CHAPTER 1

General Introduction

General introduction on sol-gel processing for the preparation of glasses and its advantages are given. Structural changes during gel to glass transition are briefly discussed. Spectroscopic properties of rare earth ions in glasses, principally europium ions are described. A brief discussion on the semiconductor nanocrystallites and their properties in sol-gel glasses are presented. The advantages and merits of sol-gel glasses as hosts for various rare earth ions and luminescent species are detailed. The various applications of these active species in industry and research are also outlined.
1.1 Glass

Glass is one of the most ancient materials known to mankind. The word glass is derived from a late-Latin term glaesum used to refer to a lustrous and transparent material. Glass is an extremely important material in science being used in a wide variety of ways: from lenses, mirrors, optical switches and fiber optics to filters and substrates for active materials. Glass is essentially a noncrystalline solid obtained by freezing super cooled 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 are 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. The short range order is of great significance to the optical and spectroscopic properties as all the electronic movements take place in the short range region within or among the atoms or ions. 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. 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\textsuperscript{1} adopted the definition “A glass is a noncrystalline solid exhibiting the phenomenon of glass transition.” He named the corresponding physical state as vitreous state originating from the Latin word vitrum. Varshneya\textsuperscript{2}
adopted the definition glass as a ‘solid with liquid like structure’, ‘a noncrystalline solid’ or ‘simply an amorphous solid’. The American Society for Testing Materials (ASTM) defined glass as “An inorganic product of fusion, which has been cooled to a rigid condition without crystallization”. The sol-gel process of making a glass avoids the normally high temperature employed for fusion of glass.

1.2 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 on the atomistic viewpoint correlating the nature of the chemical bond and the geometrical shape of the groups involved\(^\text{3}\). 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\(^\text{4}\). 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\(^\text{5}\) postulated that, as in crystals, the atoms in glass must form extended three dimensional networks. However, Hagg\(^\text{6}\) 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\(^\text{7}\) mixed chemical bonding in a material is necessary for glass formation. Sun\(^\text{8}\) showed that bond strengths in glass forming oxides are particularly high. Turnbull\(^\text{9}\) 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\(^\text{10}\)
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 glass transformation to a more satisfactorily extent.

1.3 Sol-Gel Processing

The sol-gel technology by which inorganic or composite organic-inorganic materials are made at relatively low temperature, consists of hydrolysis of the constituent molecular precursors and subsequent polycondensation to glasslike form. The technology allows incorporation of organic and inorganic additives during the process of formation of the glassy network at room temperature. The sol-gel process involves chemical synthesis of oxides. Based on the sol-gel process a large number of sophisticated materials have been prepared and studied and the corresponding theories elaborated.

Sol-gel process leads to the preparation of thin films, glasses, fibres etc from gels. A schematic diagram of the process which leads to different final products is shown in Figure 1.1. In 1846, Ebelmen reported the formation of a transparent solid by slow hydrolysis of silica esters. As early as 1864, Thomas Graham 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. In this process the required ingredients are reacted at low temperature to constitute a gel, which is then dried and densified to massive glass. A high degree of homogeneity is achieved in a molecular scale because glasses are prepared at lower temperatures. The molecular level of glass formation involves the organization of glass-network elements within the gel particles and their interaction followed by the formation of three-dimensional, highly polymerized network.
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'. A great deal of scientific knowledge has been generated at this time and many new materials were prepared. In the sol-gel process, the precursors for preparation of a colloid consist of a metal or metalloid element surrounded by various ligands.
Metal alkoxides are members of the family of metal organic compounds, which have an organic ligand attached to a metal or metalloid atom $\text{M(OR)}_x$, where OR is an alkoxyl group. Metal alkoxides are popular precursors because they undergo hydrolysis depending on the amount of water and catalyst present. Two partially hydrolyzed molecules link together in condensation to form ‘polymeric sol’. Polymeric sol is one in which the solid phase contains no dense oxide particles larger than 1nm, the lower range of colloidal range. If one molecule reaches macroscopic dimensions so that it extends throughout the solution, the substance is said to be a ‘gel’. A gel consists of continuous solid and fluid phases of colloidal dimensions. Gelation can occur after a sol is cast into a mold, and if the smallest dimension is greater than a few millimeters the object is called a monolith$^{21}$. Densification is a sintering process by which the pores of a dry gel are eliminated and the material is converted into a clear massive glass. The driving force in this process is supplied by the surface energy of the porous gel$^{22}$.

1.3.1 Multi component glasses

The primary objective in all preparations of multicomponent oxide compositions is to obtain initially a solution of all components in the form of soluble precursor compound. Hydrolysis is facilitated by increase in charge density on the metal, the number of metal ions bridged by a hydroxo or oxo ligand, and the number of hydrogens contained in the ligand. Hydrolysis is inhibited as the number of hydroxy ligands coordinating metal increases. The development and disappearance of porous structure are submicroscopic or nanostructural process.

