I INTRODUCTION

1.1 General introduction

1.1.1 Definition of glass

Glass is an inorganic product of fusion, which has been cooled to rigid condition without crystallization. Glasses are characterized by certain well-defined properties which are common to all and different from those of liquids and crystalline materials. The atomic arrangement of glass is different from those of crystalline materials and lacks long range regularity. There is neither crystal lattice nor lattice point in the glass structures and, therefore, instead of diffraction peaks a halo is seen in the X-ray diffraction patterns of a glass. X-ray and electron diffraction studies show that glasses lack long range periodic ordered constituent atoms.

In general, glass is defined as an amorphous solid which exhibits a glass transition and whose shear viscosity exceeds $10^{14}$ poise [1]. At the glass transition temperature a solid amorphous phase exhibits abrupt change in the derivative of heat capacity or thermal expansion from crystal phase to liquid phase. All the glasses are amorphous but not all amorphous solids are necessarily glasses. Fig. 1.1 shows the variation of specific volume with temperature indicating transformation from molten liquid to glass through supercooled liquid stage. As temperature decreases, the specific volume also decreases. When the melting point $T_m$ is reached, an ordinary liquid releases its fusion heat and changes into a crystal. Afterwards, the volume decreases according to the expansion coefficient of the crystal. A substance that solidifies into a vitreous state does not crystallize at the melting point, but continues to be cooled in a liquid state, which is called as supercooled state. Thermodynamically it is not a stable state but it is a metastable
state. As the temperature decreases further, the volume also decreases. At the end, the volume decreases with almost the same expansion co-efficient as in crystals. At temperature $T_g$, a shift is observed indicating transition of the expansion coefficient of liquid to the solid. A supercooled liquid below this temperature is called a vitreous state. Above this temperature the liquid is in a supercooled state. These changes can be observed by monitoring the volume as a function of temperature by means of a dilatometer. This process of glass transition can be monitored by Differential Scanning Calorimetry (DSC) or Differential Thermal Analysis (DTA). In these methods the sample is heated at a constant range and the changes in heat (DSC) or temperature (DTA) with respect to an empty reference pan are measured. A schematic diagram of a typical DTA trace is shown in Fig. 1.2.

1.1.2 Inorganic oxide glass and borate glass

Glass is a continuous random network lacking both symmetry and periodicity. The basic structural units which make up the glass network have a definite geometry but are connected at corners to form a random three dimensional network, for example SiO$_4$ tetrahedra or BO$_3$ triangles [2]. Several compounds exist in an amorphous phase singly and constitute simple glass formers, for example, SiO$_2$, GeO$_2$, B$_2$O$_3$, P$_2$O$_5$ and As$_2$O$_3$. Conditional glass formers like TcO$_2$, Al$_2$O$_3$ and WO$_3$ require the presence of one or more additional compounds to form a glass. Other compounds like alkali oxides, alkaline earth oxides and other oxides such as SeO$_2$, MoO$_3$, PbO, Bi$_2$O$_3$, Ga$_2$O$_3$ and V$_2$O$_5$ modify the network when added to the glass. Anions like oxygen, halogens etc., when they bridge two network former cations they become non-bridging. Network modifier cations such as alkali, alkaline earth and higher valence state ions are accommodated randomly in the network in close proximity to non-bridging anions. Rare earth ions depending upon their size and valence state, enter a glass network as a network
Fig. 1.1. Volume-Temperature diagram for glassy, liquid and crystal states.

Fig. 1.2. Schematic DTA trace showing the (1) Glass transition (2) Crystallisation and (3) Melting.
modifier cations. Some times it is difficult to add \( \approx 1 \, \text{mol}\% \) of rare earth oxides to simple glass network formers. Bridging oxygen tightly bonds the network of these single component glasses. Trivalent rare earths can not easily enter this structure substitutionally because of size.

