CHAPTER- 1
INTRODUCTION AND REVIEW OF LITERATURE

This chapter presents the general introduction, glass transformation behavior and classification of glasses along with an insight about the borate glasses, their structural aspects and various applications. Brief theory describing the rate of nucleation and crystal growth of glass-ceramics has also been added. A detailed literature review of borate glasses and barium titanate (BT) modified glasses has been included. The objectives of the thesis have also been given at the end of this chapter.

1.1 General Introduction

Glass is one of the most ancient materials known and used by mankind. Earlier the use of glass was limited to window panes, mirrors, art objects, etc., till they got the attention of scientific community. The vast applications of glasses in various fields have fascinated and attracted enormous interest of glass researchers both scientifically and technologically. The different types of glasses have found to play a key role in numerous applications such as electronics (Boolchand 2000; Bengisu 2016), photonics (Richardson et al. 2010; Murai et al. 2013), biomedicines (Stroganova et al. 1997; Regí et al. 2003; Hench 2006), nuclear industry (Donald et al. 1997; Plodinec 2000) and many more. Today, glassy materials can be used in active devices like switches, sensors, memory devices, solar cells etc. (Kreibl 1990; Kolev et al. 2009). The importance of glasses can be summed up by Jo Marshall’s (1990) statement “It is only when one tries to imagine a world without glass that one realizes in how many ways it is used and the extent of our unthinking acceptance of it”. Hence, we live in a world where glasses play a very important role in all aspects of our daily life providing us an ample reason to study the science of these glasses.

The reason for enormous usage of glasses is because of their certain distinctive properties which are not found in other engineering materials such as the combination of hardness and transparency at room temperature along with sufficient strength, excellent corrosion resistance etc. Owing to these properties of glasses the number of its applications is constantly evolving and is progressively being used in combination with other material for high-tech applications.
1.2 Definition of Glass

According to American Society for Testing Materials (ASTM), a glass can be defined as “an inorganic product of fusion, which has been cooled to a rigid condition without crystallization” i.e. a glass is an amorphous material obtained by melt quenching process. Conventionally, glasses are formed by rapidly cooling the melts but they can also be prepared by vapor deposition, sol gel processing of solution and by neutron irradiation of crystalline materials. And so, most scientists regard the term ‘glass’ as covering ‘all non-crystalline solids that show a glass transition’ irrespective of their synthesis process. All the glasses found till date have two common characteristics. One, no glass has a long range, periodic atomic arrangement and the other is, that every glass exhibits a time-dependent glass transformation behavior, which occurs over a temperature range known as the glass transformation region. Thus, we can define a glass as “an amorphous solid completely lacking in long range, periodic atomic arrangement and exhibiting a region of glass transformation behavior.” So, any material whether organic, inorganic or metallic, formed by any method, which exhibits glass transformation behavior is a glass (Shelby 2005).

It is to be understood that all glasses are amorphous but all amorphous materials are not necessarily glasses. For example, materials can be converted into amorphous state by a number of other methods such as condensation of vapours on cold substrates, bombardment of crystalline solids by neutrons or other heavy particles, gelation of solutions further followed by removal of solvents, mechanical shear, solvent evaporation or even by applying high pressures. The resulting material obtained in all above cases give rise to the X-ray diffraction patterns, which show the absence of sharp diffraction peaks confirming the lack of crystalline features. But many such amorphous materials do not exhibit glass transition and hence are not glasses. Glass transition temperature is the main characteristic for any amorphous material to be a Glass.

When a liquid is allowed to cool from a high temperature to its melting point, it usually solidifies to a crystalline material. So, to obtain a glass, the rate of cooling should be such that it bypasses crystallization which can be achieved through rapid quenching process. Thus, the cooling rate also called as quenching rate \( Q \), which is a
kinetic parameter, is quite significant for the glass formation. Crystallization is governed by two factors, nucleation and growth. Both the nucleation and growth rates show a rapid increase which is followed by slowing down as the temperature is lowered below $T_m$ (Rao 2002).

1.3 The Enthalpy-Temperature Diagram

As defined, any material which exhibits a glass transformation behavior is a glass. The glass transformation behavior is usually discussed on the basis of either enthalpy or volume versus temperature diagrams, as shown in Fig. 1.1. Since enthalpy and volume behave in a similar manner, the choice of the ordinate is rather arbitrary. Consider a small volume of a liquid at a temperature well above the melting temperature of that substance. Now, as we cool the liquid, the atomic structure of the melt will change gradually and will be characteristic of the exact temperature at which the melt is held. Cooling of the substance to any temperature below its melting temperature would normally result in the conversion of the material to the crystalline state, with the formation of a long range, periodic atomic arrangement.