1.3.1.1 All- alkoxide method

Metal alkoxides having the general form $\text{M(OR)}_x$ are used in this method where M is the metal, R is an alkyl group and x is the valence state of the metal. The hydrolysis reaction can be represented as
The byproduct ROH is an aliphatic alcohol and removed by volatilization. Silicon alkoxides require an acid or basic catalyst for hydrolysis and the reaction rate is slow.

The simplest method of preparation of multicomponent system involves making a solution of all the components as alkoxide precursors in a suitable organic solvent and then reacting the solution with water to form the oxide mix. The reaction for three component system is

\[
M(OR) + xH_2O \rightarrow M(OH)x + xROH
\]

\[
2M(OH)x \rightarrow M_2Ox + xH_2O
\]

This involves first hydrolysis of metal alkoxide groups to metal hydroxide groups and subsequent condensation of these groups with each other or with unhydrolysed alkoxide groups to give products containing M-OM linkage. The polymeric products become insoluble due to crosslinking and gelation or precipitation results. Soluble polymerized products are initially formed followed by a viscosity increase and eventual gelation.

### 1.3.1.2 Alkoxide- Salt method

The normal method of sol-gel preparation using salts is first to form a solution of all components which are to be added to be as alkoxides, and then add one or more salts as solution in alcohol or in water for further hydrolysis. All components are then uniformly dispersed and subsequent gelation should then freeze all elements in a gel network. This method is used in case of group I and II elements whose alkoxides are solid, nonvolatile and in many cases with low solubility or difficulty in getting pure form. Sol gel preparation involving salts are more complex because the hydrolysis requires thermal or oxidative degradation.
The formation of pure silica gel involves a polymerization mechanism with three essential stages,

(a) polymerization of monomer to form primary particles
(b) growth of particles
(c) linking of these particles together in chains, then into three dimensional networks

\[ -\text{Si} - \text{OH} + \text{HO} - \text{Si} \rightarrow -\text{Si} - \text{O} - \text{Si} - + \text{H}_2\text{O} \]

Tetraethyl orthosilicate (TEOS) is an alkoxide precursor commonly used for preparing silica sol-gel materials. The basic chemical reactions are as given 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, Si(OR)_{4-n}(OH)_n. Two partially hydrolysed molecules can link together in a condensation reaction such as,

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

or

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

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 depend on the following factors.\textsuperscript{23}

1. Structure and chemical reactivity 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

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. 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. 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 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.

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$^\circ$C 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.

The gel to glass transition takes place in following steps,

1) Desorption of the water and alcohol
2) Combustion of residual organic matter
3) Polymerisation
4) Volume relaxation and
5) Pore collapse and viscous sintering

1.3.2 Phase separation in gel

Phase separation is the name given to the process of separation of a homogeneous liquid into two liquid phases as it enters an immiscibility dome. As the ratio $z/r$ (cation charge/cation radius) of the modifying cation increases, the tendency to immiscibility increases. There was a greater degree of crystallization in the gel glasses than in ordinary glasses for any given heat treatment. The phase transformation behaviour of gel and ordinary glasses may differ. Many glass forming systems containing two or more components have been observed to undergo liquid-liquid phase separation in particular temperature regimes. Immiscibility regions in glass forming systems are characterized as being stable or metastable depending on temperature regime where the unmixing occurs (above or below liquidus temperature). Schematic characteristic curve which delineates the two phase and single-phase regions for a given conditions of temperature and composition is shown in Figure 1.2. The region under the curve corresponds to the two-phase region while the

![Figure 1.2. The phase transition diagram](image-url)
region exterior to the curve is the single phase region. The bounding curve which indicates the temperature at which a composition will transform from a single phase to a two phase region is termed binodal and the transformation temperature is termed as the immiscibility temperature, $T_m$. The elevation of the immiscibility temperature of the gel glass was explained in terms of the enhanced water content. Water is contained in glass primarily in the form of bound hydroxyl groups. Molecular water is transformed into the network structure by the reaction.

$$\equiv \text{Si} - \text{O} - \equiv \text{Si} + \text{H}_2\text{O} \rightarrow 2\equiv \text{SiOH}$$

Thus glass with an enhanced water content would possess a smaller degree of structural coherency since as a result of the above equation such glass would be expected to have fewer bridging oxygens. This reduction in the connectivity of the gel glass framework could possibly account for its elevated immiscibility temperature.

The water concentration of the glass cannot be the sole cause of the anomalous behaviour of $T_m$. The arrangement of the hydroxyl groups in the gel glass is also responsible for the immiscibility temperature. The most influential impurity cations alter $T_m$ by at most $10^\circ \text{C}/0.1 \text{wt} \%$. As gels are heated to increasingly high temperatures, their structure and properties begin to approach those of glassy state, if crystallization does not intervene.