Silica and Silicate glasses are used mostly for various commercial applications. Recently, non-silicate glasses like phosphate, borate, germanate and telluride are also used as key components of various devices in the field of optics, electronics and optoelectronics. Although non-silicate glasses are not generally applied to mass production due to the high cost of raw materials, they do show unique properties that can not be obtained for silicate glasses. The formation of these non-silicate oxide glasses is also made by melt quenching technique. Phosphate glasses have a lower softening point than silicate glasses and are used as the enamel for aluminum metal and as solder glasses for glass-to-glass bonding [3, 4]. Multi component borate glasses, which consist of \( \text{BO}_3 \) triangles and \( \text{BO}_4 \) tetrahedra are formed by combination with alkali, alkaline earth oxides and alumina etc. [5]. Due to high compatibility with rare earth elements, borate glasses are used in optics and opto-electronic fields.

\( \text{B}_2\text{O}_3 \) is the basic network forming oxide of borate glasses. From the vibrational spectrum of amorphous \( \text{B}_2\text{O}_3 \) and from the other studies, boroxol rings were thought to be major constituents of the structure [6-9]. Guha and Walrafen [10] postulate that the structure of vitreous \( \text{B}_2\text{O}_3 \) is comprised of an equal proportion of boroxol rings and \( \text{BO}_3 \) triangles, whereas the conclusion of some molecular dynamics studies [11, 12]. X-ray and neutron diffraction data was that a glass structure consists of a random net work of \( \text{BO}_3 \) triangles but without boroxol rings. Nuclear Magnetic Resonance (NMR) data of Silver and Bray [13] confirmed the three coordinated structure of boron in \( \text{B}_2\text{O}_3 \) glass. The \( \text{BO}_3 \) triangles, like the
SiO$_4$ tetrahedra are interlinked to form a continuous three-dimensional network but the structure of B$_2$O$_3$ is more complex than that found in SiO$_2$. The Raman spectra of vitreous B$_2$O$_3$ and crystalline B$_2$O$_3$ are quite different [14]. In crystalline B$_2$O$_3$ the boroxol rings are absent and it consists of a chain of BO$_3$ triangles. Krogh-Moe [15] provided a detailed review of the structure of B$_2$O$_3$ glass.

With the addition of alkali oxides, the structural variations that take place in B$_2$O$_3$ are quite different compared to silicates. In borate glass, conversion of BO$_3$ units to tetrahedral BO$_4$ units takes place without the creation of non-bridging oxygens. From the X-ray diffraction study of a series of alkali borate glasses, Biscoe et al. [16] have first observed the evidence for this change in the boron coordination. For alkali borate glasses, the abrupt property changes were observed nearly at 15-20 mol% modifier oxide [17]. This peculiar and anomalous behavior, referred to as ‘borate anomaly’ was first explained in terms of the unique ability of boron to exist in two distinct coordination states, the trigonal and tetrahedral. The addition of alkali oxide to boric oxide results in conversion of boron from trigonal to tetrahedral co-ordination up to 20 mol% and at 20 mol% of R$_2$O (R=Li, Na, K, and Rb) the tetraborate reaches maximum concentration, the boroxol group disappears and the formation of diborate starts. Shelby [18] correlated these abrupt changes in properties of alkali borate glasses with increasing alkali content with changes in the concentration of the structural groups rather than the concentration of BO$_3$ and BO$_4$ units. He related the minima observed in the thermal expansion coefficient of alkali borate glasses at 20 mol% R$_2$O to the maximum concentration of tetraborate groups and the disappearance of boroxol and appearance of diborate groups which occur at this composition. But the recent studies [19] have indicated that, with the addition of alkali oxide, boroxol rings are getting converted into pentaborate units and not into tetraborate or triborate groups. The incorporation of a second BO$_4$ tetrahedron into a pentaborate group results in the formation of a
dipentaborate group. At higher contents of alkali oxide the NBO's are present in the form of orthoborates, pyroborates, ring and chain type metaborates. The different structural groups that are present in alkali borate glasses are shown in Fig. 1.3.