![Enthalpy-Temperature Diagram](image)

**Figure 1.1:** Variation in enthalpy of a glass forming melt as a function of temperature (Shelby 2005).
During this process the enthalpy will decrease abruptly to the value appropriate for the crystal. The continued cooling of the crystal will further result in a decrease in enthalpy due to the heat capacity of the crystal. If the liquid can be cooled below the melting temperature of the crystal without crystallization, a supercooled liquid is obtained, whose structure continues to rearrange with the decrease in temperature. But there will be no abrupt decrease in enthalpy due to discontinuous structural rearrangement. As the liquid is cooled further, its viscosity increases and this increase eventually becomes so great that the atoms can not rearrange completely to the equilibrium liquid structure, during the time allowed by the experiment. Thus, the structure begins to lag behind that which would have been present if sufficient time were allowed to reach the equilibrium. The enthalpy starts deviating from the equilibrium line and follows a curve of gradually decreasing slope, until the viscosity becomes so great that the structure of the liquid becomes fixed and is no longer temperature-dependent. This temperature region that lies between the limits where the enthalpy is that of the equilibrium liquid and that of the frozen solid, is known as the “glass transformation region”. The frozen liquid is now a glass. Since, the temperature where the enthalpy deviates from the equilibrium curve is controlled by the viscosity of liquid, i.e. by kinetic factors. So, the use of a slower cooling rate will allow the enthalpy to follow the equilibrium curve to a lower temperature, resulting in a shift of the glass transformation region to lower temperatures and the formation of a completely frozen liquid, or glass, will not occur until a lower temperature. This obtained glass will have a lower enthalpy than that obtained using a faster cooling rate. The atomic arrangements will be the characteristic of the equilibrium liquid at lower temperature than that of the rapidly cooled glass.

It is noted that the glass transformation actually occurs over a temperature range, it is convenient to define a term that can explain the difference in thermal history between these two glasses. If we extrapolate the glass and supercooled liquid lines, they intersect at a temperature defined as the fictive temperature where structure of the glass is considered to be that of the equilibrium liquid. Howsoever, the fictive temperature concept is not a completely satisfactory method for characterizing the thermal history of
glasses but it does provide a useful parameter for discussion of the effect of changes in cooling rate on glass structure and properties.

As indicated above, since, the glass transformation occurs over a range of temperatures, so, it cannot be characterized by a single temperature. It is, however, convenient to assign a single temperature that can be used as an indication of the onset of the glass transformation region during the glass heating process. This temperature is termed as either the glass transformation temperature, or the glass transition temperature, \( T_g \) and is rather inexplicitly defined by the changes in either thermal analysis curves or thermal expansion curves. Also, the values obtained from these two methods, are similar but not identical. The value obtained for \( T_g \), is also a function of the heating rate used to yield these curves. Since \( T_g \), is a function of both, the experimental method as well as the heating rate (used for the measurement), so, it cannot be considered as a true property of the glass, though it can be a useful indicator of the approximate temperature where the supercooled liquid changes to a solid on cooling, or, conversely, of which the solid begins to behave as a viscoelastic solid on heating (Shelby 2005).

### 1.4 Classification of Glasses

Glasses are found in a wide variety of systems but one of the main and most exploited class of glasses is the oxide glass, based on silicate, borate, phosphate and germanate etc. There are also other types of glasses which are of great importance and it includes chalcogenide glasses, halide glasses, heavy metal fluoride glasses, metallic glasses and organic glasses. A brief description about the different structural aspects and properties of these glasses has been given in the following section.

#### 1.4.1 Oxide Glasses

##### 1.4.1.1 Silicate Glasses

Silicate glasses are of great technological and commercial importance due to their chemical and weathering stability. The basic building block of the structure is the SiO\(_4\) tetrahedron where each oxygen acts as a bridge between the neighbouring tetrahedra, and hence is called bridging oxygen. The addition of alkali oxides causes
some modifications in the silica glass such as breakage of Si-O-Si bonds and creation of nonbridging oxygens e.g. addition of Na₂O to silica glass breaks the Si-O-Si linkage and forms Si-O’ terminations; the oxygen bridge in the structure is broken. Hence, the structure is said to be 'depolymerised' or 'modified'. The oxygen in the Si-O-Si linkage is known as a 'bridging oxygen' (BO) and that in Si-O’ is known as 'non-bridging oxygen' (NBO). The ionic oxide (here Na₂O), which leads to the NBO→BO conversion, is known as a network 'modifier' and SiO₂ itself is referred to as a 'network former'. The degradation of the network is assumed to be systematic with an increasing alkali content. The modifications have been found to result in the formation of meta, pyro and ortho-silicates in that order. The different silicon structural units, [SiO₄]₀, [SiO₃/2]²⁻, [SiO₂/2]²⁻, [SiO₁/2]³⁻ and [SiO₄]⁴⁻, present in modified silicate glasses, have been designated as Q₄, Q₃, Q₂, Q₁ and Q₀ respectively, where the subscripts indicate the number of BO’s centered on the given Si atom through which it is further connected to other Si atoms in the glass structure (Mysen and Richet 2005).