1.4. Advantages of sol-gel process

Advantages of sol-gel process are:

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. If a typical sol-gel solution prior to conversion contains all the components mixed at or near molecular level, and if this level is maintained during subsequent condensation, the product is highly homogeneous. The purity of the sol-gel composition depends on the purity of the starting materials and the care taken in the conversion to oxide. Metal alkoxides are particularly good reagents for high purity products because many of them are volatile. The ability to dope sol-gel derived silica hosts with controlled amounts of lasing species affords the possibility of developing a new generation of advanced tunable solid state lasers.27

1.5. Rare Earths

The unsaturated 4f electronic structure of rare earth elements makes them have special properties in luminescence, magnetism and electronics, which could be used to develop many new materials such as phosphors, magnetic and magnetostrictive materials, hydrogen storage materials and catalysts. Rare earth occurs as two groups, known as lanthanides and actinides, characterized by the progressive filling of the 4f or 5f shells of their electronic configuration.

1.5.1 Lanthanides

The lanthanide series of elements are characterized by a partially filled 4f-electron shell, start with element Cerium (Z=58) and end with Lutetium (Z=71). The chemical properties of the lanthanides are related to the decreasing ionic size, which is popularly known as lanthanide contraction. As we proceed through the lanthanide series, the nuclear charge together with the number of 4f electrons increases and with each increase the effective nuclear charge increases causing a reduction of the entire 4f\(^n\) shell. As a result of this
contraction the f shell behaves as an inner shell and the direct manifestation is in the regular decrease in size of the lanthanide with increasing atomic number followed by decrease in the ionic radii with increasing ionization. The elements generally exhibit strong electropositive ionic state in M$^{+3}$ form.

Sharp 4f-4f spectral lines are possible for lanthanides because their 4f electron orbitals lie within the shell of outer 5s and 5p electrons. The 4f electrons are largely shielded from the surrounding crystal field and are not involved in chemical bonding. However some interaction with the crystal field does take place, because depending on its symmetry, higher energy electronic states of opposite parity can be mixed with the 4f electronic states. It is this mixing of states which makes electronic dipole transitions possible. Without mixing only magnetic dipole and quadruple transitions could occur, and all optical transitions would be electric dipole forbidden. Ultimately any transition occurring within the lanthanides 4f orbital is going to be only weakly coupled to crystal lattice vibrations, and the resulting spectra will appear free-ion-like. The exemptions are higher energy transitions to levels above the 4f$^{n}$ electronic states, viz. 4f$^{n} \rightarrow 4f^{n+1}$5d transitions and/or charge transfer transitions which are parity allowed. Unlike the 4f- electrons, the 5s and 5p shells do not shield the 5d shell. These 4f$\rightarrow$5d transitions are greatly influenced by their surroundings and result in the broadband structure.

The absorption spectra of rare earths in the optical region arise from transitions within the 4f$^N$ configuration. Because of the shielding nature of the 5s and 5p shells, perturbations by surrounding neighbours do not take place resulting in sharp line spectra. The wavelengths of the emission and absorption transitions are relatively insensitive to the host material, the intensities of transitions are weak, the lifetimes of the metastable states are long and the quantum efficiencies tend to be high except in aqueous solutions. In condensed matter the trivalent (3+) level of ionization is most stable for lanthanide ions, and most optical devices use trivalent ions. For a few notably
Ce$^{3+}$ and Pr$^{3+}$, 5d levels lie low enough to produce strong, broad absorption bands in the ultraviolet. The consequences for the static interactions are energy levels that are relatively insensitive to host, have small host induced splitting, and are only weakly mixed with higher energy states. The dynamic consequences are little or no vibronic structure (phonon assisted transition) and weak nonradiative relaxation of excited states, which occur through phonon emission. The net results are optical transitions between 4f states that manifest themselves as narrow, wide bands or sharp lines, and emission that can be highly efficient.

1.5.1.1 Europium Ion

Europium is a member of the lanthanide series of elements, characterized by partially filled 4f- electron shell. The element europium is characterized by

![Figure 1.3. Luminescence channels of Eu$^{3+}$ free ions](image-url)
having two stable valencies Eu(II) and Eu(III). Transitions within the 4f⁶ shell (S=3, L=3 and J=0) of Eu³⁺ are responsible for the observed spectra. Eu₂O₃ is the commonly used source of Eu³⁺ ions in the production of phosphors and laser materials. The radius of the ion is 0.121 nm. In these materials Eu³⁺ ions are dispersed within an insulating host to eliminate energy transfer and concentration quenching. When Eu³⁺ ion occupies a crystallographic site that does not coincide with a center of symmetry magnetic dipole and electric dipole transitions are possible. Figure 1.3 gives the luminescence channels for the Eu³⁺ ion. In the case of Eu³⁺ there is in addition to the 4f⁶ levels, a charge-transfer state which plays an important role in thermal quenching processes. The intraconfigurational 4fⁿ⁻⁴fⁿ transitions are treated in a weak–coupling limit, whereas the interconfigurational f-d transitions are of intermediate coupling. The effective mediating phonon frequency in the latter case is less than half that of maximum frequency. In the weak coupling limit, the mediating phonon frequency does not differ greatly from the maximum phonon frequency.