Chong et al. [20] showed that mixed alkali borate glasses have structures that are quite similar to the binary borate glasses. Zhong and Bray [21] studied the changes in the concentration of BO$_4$ groups in different mixed alkali borate glasses and found that the measured values are less than the expected from simple superposition of constituent alkalis. When one alkali is progressively substituted for another, many physical properties of oxide glasses show nonlinear behavior as a function of alkali content. This phenomenon is known as mixed alkali effect [22]. Different models were proposed to explore the origin of this phenomenon. Inspite of extensive investigations, there appears to be no universally accepted mechanism for the various mixed alkali effects. According to the Weak Electrolyte Model [23, 24], in a mixed alkali glasses, the mixed alkali effect in the ionic conductivity is explained by the three assumptions, a) a very small fraction of the alkali ions which are presented in the form of interstitial pairs, b) there is a preponderance of mixed alkali ion pairs and c) the pairs consisting of unlike alkali ions having much lower mobility and therefore do not contribute to electrical conduction. The second assumption in this model gives a clue for the structure of mixed alkali glasses.

1.1.3 Optical properties of glasses

The optical properties of glasses are important in many wide ranging industries as well as research applications like windows, glass containers, camera lenses to lasers, waveguides and optical fibres for optical communications. Over the past few years, there has been a great deal of interest shown on the preparation and characterization of a wide variety of inorganic glasses comprising the oxides,
Fig. 1.3. Different structural groups present in alkali borate glasses.
silicates, borates, phosphates and fluorides for their possible applications in the laser glass technology [25-30]. Glasses are good host matrices for rare earth lasers [31, 32]. Optical spectroscopy has been used as an important tool to study the nature of glasses for their various applications. For practical applications of glasses, the wavelength range studied is from 200 nm to 2400 nm with visible range lying between 400 nm to 750 nm.

Glasses of oxide and fluoride systems that have a wide gap between the conduction and valence bands are generally transparent to light in visible and near infrared regions. Due to its high transparency to visible light, glass is used as an important material for various optical components. By varying the chemical composition of glass matrices, number of commercial optical glasses have been developed so far. The primary requisite for an optical glass are high purity and high homogeneity to allow the propagation of light beam with minimum optical loss. Glass plays an important role in rare earth laser systems, because glass can be made with uniformly distributed rare earth concentrations and has great potential as a laser host medium. Materials for laser operation must possess sharp fluorescent lines, strong absorption bands and reasonably high quantum efficiency for fluorescent transition of interest. These characteristics are generally shown by solids, which incorporated a small amount of active ions in which the optical transition can occur between states of inner incomplete electron shells. Trivalent lanthanide ions have been the most extensively used active ions because there are many fluorescing states and wavelengths to choose from among the 4f electron configurations. The absorption and fluorescence bands in rare earth ions are due to the electronic transitions which occur within the 4f shell, which is well shielded by the outer 5s and 5p shells. On the other hand, in transition metal ions the electronic transitions occur in the 3d shell, which is outer most shell. The strong/sharp line absorption and fluorescence from rare earth doped glasses allow them to be used
extensively as active media in optically pumped laser devices. In glasses, disorder in structure produces in-homogeneously broadened lines. This raises the threshold and reduces the amplified spontaneous emission losses. This property is utilized for Q-switched applications. Shorter pulses can be obtained by mode locked operation using broader fluorescence lines of glasses.

1.2 Optical absorption and fluorescence

At normal laboratory temperatures, the atoms and molecules would be in the ground state. When they absorb the incident electromagnetic radiation, the system raises to higher energy excited states. The variation of intensity of absorption with wavelength or frequency is called the absorption spectrum. During the process of absorption, the atom may have an electron displaced from the ground to the higher energy levels. The atomic spectra thus resulting from electronic transitions are often called as electronic spectra. The optical absorption spectroscopy in the Ultra Violet-Visible-Near Infrared (UV-VIS-NIR) region is a sensitive technique to understand the optical absorption properties of rare earth ions in glasses. The study of optical absorption and fluorescence of rare earth doped glasses is an attractive area of research both from the fundamental and technological viewpoint.