The pure silica is perhaps the only single component glass having a number of practical applications but the synthesis of pure SiO₂ glass is very expensive as the working temperatures required for shaping pure SiO₂ glass is around 2000 °C.

1.4.1.2 Borate Glasses

Boron trioxide (B₂O₃) is a significant component of glasses and enamels, and B₂O₃ based glasses have been a subject of severe surveys due to their scientific and technological prominence as they are chemically inert, optically transparent and electrically insulating (Shaaban et al. 2008; Majhi and Varma 2010; Swapna et al. 2014). Since, B₂O₃ does not crystallize by itself even after being cooled at the slowest rate, therefore, B₂O₃ is considered to have the highest glass formation tendency. B₂O₃ can be crystallized only under sufficient pressure. Due to its hygroscopic nature it is somehow difficult to prepare pure borate glasses without any moisture content under normal conditions. The moisture free borate glasses were prepared by Poch by melting orthoboric acid for several hours at a pressure of 1 mm of Hg (Poch 1964).

Recently, pure borate glasses have been explored for their applications in biomedical industry (Richard 2000). Richard was the first one to investigate the 45S5
(45SiO$_2$-24.5CaO-24.5Na$_2$O-6P$_2$O$_5$) glass by replacing SiO$_2$ completely with B$_2$O$_3$ and it was observed that replacement of SiO$_2$ by B$_2$O$_3$ not only promoted bone formation, but did so at a faster rate than the silicate based 45S5 glass. The borate glass has been found to provide a marginally suitable environment for the growth of cells due to the release of boron.

Borate based glasses are widely used for optical components, glassware and semiconducting applications. The incorporation of transition metal oxides such as V$_2$O$_5$, Fe$_2$O$_3$, WO$_3$ etc. to the borate glasses imparts them semiconducting behavior (Bandyopadhyay et al. 1978; Saleh and Gawish 1980; Seth et al. 1988; Mansour et al. 2001; Sindhu et al. 2007; Sanjay et al. 2009; Sheoran et al. 2011) making them a potential candidate for uses in electrical and optical memory switching (Ahmed and Hogarth 1987, Singh and Ratnam 1988), optical fibers (Eloker et al. 2006), laser glasses (Karthikeyan and Mohan 2003; Lakshminarayana and Buddhudu 2006) and solid state ionic devices (Laorodphana et al. 2009; Arora et al. 2011) such as fuel cells. Rare earth doped borate glasses are used to manufacture lens systems with high numerical aperture and low spherical aberrations, UV-sensors, tunable visible lasers, optoelectronic devices, optical switches, data storage, optical amplifiers, and planar waveguides etc. (Lin et al. 2005; Jamalaiah 2009; Ravi et al. 2012). The detailed structure of borate glasses is explained in section 1.5.

1.4.1.3 Phosphate Glasses

The network structure of phosphate glass is a polymeric arrangement of PO$_4$ tetrahedral units. These glasses have comparatively low glass transition temperature ($T_g$) that makes them easily processable. Owing to the various properties of phosphate glasses such as low glass transition temperature ($T_g$), low melting temperature ($T_m$), high thermal expansion coefficient ($\alpha$) and their biocompatibility (Brow 2000; Pavie et al. 2014), they have found numerous applications such as in solid state lasers (Shah et al. 2006; Arbuzov 2013), fast ion conductors (Martin 1991; Mugoni et al. 2014; Sdiri et al. 2015), non linear optical devices (Nazabal et al. 2000), nuclear waste vitrification (Masko and Day 1999; Krishnaiah et al. 2014) and biomedical industry (Vogel et al. 1997; Knowles 2003; Hench 2006). Due to low dispersion and relatively high refractive
index of phosphate glasses (as compared to silicate based optical glasses) they have also been developed as achromatic optical materials.

In phosphate glass, basic building block is a 3-connected and 4-coordinated tetrahedral unit, where one of the coordination arises from P=O, which has distinctly shorter bond distance compared to the other three bonds (r_{P-O}=1.581 Å, r_{P=O}=1.432 Å). Modification of P$_2$O$_5$ glass by introducing alkali oxides results in the formation of various Q$_n$ species in the same manner as in silicates. The modification of the primary network in glass results in the formation of chemically different types of oxygens in the network and it can be a BO or an NBO or oxygen double bonded to P, often called the terminal oxygen. Like in binary silicate glasses, addition of modifier oxides to vitreous P$_2$O$_5$ leads to the conversion of BO to NBO.

Since, phosphate glasses are easily affected by moisture and degrade rapidly with time, therefore, initially these glasses were of less commercial importance. But eventually the problem of durability has been solved by the inclusion of suitable intermediates like Al$_2$O$_3$, In$_2$O$_3$, Fe$_2$O$_3$ etc. (Ghosh and Chaudhuri 1988; Day et al. 1998; Guo 1998; Guo 1999).

