during drying and densification process. Measurements of wavelength shape, intensity and width of optical spectra and of excited state lifetimes can reveal the existence of rare earth clustering and the presence of water and other additives in the immediate vicinity of the rare earths.

1.7 Spectroscopy of rare earths in solid hosts

1.7.1 General

The rare earths otherwise referred to as the lanthanides, comprise the series of elements in the sixth row of the periodic table stretching from lanthanum to ytterbium. They are characterized by a partially filled 4f shell that is shielded from external fields by 5s² and 5p⁶ electrons. The energy levels of elements in this series are therefore largely insensitive to the environment in which they are placed. When incorporated in crystalline or amorphous hosts, the rare earths exist as 3⁺, or occasionally 2⁺, ions. The 3⁺ ions all exhibit intense narrow-band intra-4f luminescence in a wide variety of hosts, and the shielding provided by the 5s² and 5p⁶ electrons means that rare earth radiative transitions in solid hosts resemble those of the free ions and electron phonon coupling is weak. Although some of the divalent species also exhibit luminescence (principally samarium and europium), it is the trivalent ions that are of most interest.

As a result of the shielding of the 4f electrons, the positions of rare earth – electronic levels are influenced much more by spin orbit interactions than by the applied crystal field. The intra-4f transitions are parity forbidden and are made partially allowed by crystal field interactions mixing opposite parity wave functions. Luminescence lifetimes are therefore long, and line widths narrow. By careful selection of the appropriate ion, intense, narrow band emission can be obtained across much of the visible region and into the near infrared.
A number of excitation pathways are available for rare earth luminescence in solid hosts. These can be broadly classified as either direct or indirect mechanisms. Amongst the former are, resonant optical excitation by the interaction of photons of appropriate wavelengths with specific rare earth 4f absorption bands, cathodoluminescence and electroluminescence in semiconductor hosts involving hot electron collision with rare earth centers. Indirect mechanism include carrier–mediated excitation transfer in semiconductors, and dipole–dipole Forster–Dexter coupling in insulators. Carrier mediated excitation is of particular importance for the production of optoelectronic devices, and there has been much work directed at an understanding of such processes in a range of semiconductor hosts [53].

1.7.2 Symmetry considerations
Although the shielding of the 4f shell means that the rare earth ion energy levels are largely independent of host, Stark splitting broadens the levels as a result of the applied crystal field. Full Stark splitting is observed for rare earth ions in glasses, as a result of the low point symmetries of the rare earth sites in amorphous matrices [54]. For example, Er$^{3+}$ ions in silica exhibit \((2J+1)/2\) Stark levels due to splitting of the \(J\) manifold, which leads to a total of 56 possible \(^4I_{13/2}\) to \(^4I_{15/2}\) transitions. However, these levels may only be resolved in emission spectra of crystalline hosts taken at low temperature, and at room temperature the Stark levels broaden and overlap to produce an inhomogeneously broadened emission band.

1.7.3 Term symbols
Energy levels in rare earth ions are conventionally labeled according to their angular momentum and spin quantum numbers using term symbols such as \(^4I_{13/2}\) or \(^2F_{7/2}\). Here the letter refers to the total orbital angular momentum of the ion obtained by combining the orbital angular momentum of the individual electrons in the ion according to the Clebsh–Gordan series. The left superscript is the number of possible orientations of the total spin of the ion, given as
2S + 1, where S is the total spin of the ion. The right subscript gives the total angular momentum of the ion and is determined using the Russel-Saunders coupling scheme.

1.7.4 Judd-Ofelt theory

It is important to know the transition probabilities, or oscillator strengths, for the various transitions between energy levels in rare earth ions. Unfortunately, these are extremely difficult to measure, and instead must be calculated using Judd-Ofelt theory [55-56]. This states that the oscillator strength for the transition between two states $^{2S+1}L_J$ (described by the wave function $\psi_i$, specified by the $f^N$ configuration for a partially filled $f$ shell, the quantum numbers $S$, $L$ and $J$ and a factor $\gamma$ to distinguish electronic states that share the same values of $S$ and $L$) and $^{2S+1}L_J'(\psi_f$ specified in a similar way) is given by

$$S = \frac{1}{e^2} \left| \langle \psi_i | H | \psi_f \rangle \right|^2 = \sum_{k=2,4,6} \Omega_k \left| \langle f^N S' L' J' U^k | f^N S L J \rangle \right|^2$$

here $H$ is the electric dipole Hamiltonian, expressed in tensor form as $U^k$, and the $\Omega_k$ coefficients are the Judd-Ofelt parameters. Physically, these may be considered as a set of coefficients describing the influence of the external crystal field on the radiative transition probabilities of the intra-4f transitions.