The absorption of electromagnetic radiation in the visible region can be classified into three different types. In the first type, electron leaves an orbital located largely on one ion or atom and it occupies an orbital located largely on another ion or atom. Such transitions are called interionic transitions or charge transfer transitions and they are allowed transitions. The absorption bands associated with these transitions are very intense. Intraionic transitions are the second type which involve excitation of ligand electrons to higher levels localized on the same ligand. These transitions are also allowed and are very intense. In the
third type, transitions occur between non-degenerate energy levels of ions with unfilled inner electron shells. These transitions are spin forbidden and hence the intensity of absorption bands is much lower. The optical absorption spectra of triply ionized rare earth ions originate from intraionic electronic transitions. The 4f orbits of rare earth ions lie well inside the electronic shell and are well protected by the surrounding 5s\(^2\) and 5p\(^6\) closed shells so that the sharp line optical absorption can be obtained not only in the ground state but also in most of the excited states. Thus the 4f electrons are only weakly perturbed by the charges of the surrounding ligands. The positions of absorption lines arise from a combination of the coulomb interaction among the electrons, spin-orbit coupling and the crystalline electric field. The resultant splitting of the 4f\(^n\) configuration are shown in Fig. 1.4.

The optical absorption properties of rare earth ions in the glass matrix depend on surrounding environment of the rare earth ion and the interaction of rare earth ion with ligands. Spectral intensities of a set of absorption lines for a particular rare earth ion in any glass matrix is characterized by three intensity parameters. These parameters depend on the symmetry of the crystal field at the rare earth site and the strength of the covalence of rare-earth oxygen bond. From these parameters, several important lasing characteristics can be studied.

Luminescence is a general term used to describe the emission of radiation from the substance which can be excited by various methods. If the excitation takes place by the absorption of electromagnetic radiation, it is called photoluminescence. If the excitation takes place by bombardment with electrons, it is called electroluminescence. Chemiluminescence is luminescence produced by chemical reaction. Photoluminescence is further classified into fluorescence and phosphorescence depending on the nature and duration of the emission following the removal of excitation. When the emission of light is instantaneous, the
Fig. 1.4. Schematic diagram of the splitting of rare-earth energy levels due to the electrostatic, spin-orbit and crystal field interactions.
phenomenon is called fluorescence, but emission occurs when after some time lag, it is known as phosphorescence. Phosphorescence has a lifetime longer than $10^{-4}$ sec, whereas the lifetime of fluorescence is generally of the order of $10^{-10}$ to $10^{-1}$ sec. The emitted photon energy is different (generally lower) than the energy of excitation for both fluorescence and phosphorescence.

When an electron is excited from a ground state to an excited state, it will return to the ground state and emit energy via two distinct processes: 1) radiative decay with the emission of a photon 2) Non-radiative decay where the excitation energy is converted into vibrational quanta of surroundings. The radiative decay is affected by the asymmetry of the surrounding binding forces. In a glass matrix, these binding forces are determined by the immediate neighborhood of the fluorescing ion. Therefore, potential fluorescent centers may find themselves in different environments within a glass. In general, this leads to broadening of fluorescence bands as compared to the bands of similar centers in crystals. Hence, the position, intensity and full width at half maximum of the fluorescence line would be affected by the structure of the glass matrix. Therefore it is of interest to study the fluorescence spectra of rare earth doped glasses. Rare earth doped glasses find variety of applications such as in optical amplifiers, lasers and other opto-electronic devices.

1.2.1 UV-Absorption: Fundamental absorption edge

The measurement of optical absorption and absorption edge is important in connection with the theory of electronic structure of amorphous materials. The rapid rise of absorption-coefficient is referred to as the “UV cut off” or “fundamental absorption edge”. The UV absorption is generally believed to involve in the excitation of the electrons associated with oxygen anions in glasses. For the first time Stevels [33, 34] discussed the UV absorption mechanism in
glasses theoretically. McSwain et al. [35] studied the effect of composition on the UV spectra of borate and silicate glasses and concluded that for both alkali silicate and borate glasses there is shift of the UV transmission cut off to longer wavelength as the alkali content increases. The spectroscopic study of some borate and vanadate glasses has also been reported by Ahmed and Hogarth [36]. Krogh-Moe [37] reported IR studies of boron oxide glass and alkali borate glasses. Hogarth and Hosseini [38] and Bae and Weinberg [39] made a detailed study of the effect of composition on the absorption edge. The information obtained from this study is valuable in the development of UV transmitting glasses for application like bactericidal lamps.