1.4.1.4 Germanate Glasses

GeO$_2$ is another glass forming oxide whose structure is expected to be very similar to SiO$_2$. Investigations in GeO$_2$ glasses have been largely of academic interest because of their high melting point and absence of large volume applications. Modification of GeO$_2$ by alkali oxides results in the conversion of Ge to octahedrally coordinated Ge, thereby, increasing the cross-linking in the network. As the alkali oxide content increases above 15-20%, the octahedrally connected structure breaks down rapidly giving rise to various Q$_n$ species, (Q$_n$ = [GeO$_{n/2}$O$_m$]$^{m-}$ (n+m) ≤ 4). It further has consequences on various properties of alkali germanate glasses, which exhibit anomalous variations. This 'germanate anomaly' was first observed in infrared spectroscopic investigations by Murthy and Kirby (1964).

1.4.2 Chalcogenide Glasses

The three elements sulphur (S), selenium (Se) and tellurium (Te) of Group VI of the periodic table, known as chalcogens, give viscous liquids on melting which rapidly
form glasses on cooling. The band gap of chalcogenide glasses is of the order of 1-3 eV hence, they show semiconducting behavior and usually have electronic conductivities in range $10^{-3}$ to $10^{13}$ ohm$^{-1}$ cm$^{-1}$. A variety of glassy or amorphous semiconductors can be made from the chalcogens either alone or in combination with other elements from III, IV or V group of the periodic table. These glasses have covalently bonded atoms in their structure and their melt contains rings and chains of S, Se and Te atoms. Chalcogenide glasses are the potential candidate for applications in infrared transmission, xerography, switching devices for computer memories, fiber optics and X-ray imaging plates etc. (Fairman and Ushkov 2004).

1.4.3 Halide Glasses

Halide glasses like BeF$_2$ and ZnCl$_2$, known for a long time, are obtained by quenching halides from their molten state (Van Uitert and Wemple 1978; Weber 1986; Lucas 1991). The structures of simple BeF$_2$ and ZnCl$_2$ seem to be based on tetrahedrally coordinated Be and Zn, with halogens forming bridges between the tetrahedra. Chloride bridges are found to be much weaker than the fluoride bridges and so the glasses are inherently unstable towards devitrification. Since, BeF$_2$ has very low linear and non-linear refractive indices, therefore, BeF$_2$ glasses doped with transition metal ions like Nd$^{3+}$ are very good material for high-power lasers. Trivalent halides like AIF$_3$, FeF$_3$, CrF$_3$ and GaF$_3$ (Jacoboni et al. 1983) can also form glasses but only in combination with divalent fluorides such as ZnF$_2$, MnF$_2$ and PbF$_2$.

1.4.4 Heavy Metal Fluoride Glasses

Of the non-oxide glasses, the heavy metal fluoride glasses (HMFGs) exhibit very low optical attenuation. Owing to their predicted ultralow loss and long transparency range heavy metal fluoride glasses are very promising optical fiber materials. But they are extremely difficult to form and show poor resistance to moisture and other environmental attacks. The ZBLAN glass with composition (53ZrF$_4$-20BaF$_2$-4LaF$_3$-3AlF$_3$-20NaF) is the most promising of these materials and has main technological application as optical waveguides in planar and fiber form. Conventional silica fibers have attained their theoretical minimum loss of 0.15 dB/km whereas fluoride glasses have the potential to yield losses of only 0.001 dB/km. Also, Fluoride
glasses exhibit transparency into mid-IR frequencies, a region inaccessible to silica fibers. However, instability of this group of glasses to devitrification during both bulk glass synthesis and fiber-drawing has limited their commercial exploitation to a small niche market in the laser industry. Currently, these glasses have found applications as hosts for high power lasers and as infrared windows. These glasses have also been employed for making fibers for fiber-optic communication (Dunkley et al. 2004).

1.4.5 Metallic Glasses

Metallic glasses are the solid alloys with liquid like atomic structure. They are prepared by rapid quenching (~of the order of $10^6$ K per second) because of their high propensity to crystallize. Recently, critical cooling rates, for a wide range of multicomponent alloys, have been dramatically lowered to permit casting in bulk (i.e. with minimum dimension >1 cm). These Bulk metallic glasses (BMGs) show better elastic limit and corrosion resistance as compared to crystalline metals (Inoue et al. 2008). There are two main categories of metallic glasses, the first one is metal-metalloid system where metal could either be a transition or a noble metal and the metalloid content (Si, B, P or C) lies between 15 to 25 atom%. Some examples of this category are Au-Si, Pd-Si, Co-P, Fe-B, Fe-P-C, Fe-Ni-Pb, Ni-B-Si. The second category of metallic glasses is formed by the combination of two transition metals, one early transition metal (like Sc, Ti, V) and the other, a late transition metal (like Mn, Fe, Co, Ni) e.g. Zr-Ni, Y-Cu, Zr-Cu, Nb-Ni, Ta-Ir, W-Fe, Zr-Fe etc. (Rao 2002).