The theory has been applied to rare earth ions in variety of glass hosts in the past with a considerable degree of success. However this standard theory is found to be inadequate in the case of Pr$^{3+}$ ions in glassy as well as crystalline hosts. Many groups tried to solve this problem [57] by modifying the basic JO theory. Recently Jose et.al [58-59] have successfully applied the modified theories proposed by Kornienko et al.,[60] and Florenz et al. [61] and arrived at better results.

1.8 Radiative and nonradiative transitions

When an optically active ion in a solid is raised to an excited state, it may lose its excitation by radiative emission (Fig 1.10 a) or by a number of non-
radiative processes: by multiphonon emission to the next lower state (1.10 b), by cross relaxation (1.10 c), or by energy transfer resulting in loss of excitation to some non-radiative center in the solid (1.10 d). A number of these deexcitation processes may be operating simultaneously. Processes (c) and (d) can be eliminated by going to small concentrations of active ions, while processes (a) and (b) are intrinsic to the particular ion-host combination.

![Diagram](image)

**Figure 1.10** Deexcitation process out of the excited state (a) is the radiative process (b) is the non-radiative multi-phonon process (c) shows cross-relaxation with an adjacent similar ion followed by transfer to a center which then decays non-radiatively.

Radiative transitions between 4f electronic states of rare earth ions in crystals are characterized by very sharp optical transitions—a consequence of (i) the weak coupling between the 4f electrons and the ionic lattice environment of the rare earth ion, and (ii) the fact that the rare earth ions generally enter identical sites in the crystal [62]. In contrast to the situations in crystals, rare earth ions in glass find a range of site types available to them and this leads to relatively large inhomogeneous broadening. The first quantitative studies of nonradiative processes on rare earth ions in glasses were carried out by Reisfeld and coworkers [63]. The nonradiative decay rate at low temperatures is given by to good approximation by the empirical formula

\[ W_{nr} \approx 10^7 \exp[-\beta(p - 2.4)] \]

where \( \beta \approx 2 \), \( p \) is the number of phonons involved in the relaxation process and \( p = E/\hbar \omega \), where \( E \) is the energy gap to the next lower level, and \( \hbar \omega \) is the phonon energy. From the earliest experiments on oxide glasses, it was clear that a smaller number of luminescent states are observed for rare earth ions in
these glasses than is the case for rare earth ions in oxide crystals. Since radiative decay rates on rare-earth ions in crystals and glasses are of the same magnitude, this implies an enhanced nonradiative decay rate in glasses. In oxide glasses the luminescence transitions are exceedingly weak, the intensity decreasing in the order borate< phosphate< germanate< tellurite [63]. The enhanced nonradiaitve decay in the oxide glass is attributable to the presence high frequency vibrations in these glasses, in the range of 700-1400cm⁻¹, larger than that found in common crystalline host materials. For oxide glasses the large energy of the phonons engaged in the nonradiative process means that the probability of nonradiative decay across the same energy gap is much larger for these glasses than for crystalline materials. This creates a limitation to the to the efficient long wavelength luminescence from oxide glasses.

In contrast to the case of rare earth ions, whose electrons are partially shielded from interaction with the environment, for transition metal ions the active 3d electrons are on the outside of the ion, so that the 3dⁿ electronic states are much more sensitive to variations in the ionic environment. As a consequence, the electron lattice interaction is much larger for transition metal than for rare earth ions. There are two consequences of this. One is a stronger nonradiative process for transition metal ions in crystals and in glasses than is the case for rare earth ions. The second is that due to the wide range of sites in glass, the inhomogeneous broadening of optical transitions in glass is much more for transition metals than for rare earth ions.
References

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Spectroscopic Studies and Optical Constants of Phthalocyanines in Glassy Medium

Optical absorption and emission spectral measurements of various phthalocyanine (Pc) doped borate glass matrices are reported. Absorption measurements have been done corresponding to photon energies between 1.1 to 6.2eV for free base, manganese, iron, nickel, molybdenum, cobalt and copper phthalocyanines. Several new discrete transitions are observed in the UV-VIS region of the spectra in addition to a strong continuum component of absorption in the IR region. Values of some of the important optical constants viz, absorption coefficient (α), molar extinction coefficient (ε), absorption cross-section (σ_a), bandwidth (Δλ), electric dipole strength (q^2) and oscillator strength (f) for the relevant electronic transitions are also presented. All the data reported for Pc-s in the new matrix have been compared with those corresponding to solution, vapor and thin film media. All the emission spectra show intense fluorescence peaks in the 765nm region upon excitation in the B-band (330nm) and Q-band (700nm). Fluorescence intensity is found to be minimum in the free base phthalocyanine (H_2Pc) whereas maximum in the MoOPc. Analysis of the data yielded spectral parameters favoring high optical amplification in the 765 nm region.