1.6 Spectroscopy of Rare Earths in Glass

The spectral bands of materials doped with rare earth ions exhibit a fine structure, which appears in crystals as groups of narrow lines (Stark splitting) and in glasses as a more or less pronounced maxima in complex contour. The smoothing of the Stark structure for glasses is naturally explained by the inhomogeneous broadening caused by the disordered glass structure. 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. Rare earth activated lasers were reported by Snitzer as early as 1961. He demonstrated 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.33

Sol-gel matrices were also found to be a good host of rare earth ions. Neodymium has been incorporated into sol-gel SiO$_2$ at concentrations upto 5-10wt% without crystallization.27,34,35 Careful comparison of the spectra of sol-gel and melted silica containing 0.5% Nd$_2$O$_3$ 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 life times can reveal the existence of rare earth clustering and the presence of water and other additives in the immediate vicinity of the rare earths.

Rare Earth products are used in glass applications as colorants, stabilizers and UV absorbers. They are also used as modifiers to increase the refractive index and decrease dispersion of high purity glass. Concentrates are used in mirrors, cut crystal glass, TV screens and cathode ray tubes and polishing compounds. Purified compounds are also used as additives to optical safety, radiation shielding and crystal glass and for lasers, fluorescent lights and opticals.

La-containing glass has high refraction and low scattering, thus being used in lenses for all kinds of cameras. Er-containing fiber optics is used to replace the relay stations in the traditional optical transmission. Cerium is used in television glass to absorb UV rays and is added to glass to add or suppress color. Cerium is also used as a polishing agent for production of high performance optical glass such as lenses for digital cameras and telescopes. Nd-containing glass is a wonderful material for lasers. Gd and Y are used to produce special glass.
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 the expanding field of optics and optoelectronics. In oxide glass systems, besides traditional silicate glasses, borate, phosphate, germanite etc. have emerged and new glass forming systems have also been expanded to non-oxide glasses, such as halide and chalcogenide glasses. Since the emergence of lasers, transition element doped glasses (rare earth ions and transition metal ions) have become some of the most important laser materials. Special emphasis has been put on optical and spectroscopic properties of doped inorganic glasses in a lot of research activities. In addition to the conventional absorption spectra, the emission, relaxation and laser spectra were investigated in detail. Newly developed laser spectroscopic techniques are the most powerful tools for studying the optical properties of rare earth doped glasses. The interaction of intense laser radiation with glass media gives rise to a series of non-linear optical effects, such as self-focusing, laser induced damage, stimulated light scattering etc. Hence one must study the fundamental non-linear optical and spectroscopic properties of glasses.

The rare earth doped in a solid state matrix can be suitably processed to get the laser action in the infra red, entire visible and ultra violet regions. Spectroscopy provides with measurements involving some effective average over the distribution of physically different environment in glass. The spectra of the rare earth ions are composed of a set of sharp levels, which can be directly traced to their free-ion Russell-Saunders\(^{36}\) origin. The majority of commonly encountered transitions are intraconfigurational i.e., 4f-4f and...
hence are weak because of parity selection rules. The special optical properties of trivalent rare earth ions result from the fact that the electrons of their partially filled 4f shell are shielded from the surrounding completely filled 5s and 5p shells. The energy levels of the 4f shell arise from spin-spin and spin-orbit interactions are often denoted using Russel–Saunders notation $^{2S+1}L_J$ arise in which S is the total spin quantum number, L the total orbital angular momentum and J the total angular momentum. The most important feature of energy levels of rare earth ions is that all the levels of a particular ion have the same electronic configuration and consequently all of them have the same parity. Since the electric dipole matrix elements between the two states of the same parity are identically zero, electric dipole transition between any two levels of the ions is totally forbidden. However in a solid, the slight mixing with odd parity wave functions makes the transition slightly allowed. The absorption and emission cross-sections are therefore small and the luminescence life times can be quite long [ms].

The source of absorption in glasses is of three types : (1) Electron transitions within the unfilled orbits of the transition elements (2) Plasma resonance and (3) electron transitions across the bandgap. The transition elements are characterised by unfilled inner electron shell. The transition ion $M^{m+}$, is surrounded by negative ions or oriented dipoles called ligands in glass. Together they form a complex. The electric field of the ligands causes the degenerate energy levels in $M^{m+}$ to split. The energy difference between the two sets of split levels is the ligand field, denoted by 10Dq. The ligand field strength 10Dq is computed by estimating the ligand or crystal field stabilization energy (CSFE)$^2$. The optical properties of trivalent 4f ions in the crystals in the visible and near infrared are well understood in terms of the weak crystal field approximation.$^{37,38}$ There are two important effects that the crystal fields have on the energy levels of the rare earth ions. Firstly the previously (2J+1) degenerate LSJ levels are split into a number of Stark
levels. Due to the shielding of the 4f electrons by the 5s\(^2\), 5p\(^6\) electrons these Stark shifts are quite small only around a few hundred inverse centimeters. Secondly the crystal field breaks the inversion symmetry of the ions environment and this now permits electric dipole transition to occur between Stark levels in different LSJ multiplets. The oscillator strengths of these transitions are very small of the order of \(10^{-6}\), which reflects the weakness of the interaction of the 4f electrons with the crystal field. The magnetic dipole transitions, which are typically many orders of magnitude weaker than fully allowed electric dipole transitions, may nevertheless take place. Broadening of the rare earth ion fluorescence and absorption bands in glass is necessarily more complicated than in crystals, since glasses have by definition a random structure with each rare earth ion seeing a different electric field and therefore having a different set of Stark levels. For a first approximation it is considered that at room temperature the broadening of the absorption and fluorescence bands of rare earth doped glasses is homogeneous in nature. The fluorescence efficiency of an active ion in a material depends on various spectroscopic parameters such as absorption and emission cross section, transition probabilities, life times of the metastable levels, concentration of the dopant ions, and also the effect of ligand field on them.