As compared to the conventional metallic materials, the defining characteristic of metallic glasses is their lack of crystallinity and associated lack of microstructural features such as grain and phase boundaries, which imparts them distinctive mechanical and magnetic properties. The excellent magnetic properties such as low hysteresis and high values of magnetization, of metallic glasses, have led to their applications in transformer cores, magnetic read-heads and magnetic shielding (Schulz et al. 1988; Ashby and Greer 2006).

1.4.6 Organic Glasses

Organic glasses are the amorphous materials consisting of carbon-carbon chains which are entangled in such a way that rapid cooling of the melt inhibits their
rearrangement into crystalline regions. Their structures have a close resemblance to those of vitreous sulphur and selenium, which also consist of entangled chains. The chains in organic glasses can also be crosslinked, the way as they are found in chalcogenide glasses, with subsequent changes in their properties. Increase in the degree of crosslinking increases the melt viscosity and glass transition temperature ($T_g$). In general, the properties of organic glasses bear a resemblance to those of inorganic glasses having chain based structures, including the ability of producing materials with oriented properties by applying stress during formation. Organic glasses often exhibit small regions of oriented chains so that many of these materials resemble low crystallinity glass ceramics. The simplest glass known as polyethylene is formed from long chains of $-\text{CH}_2-$ moieties and they are used for producing polyvinyl chloride (PVC) bottles, optical lenses and to protect glass articles (Titow 1984). Polycarbonate (PC), Polystyrene (PS) and Polymethylmethacrylate (PMMA) are some other examples of most widely studied organic glasses (Wetton and Moneypenny 1975).

1.5 Structure of Borate Glasses

Pure $\text{B}_2\text{O}_3$ can form a glass by itself and binary borates with many other oxides. Borate glass is considered to have a mixture of $\text{BO}_3$ triangles and $\text{BO}_4$ tetrahedra depending on the composition. An important constituent of vitreous $\text{B}_2\text{O}_3$ is boroxol group which is a planar, six membered ring of alternate boron and oxygen atoms connected in a 3-D network by sharing all three oxygen atoms with adjacent $\text{BO}_3$ unit (Wright et al. 1997) as shown in Fig. 1.2. The addition of alkali oxide to glassy $\text{B}_2\text{O}_3$ gives rather different results than those obtained in the corresponding alkali silicates and an effect known as the boron oxide anomaly is observed. It has been observed that a gradual change in the coordination number of boron from three to four occurs as alkali oxide is added. The various structural groups present in these glasses have been clearly identified by combining the Raman scattering studies and the NMR studies with the available crystallographic data. Fig. 1.3 shows the several structural groups present in various borate compounds.


Figure 1.2: Schematic representation of Boroxol group.

Figure 1.3: Structural groupings in borate glasses, where boron is represented by (●) and bridging oxygens by (○).

The addition of modifier oxides may lead to the following modifications in the network:

(a) Breakage of Boron-Oxygen-Boron (B-O-B) bonds by oxygen anions to form NBOs.

(b) Change of hybridization of the boron atom to the sp³ tetrahedral arrangement resulting in the formation of BO₄ tetrahedron with three BO’s and one NBO (via
overlapping of a filled orbital of an oxygen anion with an empty p-orbital of a boron atom)

(c) Change in the coordination of two borons from sp$^2$ to sp$^3$ hybridization with no NBO (via contribution of an electron pair by an oxygen atom to two BO$_3$ units).

According to Biscoe and Warren (1938), the addition of alkali ions to boron oxide results in the conversion of some borons from BO$_3$ state to BO$_4$ state with no NBOs formation. Such a change increases the connectivity of the network causing the thermal expansion to decrease and viscosity to increase. A continued increase in the alkali oxide content results in further shift of borons from 3-fold to 4-fold coordination. But when even more alkali oxide is added to boric oxide, it causes the production of NBOs along with a resultant increase in thermal expansion coefficient and decrease in viscosity. This extreme behavior is not seen in borate-free glasses and hence was termed the boron anomaly e.g. in case of B$_2$O$_3$-Na$_2$O system, upon adding Na$_2$O to B$_2$O$_3$ glass, up to 33 mol%, there is a progressive conversion of trigonal boron structural units (BO$_3$) to tetrahedral boron structural units (BO$_4$) but as the concentration of Na$_2$O is increased above 33 mol%, relative concentration of BO$_4$ units starts decreasing (Jellison and Bray 1978).