1.3 Review of the literature

Many systematic studies of optical absorption and fluorescence of rare earth doped glasses were made by several authors [40-47]. Studies on spectroscopy of Sm\(^{3+}\) doped different glassy matrices were reported by various authors [48-52b]. Annapurna et al. [53] reported temperature dependent luminescence characteristics of Sm\(^{3+}\) doped silicate glass. Jayasankar et al. [54] reported high-pressure fluorescence study of Sm\(^{3+}\) in lithium fluoroborate glass. Spectroscopic properties of Sm\(^{3+}\) ions in fluorophosphate glasses were given by Binnemans et al. [55]. Saisudha and Ramakrishna reported optical absorption of Sm\(^{3+}\) in bismuth borate glasses with large radiative transition probabilities [56]. Judd-Ofelt analysis and multiphonon relaxations of Sm\(^{3+}\) ions in fluorohafnate glasses were analysed by Cases and Chamarro [57]. Vijaya Prakash reported absorption spectral studies of Sm\(^{3+}\) doped in NASICON type phosphate glass, Na\(_4\)AlZnP\(_3\)O\(_{12}\) [58].

Similarly, spectroscopic investigations of Dy\(^{3+}\) doped glasses were presented by various authors [55, 59-62]. Shin and Heo [63] studied mid-infrared emission and multiphonon relaxation in Dy\(^{3+}\) doped chalcohalide glasses. Dy\(^{3+}\)
doped stabilized GeGaS glasses for 1.3 μm optical fibre amplifiers were presented by Guimond et al. [64]. Nachimuthu et al. [50] gave absorption and emission spectral studies of Dy$^{3+}$ ions in PbO-PbF$_2$ glasses. Hormadaly and Reisfeld [65] studied intensity parameters and laser analysis of Dy$^{3+}$ in oxide glasses. Optical properties of fluorozincate glasses doped with Dy$^{3+}$ ions were studied by Cases et al. [66]. Dysprosium phosphate glasses with compositions Dy$_2$O$_3$(1-x)P$_2$O$_5$ (x = 0.18 to 0.30) have been synthesized and analyzed using infrared, far-infrared and laser Raman spectroscopy by Sun and Risen [67]. Tanabe reported optical transitions of rare earth ions for amplifiers and the working of local structure in glass [68].

Reisfeld et al. [69] studied absorption and fluorescence of Ho$^{3+}$ in La$_2$S$_2$.3Ga$_2$S$_3$ glass. Blue and green upconversion fluorescence of Ho$^{3+}$ in fluoride glasses was reported by Zou and Toratani [70]. Buddhudu and Bryant [71] reported optical properties of Ho$^{3+}$ alkali mixed fluoride glasses. Allain et al. [72] reported holmium in ZBLAN interplay of lasing, co-lasing and excited state absorption. Kishimoto et al. [72a] studied Upconversion fluorescence in Ho$^{3+}$ doped ZnCl$_2$ glass. Some of the authors reported optical transitions and various spectroscopic parameters of Ho$^{3+}$ in YAG and LiYF$_4$ crystals [73, 74].

Several spectroscopic investigations were made on Tm$^{3+}$ doped glasses for their various applications [75-80]. Zou and Toratani reported spectroscopic properties and energy transfer in Tm$^{3+}$ singly and Tm$^{3+}$/Ho$^{3+}$ doubly doped glasses [81]. Binnemans et al. [55, 61] reported spectroscopic properties of Tm$^{3+}$ ions in fluorophosphate glasses and NaPO$_3$-BaF$_2$ based fluorophosphate glass. Florez et al. [82] studied optical properties of thulium doped chloroindate glasses. They also studied the influence of third order effects through odd intensity parameters in Tm$^{3+}$ doped fluorooindate glasses [83]. Lakshman and Ratnakaram [84] studied the spectroscopic investigations of Tm$^{3+}$ ion in sulphate glasses
In addition to the above academic review, some of the relevant studies on Sm\(^{3+}\), Dy\(^{3+}\), Ho\(^{3+}\) and Tm\(^{3+}\) ions in various glass matrices were also included in the respective chapters. However, it could be inferred that much work did not take place to analyze the absorption and emission properties of Sm\(^{3+}\), Dy\(^{3+}\), Ho\(^{3+}\) and Tm\(^{3+}\) ions in various mixed alkali borate glasses. Hence the author studied these properties and reported in the present thesis.