\[
H = H_{\text{free ion}} + V_{\text{ion-static lattice}} + V_{\text{ion-dynamic lattice}} + V_{\text{EM}} + V_{\text{ion-ion}}
\]

First two terms give rise to observed electronic structure. The quantum numbers (L,S,J and another arbitrary one ) defines the terms of the configuration, all of which are degenerate in the central field approximation for Lanthanides and Actinides. While both the electrostatic and spin-orbit interactions increases with increasing atomic number, spin orbit increases more rapidly and LS mixing is more significant for the high Z rare earths\(^{39}\).

### 1.7. Rare earths complexes in sol gel glasses

Luminescent materials based on lanthanides are attractive as labels for
advanced time-resolved fluoroimmunoassays, and molecular markers, their potential use is also conceivable in the field of luminescent displays, molecular photonics and highly luminescent materials in hybrid organic/inorganic glasses. The lanthanide complexes trapped in sol-gel inorganic glasses based on silica and zirconia networks and their spectroscopy allows preparation of new family of such complexes in sol-gel based materials.\textsuperscript{40} Much effort has been devoted to the study of complexes which contain ligands that have high absorbance in the UV followed by efficient energy transfer to excited f states of rare earth. The dominant characteristics which determine the luminescence quantum yield of these complexes are the energy gap law corresponding to the difference in energy between the excited emitting state and the highest state of the ground $^{2J+1}L$ term, the location and influence of ligand metal charge transfer (LMCT) states, and the competition with non radiative decay processes. Inter- and intramolecular dynamics also affect the luminescence properties of lanthanide(III) complexes\textsuperscript{41}. These are severely reduced in solid samples, and, more recently, in experiments in which the luminescent species have been incorporated into transparent sol-gel. Incorporation of rare earth ions into silica matrix along with semiconductor nanocrystallites allowed to obtain better luminescence than in silica matrix.\textsuperscript{42} The emission spectra of the complexes when compared to non complexed europium show a dramatic increase in emission intensity of the europium. When normalized to the absorption an increase is observed in Eu$^{3+}$ luminescence in silica codoped cadmium sulphide as compared with zirconia glass. The incorporation of the cryptate complexes into zirconia films results in dramatic increase of the emission intensity as well as in the increase of the absorption intensity of Eu. The former results from the shielding of OH– vibrations responsible for the non-radiative relaxation and lowering of the symmetry site in which Eu is situated. The most dramatic effect must arise from energy transfer from the organic ligand to the Eu.
1.8. Quantum dots in sol-gel glasses

Nanoparticles of metals, semiconductors and dye aggregates have atomic arrangements in aggregates of the size ranging between molecular clusters and infinite solid state arrays of atoms. ‘Clusters’ are used for agglomerates of very few atoms, ‘nanoparticles’ are used for larger agglomerates and ‘quantum dots’ are used for semiconductor particles and islands where quantum confinement of charge carriers or excitons determine their properties. Their properties are determined by the extent of confinement of highly delocalized valence electrons. An ideal nanocrystal is considered to be a bit of a crystal with a spherical or cubic shape, called as a ‘quantum dot’. Nanocrystals dispersed in a transparent host environment exhibit a variety of guest-host phenomena known for molecular structures. Semiconductor doped glasses (SDG) have large non linear susceptibilities for optical transitions near their optical band gap and a fast electron hole recombination time of picosecond order. When introduced into glasses their spectroscopic properties can be measured and the shifting of the discrete energy levels compared to the continuous band energies determined.

In an infinite and perfect semiconductor, there is a strict periodicity of the atoms in the lattice. This implies that the there is a periodical interaction

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure1.4}
\caption{(a) The band structure of an infinite and perfect semiconductor with a band gap $E_g$ at 0K.
(b) The band structure for a nanocrystal with a crystal size $r$ and a size dependent bandgap $E_g(r)$.}
\end{figure}
between the electrons and the potential generated by the lattice atoms, which results in a band structure. In the nano-regime, the electronic, structural, magnetic and thermodynamic properties are essentially size dependent. The cause of this behaviour is due to the fact that the electronic energy levels in a quantum dot are not continuous as in bulk, but are discrete. The discreteness is caused by the confinement of the electron wave function in finite physical dimensions of the particle.