Several attempts (Pye et al. 1978) have been made in order to explain the structure of borate glasses on account of various imaginative structural models and all of these models were built around the relatively unique ability of boron to exist in two distinct coordination states. NMR studies (Svanson et al. 1962; Bray and Keefe 1963) however, revealed that the four coordinated boron varies smoothly as $x/(1-x)$ where $x$ varied from 0 to 30 mol% modifier oxide without any unusual behaviour in the critical range 15-20 mol% of modifier oxide. The BO$_4$ units are bonded to the rest of the structure in four directions and hence, the structure is tied together in 3-dimensions rather than two. This induces a noticeable increase in the strength and tightness of the structure. With the help of B$^{11}$ NMR spectroscopy, Bray revealed (Bray et al. 1978; Bray and Gravina 1985) that as alkali oxide is added to B$_2$O$_3$, there is a gradual change in the coordination number of boron from three fold to four fold. As the amount of
alkali content added reaches 30 mol%, approximately 40% of the borons change to
tetrahedral coordination, independent of the nature of the alkali added.

Krough-Moe (1960) also carried out extensive investigations on crystalline and
glassy borates and suggested that borate glasses are not merely a random network of
BO$_3$ triangles and BO$_4$ tetrahedra joined at the corners, but, they actually contain well-
defined and stable groups as segments of the disordered frame work. They also pointed
out that the borate groups included in the glass structure should be identical with the
groupings that exist in crystalline borates. The experimental results obtained from
thermodynamic studies (Krough-Moe 1962) and infrared studies (Krough-Moe 1965)
suggested that the structural groupings in borate glasses can be classified into four
different groupings. viz., boroxol, pentaborate, triborate and diborate groups (Fig. 1.3).
However, the pentaborate and triborate groups will always occur in pairs and are
referred as tetraborate groups.

1.6 Glass Ceramics

Glass ceramics (GC) are the polycrystalline solids with crystals (nanometers to
micrometers size) embedded in the host glass matrix. The glass ceramics are produced
by devitrification of glasses. The first step towards the production of glass ceramics
involves the synthesis of glass by conventional techniques such as melt quench, sol-gel,
chemical vapor deposition etc. The obtained glass is then subjected to a controlled
crystallization process (Beall and Duke 1969; Jean et al. 1995) which results in the
separation of a crystalline phase from the glassy parent phase in the form of tiny
crystals. The number of crystals formed, their rate of growth and the final size are
controlled by suitable heat treatment (McMillan 1964).

Glass ceramics (GC’s) comprising nano/micro crystallites have attained a vast
popularity among the glass researchers owing to their several functionalities,
comparatively easy preparation methods and their potential applications in optical and
electronics devices (Al-Assiri et al. 2009; Chen et al. 2010; Szreder et al. 2014; Al-
Syadi et al. 2014; Abdel-Khalek and Ali 2014). The ceramic materials could be
prepared by several methods such as solid state reaction method, sol gel method,
hydrothermal and aerosol method etc. But there are certain drawbacks and difficulties
associated with these methods such as high temperature requirement for preparation process or the longtime of reaction (Dutta et al. 1994; Funakubo et al. 1997; Beck et al. 1998; Berbenni et al. 2001). Such difficulties are overcome in glass ceramics since processing of glass-ceramics is generally a simple regulated thermal process. As, the name indicates, GC’s have the combination of both glassy and crystalline phases. They have the benefit of easy fabrication of glass as well as special properties of ceramics. Since, there is no pressing and sintering involved in glass ceramic synthesis process, so, unlike sintered ceramics, GC’s have zero porosity. Glass-ceramics possess some interesting optical, chemical, thermal, dielectric properties (Sung 2000; Jun et al. 2006; Miller et al. 2006; Bhakta et al. 2008). All these properties can be altered by controlling the base glass composition and by varying the nature and concentration of crystal phases through a controlled heat treatment/crystallization of the base glass.

1.6.1 Theory of Nucleation

Nucleation is the process of formation of a stable nuclei i.e. crystalline embryo of critical size, which may sustain the further growth. There are two main mechanisms of nucleation: homogeneous nucleation and heterogeneous nucleation. In homogeneous nucleation, a new solid phase develops (in the absence of any foreign boundaries) due to local fluctuations in the density and kinetic energy of the melt whereas in heterogeneous nucleation, a solid phase forms on a foreign particle or surface which catalyzes the nucleation event. The formation of uniform crystallization in glass ceramics by incorporating the nucleating agents such as impurity particle/fine metal particle to initiate the growth of required phase, is of heterogeneous type.