The most simple band structure is shown in the figure 1.4(a), where the lower band, the valence band (VB) consists of electronic states that are all occupied. The higher band, the conduction band (CB), is comprised of unoccupied states. The width (in energy) of the region where no electrons or holes are allowed is denoted by $E_g$, the band gap energy. When a semiconductor crystal is illuminated with photons of sufficiently high energy the light can be absorbed by the material. The absorption of light by the semiconductor usually results in the promotion of an electron from the valence band to the conduction band results in the formation of electron-hole pair or an exciton.

The exciton is considered as a composite particle with a center of mass motion having a reduced mass

$$\mu = \frac{1}{\left[m_e^*\right]^2 + \left[m_h^*\right]^2} \quad (1.1)$$

where $m_e^*$, $m_h^*$ the effective mass of electron and hole respectively. These effective masses are related to the degree of interaction of the electron and hole with the semiconductor lattice. The size of this quasi particle is referred to as exciton Bohr radius written as

$$a_B = \frac{4\pi\varepsilon_0 e^2 h^2 \left(m_e^* + m_h^*\right)\left(m_e^* m_h^*\right)}{m_0 e^2} \quad (1.2)$$

where $\varepsilon_0$ is the dielectric constant of the semiconductor.
When a semiconductor becomes sufficiently small, the bulk exciton Bohr radius can become comparable to, or even bigger than the crystal dimensions. As a result, the total exciton will have to be squeezed to fit into the crystal. This results in an increase in the kinetic energy of the exciton, usually called the confinement energy. When this happens there will be a change in the band structure of the semiconductor as shown in figure 1.4(b). Because of increasing confinement energy for decreasing crystal size, the valence band will move downward and the conduction band will move upward. The net effect is the increase in the band gap. This results in a blue shift of the excitation energy of the semiconductor. When small amounts of dopant ions are incorporated into a semiconductor many interesting applications are possible. The substitutional dopants are located on a host lattice site and do not belong to the host lattice material and these materials are responsible for the luminescence.

The science and technology of nanomaterials need to take into account a bandgap, which is different from that of the bulk. The quantum size effect (QSE) predicts formation of a bandgap with decreasing particle size for metals and widening of intrinsic gap for semiconductors. The bandgap for semiconductor is usually well described by an extended effective mass approximation (EMA), which describes a bandgap increasing with decreasing particle size. These energy states of the quantum dots are positioned between the discrete energy levels of the atoms or bands of molecules and the broad band of the condensed phase. Semiconductor nanocrystals (NCs) in transparent media have, especially in sol-gel glasses, received recently a large attention due to their promising applications in non-linear optics and optical switches. Those nanometer-sized crystals, which are comparable with the bulk exciton Bohr radius, exhibit an intermediate behaviour between a bulk crystal and an isolated molecule. For example, CdS and CdSe NCs and CdTe exhibit a large optical non-linearity. The nanometer sized semiconductor crystallites of CdS, CdSe, CdTe, and PbS were formed by chemical procedure in glass.
films prepared by the sol gel method. The films are either pure silica, silica ormosils, zirconia or combined zirconia with ormosils.

As the sizes of the nanocrystallites decrease, controlled by the preparation method the band gap shifts to higher energies due to quantum size effect. Spectroscopic method of absorption and luminescence allow to determine the shift and Atomic Force microscope (AFM) and Transmission Electron Microscope (TEM) the size of the nanoparticles. X-ray diffraction for larger nanoparticles provides information on the crystallographic structure of the particles.

1.9. Energy Transfer in Doped Glasses

The weak ion phonon or lattice coupling and sharpness of transitions make 4f ions very useful as probes of various excitations and interactions in the condensed phases. The energy transfer between two inorganic ions can occur either by multipolar interaction or exchange mechanism in dilute systems or by multi-step migration in concentrated systems. Forster\(^{45}\) and Dexter\(^{46}\) developed the theory for the multipolar resonant energy transfer. According to their theory energy transfer can occur between a donor and an acceptor provided the emission transition of the donor overlaps with the acceptor absorption transition. For the exchange coupling Inokuti and Hirayama\(^{47}\) proposed a theoretical treatment assuming that the sensitizer ion is surrounded by a set of acceptor ions and during the transfer process the environment of excited acceptor ion changes with time in a non-exponential manner.