The theory of nucleation in liquid was explained by Volmer and Maurer (Volmer and Weber 1925; Maurer 1962) and later on was reviewed by Jackson (1997). In homogeneous nucleation, two barriers exist to the formation of a nucleus. First is the thermodynamic barrier that involves the free energy change in a system during the formation of nucleus. The other is the kinetic barrier, which is the result of the requirement that mass be moved or rearranged in space, to allow the growth of an ordered particle (a crystal) from a disordered liquid. The overall process of the homogeneous nucleation rate (I) is described by the expression given as:
\[ I = A \exp\left(-\left(W_c + \Delta G_D/kT\right)\right) \]  
(1.1)

where \( A \) is a constant, \( W_c \) is the thermodynamic barrier, \( \Delta G_D \) is the kinetic free energy barrier to nucleation, \( k \) is the Boltzmann constant and \( T \) is the absolute temperature (K). Here, \( W_c \) is the work required to form a nucleus of critical size, i.e., one which will grow instead of redissolving into the melt. The pre-exponential constant \( A \) in Eq. (1.1) is given by:

\[ A = 2n_v V^{1/3} (kT/h)(\gamma/kT)^{1/2} \]  
(1.2)

where \( n_v \) represents the number of formula units of the crystallizing component phase per unit volume of the melt, \( V \) is the volume per formula unit, \( \gamma \) is the crystal-melt interfacial free energy per unit area and \( h \) is Planck's constant. \( A \) is found to be essentially constant over the temperature range of nucleation measurement and, to a good approximation, it can be expressed as:

\[ A = n_v (kT/h) \]  
(1.3)

Since, the crystalline state has a lower free energy than the melt, therefore, the formation of a crystalline arrangement will lower the volume free energy which is countered by an increase in surface energy due to the formation of a new interface between regions of different structures.

The net change in energy, \( W \), for a sphere of radius, \( r \), is given by the sum of these terms:

\[ W = -\frac{4}{3} \pi r^3 \Delta G_v + 4 \pi r^2 \gamma \]  
(1.4)

where the first term represents the change in volume free energy (\( \Delta G_v \) is the change in volume free energy per unit volume) and the second term represents the surface energy change. Since nuclei are small, the surface energy term will be dominant at very low values of \( r \), so, \( W \) will increase with increasing \( r \), and the resulting nucleus will be unstable. However, if the nucleus can survive to grow to a large enough size, then as clear from the above equation, first term will become larger than the second, \( W \) will start decreasing with an increase in nucleus size, and the nucleus will become stable.
Differentiating Eq. (1.4) and equating it to zero gives the value for \( r \), known as the critical radius \( (r_c) \), where the nucleus just becomes stable:

\[
 r_c = 2 \gamma / \Delta G_v 
\]  

(1.5)

using this value in Eq. (1.4), we get the value of \( W \) for the critical nucleus, given as

\[
 W_c = 16 \pi \gamma^3 / 3 \Delta G_v^2 
\]  

(1.6)

Small clusters with \( r < r_c \), are called embryos and these embryos redissolve spontaneously unless they achieve a critical size. The embryos of critical size are known as a 'nuclei'. Nuclei, with sizes greater than or equal to critical size, \( r_c \), grow spontaneously because for \( r > r_c \) the free energy decreases continuously (Fig. 1.4).

An approximate equation for \( \Delta G_v \) for condensed phases is

\[
 \Delta G_v = -\Delta H_f (T_m - T) / V_m T_m 
\]  

(1.7)

where \( \Delta H_f \) is the heat of fusion, \( V_m \) is the molar volume of the crystal phase and \( T_m \) is the melting temperature.

The above expressions are only applicable for small undercoolings, i.e. when \( (T_m - T) \) is small. As, the degree of undercooling increases, the errors introduced by the use of these approximations also increase.

**Figure 1.4:** Free energy versus embryo radius for a given \( T < T_m \). Note that \( W_c \) goes through a maximum at \( r = r_c \).
The another barrier involved in nucleation step is the kinetic barrier that is experienced by an atom at the melt-nucleus interface for crossing over from melt onto the surface of the nucleus. The kinetic barrier of nucleation, $\Delta G_D$ can be discussed in terms of an effective diffusion coefficient, $D$, given by:

$$D = \frac{(kT^2)}{(h)} \exp(-\Delta G_D/kT) \quad (1.8)$$

where $\lambda$ is the atomic jump distance and $D$, in many cases, has been assumed to be related to the viscosity, $\eta$, of the melt via the Stokes-Einstein:

$$D = \frac{kT}{3\pi\lambda\eta} \quad (1.9)$$

Using the above two relations, Eqs. (1.8) and (1.9), and substituting them into the original expression i.e. Eq. (1.1), we get:

$$I = \frac{(Ah)}{3\pi\lambda^3\eta} \exp\left(-\frac{W_c}{kT}\right) \quad (1.10)$$

Substituting the value of $A$ from Eq. (1.3), in above expression, it can be rewritten as:

$$I = \frac{(n_TkT)}{3\pi\lambda^3\eta} \exp\left(-\frac{W_c}{kT}\right) \quad (1.11)$$

These are the expressions derived for the case of homogeneous nucleation. James indicated that the expression same as Eq. (1.1) can be used for heterogeneous nucleation on a flat substrate. For that case:

$$I_{het} = A_{het} \exp\left[-(W_{c(het)} + \Delta G_D)/kT\right] \quad (1.12)$$

where subscript “het” denotes the values for heterogeneous nucleation and $W_{c(het)}$ corresponds to the function of angle of contact between the crystal nucleus and the substrate. Expressing $A_{het}$ by an expression similar to Eq. (1.3);

$$A_{het} = n_s(kT/h) \quad (1.13)$$

where $n_s$ represents the number of formula units of the melt in contact with the substrate per unit area, we obtain the expression for homogeneous nucleation rate, given as

$$I_{het} = n_s(kT/h) \exp\left[-(W_{c(het)} + \Delta G_D)/kT\right] \quad (1.14)$$
The expressions derived above can be used to predict the shape of the curve for nucleation rate ($I$) vs. temperature. Fig. 1.5 shows the effect of temperature on the rate of nucleation and crystal growth for a glass forming melt.