The theory of non-resonant energy transfer where the energy mismatch between the energy levels of the donor and the acceptor ions is compensated by the emission or absorption of phonons was developed by Miyakawa and Dexter.\(^{48}\) The energy transfer in dilute systems has been summarised by Watts.\(^{49}\) As the concentration of the impurity ions is increased the average distance between the ions decreases which in turn causes greater interaction
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between the ions. Consequently, the excitation energy residing on donor ion can nonradiatively be transferred to acceptor ion. In rare earth doped glasses energy transfer between like ions is known as cross-relaxation and it causes concentration quenching. However unlike ions in glasses may cause dopant quenching and sensitizing. In the absence of concentration quenching an excited sensitizer may either fluoresce or transfer energy to an activator. If the sensitizer transfers its energy before it can fluoresce there will be an overall decrease in the fluorescence of the sensitizer and it corresponds to the nonradiative transfer process. In upconversion processes nonradiative energy transfer and multiphonon relaxation were observed\(^5\). On the other hand, if the ion fluoresces before transfer takes place the activator will absorb only part of this fluorescence corresponding to one of its absorption peaks leading to the process of radiative transfer.

1.9.1 Radiative and nonradiative transitions

When an optically active ion in a solid is raised to an excited state, it may get deexcited by radiative emission (Fig 1.5 a) or by a number of non-radiative processes: by multiphonon emission to the next lower state(1.5 b), by cross relaxation (1.5 c), or by energy transfer resulting in loss of excitation to some non radiative center in the solid (1.5 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](https://example.com/diagram.png)

**Figure 1.5** Deexcitation process out of the excited state (a) is the radiative process (b) is the non radiative multi-phonon process (c) cross-relaxation and (d) shows cross-relaxation with an adjacent similar ion followed by transfer to a center which then decays non radiatively.
In Eu\textsuperscript{3+} systems the cross relaxation can occur between neighboring Eu\textsuperscript{3+} ions. 
\[
\text{Eu}^{3+}(^5D_1) + \text{Eu}^{3+}(^7F_0) \rightarrow \text{Eu}^{3+}(^5D_0) + \text{Eu}^{3+}(^7F_3).
\]
When cross relaxation occurs, the \(^5D_0\) level emission of ion 1 is quenched in favour of \(^5D_0\) and ion 2 is excited to the \(^7F_3\) level. This is because the energy difference \(^5D_1 - ^5D_0\) is exactly equal to the energy difference \(^7F_3 - ^7F_0\) of ion 2. If the energy difference do not match exactly, the energy mismatch is compensated by phonon emission 
\[
\text{Eu}^{3+}(^5D_1) + \text{Eu}^{3+}(^7F_0) \rightarrow \text{Eu}^{3+}(^5D_0) + \text{Eu}^{3+}(^7F_2) + x \text{ (cm}^{-1})
\]
where \(x\) is the energy of the phonon emission.

1.9.1.1. Radiative Processes

Optical transitions between 4fn levels used for optical pumping and stimulated emission are predominantly of electric dipole in nature. Electric dipole transitions between states of 4f and 5d configuration are parity allowed. The oscillator strengths of transitions between J states are small \(\sim 10^{-6}\) while the f-d transitions have magnitudes of \(10^{-1}\) to \(10^{-2}\). Radiative transitions between 4fn 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. 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.

1.9.1.2. Non-radiative Processes

The first quantitative studies of nonradiative processes on rare earth ions in glasses were carried out by Reisfeld and coworkers. In these processes the electronic energy of the excited rare earth is transferred to vibrational energy of the host lattice or molecule. The nonradiative decay rate at low temperatures is given by to good approximation by the empirical formula

\[
W_{nr} \approx 10^7 \exp[-\beta(p - 2.4)]
\]  
(1.3)
where $\beta \approx 2$ for crystalline hosts and $\beta \approx 4$ for oxide and fluoride glasses, $p$ 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$^{53}$. The enhanced nonradiative decay in the oxide glass is attributable to the presence high frequency vibrations in these glasses, in the range of 700-1400 cm$^{-1}$, 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 efficient long wavelength luminescence from oxide glasses.

**Multiphonon process**

Multiphonon decay rates from excited states of rare earth ions determine three important properties of rare earth lasers: pump conversion efficiency, radiative quantum efficiency and lifetime of the terminal laser level. The most important factor influencing the multiphonon emission rate is the energy gap to the next- lower level. The major contribution to multiphonon processes involves the highest energy vibrations since they can conserve energy in the lowest order process. Studies of rare earths in glass demonstrate that multiphonon relaxation is predominantly to the highest frequency vibrational modes which are associated with the glass former.
1.10. Phonon Sideband (PSB) Spectroscopy

In rare earth doped glassy matrices the local crystal field symmetry produces a Stark splitting of the individual 4f levels and thus contributes to the intrinsic 4f-4f transition line width and radiative lifetime. The local vibrational density of states of the host lattice can, in addition, provide an alternative, nonradiative pathway for excited state decay characterized by a nonradiative decay rate. The parameter for classifying the decay process is the number of phonons \( p \) required to bridge the energy gap \( p = E/\hbar\omega \) where \( \hbar\omega \) is the energy of the effective phonons involved in the relaxation. In order to determine \( p \) we need to determine the frequencies of these phonons. The complete vibrational spectra of the glass can be found from the first order Raman spectrum. For each glass the highest frequency vibration is associated with the stretching mode of the glass network formers. It is the phonons of highest frequency which are involved in the multiphonon nonradiative decay process. The nonradiative processes can be particularly detrimental to the performance of amplifying devices when a population inversion is required.\(^{54}\)

The dependence of local vibration around a rare earth ion in glass can be investigated by analysing the phonon side bands associated with a particular transition.\(^{55}\) The \( \text{Eu}^{3+} \) ion has a suitable transition \( ^{5}\text{D}_{2}\leftrightarrow ^{7}\text{F}_{0} \) to measure phonon side bands because fluorescence excitation band of the pure electronic transition is observed as a single peak and the energy gap to the next higher level is quite large.\(^{56}\) The phonon side band is hardly observed for other rare earth ions because of complex spectral profiles.

The compositional dependence of the local vibrational environment around rare earth ions in \( \text{SiO}_2\text{-PbF}_2 \) glass-ceramics were studied by Takahashi et. al.\(^{57}\) The nonradiative loss due to multiphonon relaxation is crucial in assessing the radiative quantum efficiency and the excitation efficiency of the excited state absorption(ESA). The lower the multiphonon decay rate the more efficiently the upconversion emission is obtained.\(^{58}\) Further the results obtained from the
phonon sideband spectra are reported to be intriguing as they provide clues to the lattice structure around which the rare earth ion prefers to take residence in various glass hosts.\(^ {59,60,61}\)

1.11 Applications

The new materials includes:

- Luminescent solar concentrators\(^ {62}\) and antireflection coatings\(^ {63}\),
- Electrochromic\(^ {64}\), photochromic and gasochromic plates for smart windows that change their transparency according to solar irradiation,
- Sensors for environmental and biological impurities\(^ {65}\),
- Solid lasers tunable in the visible spectral range
- Active waveguides\(^ {66}\),
- Quantum semiconductor dots\(^ {42}\),
- Materials for linear and nonlinear optics, and
- Complexes of rare earth ions that can be used for diagnostics and biological markers\(^ {67}\).

Between 1997 and 2001 the demand for rare earth permanent magnets grew at 21% per year. Rare earth metals of Neodymium, Dysprosium, Samarium, Terbium and Praseodymium are widely used in the production of permanent magnets of NdFeB, SmCo and SmFeN, which are mainly used in automobile, computer, and telecommunications industries to improve performance and efficiency. One of the largest magnetic applications in the automobile industry is to improve fuel efficiency by saving weight in the motor using these small size magnets.

Rare earth compounds are known to emit distinct and different wavelengths in the electromagnetic spectrum, the three main phosphor applications using rare earths are color cathode ray tubes, tri-phosphor fluorescent lamps, and X-ray
intensifying screens, in which Y$_2$O$_3$ and Eu$_2$O$_3$ of 99.99% pure, play a key role, in addition, high purity La$_2$O$_3$, CeO$_2$ and Gd$_2$O$_3$ are used.

Some other promising applications of Rare Earth products include: Lasers, Superconductors, Data storage, Optical fibers, Nuclear uses, Magnetostrictive alloys, Magnetic refrigeration; Cement additive, Paints and coatings, etc. Magnetic refrigeration now under industrial experiment is a typical example, which is characterized by low cost and pollution free and will cause a revolution in refrigeration industry if commercialized. Giant magnetic resistance material has a capacity potential hundreds of times larger than that of commonly used information storage elements today. PDP phosphor will help realize thin and large screen for color TV and computer monitor. And fuel cell will provide the final solution for pollution free power sources for electronic products and electric vehicles.

Our efforts in understanding the mechanism of sol-gel processing have realized that the technique can be characterized as a method of glass production from liquids. Recently more focus has been paid to the studies of molecular behavior in small pores present in sol-gel glass. The total pore volume of the pores within the sol-gel glass may reach 0.5 cm$^3$/g and it is possible to manufacture sol-gel glass of average pore diameter ranging from 2 nm to 200 nm. The pores are interconnected and may be doped with almost any gas, liquid or a liquid solution of a solid. Because the pores are extremely small, the pore diameters are similar to the sizes of molecules, the sol-gel glass enables one to investigate the molecular behavior in small geometries. It is established that the process of molecular diffusion, reorientational motion, vibrational energy relaxation, liquid-solid and solid phase transitions are all affected by the geometry of the pores and are different from the properties of the bulk system.

Slow diffusion process through the network of interconnected small pores can control the flow of the dopant material into the glass to produce a desired
concentration distribution of index modifying material. Parabolic distribution of metal oxides within a cylindrical sample resulted in diverging and converging flat lenses, the so called Gradient Index, GRIN lenses. As another important application of the sol-gel processing it is found that the slow molecular transport in small geometries can be effective in the drug delivery process. After a sol-gel glass is loaded with steroids, peptides or other drugs it may be implanted, and the dopant will leach out slowly over a period of months. A constant delivery rate of a hormone on the order of a mg per day, a medically significant dosage, has been observed in rats.
Reference


39. Miniscaleo W J., Rare earth doped fiber lasers and amplifiers Chapter 2 Ed by Michel J F Digonnet, Marcel Dekker Inc.