![Figure 1.5: Temperature dependence of the rates of nucleation and crystal growth for a glass forming melt.](image)

**Figure 1.5:** Temperature dependence of the rates of nucleation and crystal growth for a glass forming melt.

### 1.6.2 Crystal Growth

A simple general model for the crystal growth mechanism can be derived using the same arguments as the nucleation rate. A general equation for the crystal growth rate, $U$, can be expressed as:

$$U = a_o v \exp\left(-\frac{\Delta E}{kT}\right) \left[1 - \exp\left(\frac{\Delta G}{kT}\right)\right]$$

(1.15)

where $a_o$ represents the interatomic separation distance, $v$ is the vibrational frequency and $\Delta E$ and $\Delta G$ are the kinetic and thermodynamic barriers to the crystal growth. If we use the arguments similar to those used for nucleation rate and introduce Eqs. (1.8) and (1.9) to describe diffusion, we obtain the expression:

$$U = \left(\frac{kT}{3\pi \sigma^2 \eta}\right) \left[1 - \exp\left(\frac{\Delta G}{kT}\right)\right]$$

(1.16)
The dependence of the crystal growth rate on temperature, as given by Eq. (1.16), is very similar to that for the nucleation rate, as is shown in Fig. 1.5. However, the major difference lies in the lack of a metastable zone for crystal growth. The region of overlap of the nucleation rate and crystal growth rate is the temperature region that has to be quickly passed over by rapid quenching in order to obtain a glass.

1.7 Literature Review

1.7.1 Borate based glasses

B$_2$O$_3$ is one of the most common glass network formers and has received great attention from researchers due to its interesting electrical, optical and luminescent properties for various technological applications. Borate glasses have found to exhibit high chemical durability and thermal stability (Shaaban et al. 2008; Majhi and Varma 2010; Swapna et al. 2014). In crystalline form, also, borates with various compositions are of exceptional importance owing to their interesting linear and nonlinear optical properties (Rajyasree et al. 2011; Farouk et al. 2013). Thus, borate based glasses have been studied widely since decades.

Lithium borate and bismuth borate are the most popular borate based glasses and have been extensively studied due to their widespread properties such as lithium borate glasses are of special interest since they are the most suitable candidate for sensors and solid state electrolyte applications. The light weight, small size and highly electro-positive character of Li$^+$ ions are the main factors that make them potential candidate for use in high energy density micro-batteries (Varshneya 1994; Rao 2002; Elalaily and Mahamed 2002; Lee 2005; Abousehly et al. 2015). Bismuth borate glasses have wide applications in the field of glass-ceramics, layers for optical and optoelectronic devices, thermal and mechanical sensors, reflecting windows etc. (El Batal et al. 2007; Sailaja et al. 2013; Farouk et al. 2013; Vedeana et al. 2013)

Obayes et al. (2016) investigated the Sr and Cu co-doped Lithium Borate (LB) glass and found them to a promising material for dosimetric applications. Thus, suggesting that Sr/Cu co-doped LB glass is potential candidate as TLD material for ionizing radiation dose measurement. Dahiya et al. (2016) carried out investigations on conductivity and modulus formulation in lithium modified bismuth zinc borate glasses
in the frequency range 0.1 Hz - 1.5 x 10^5 Hz and temperature range 573 K-693 K. ac conductivity of these samples was found to increase with increase in Li_2O content. Pawar et al. (2016) studied the physical and optical properties of Dy^{3+}/Pr^{3+} co-doped lithium borate glasses and suggested their use for white LED application.

Mhareb et al. (2015) investigated the influence of rare earth (RE) ions concentration on structural and optical response of lithium magnesium borate glass. Both physical and optical properties showed a considerable improvement with the increase of erbium ion concentration up to 0.5 mol% and the optical response observed for these samples suggested them to be useful for the development of photonic devices. Dalal et al. (2015) studied the effect of substituting iron on structural, thermal and dielectric properties of lithium borate glasses. Density and molar volume were found to increase whereas ac conductivity decreased with increase in iron oxide content. Abousehly et al. 2015 studied the electrical and mechanical properties of Li_2O-BaO-B_2O_3 glass system and reported an increase in both ac and dc conductivity with an increase in lithium content.

Ramteke and Gedam (2014) carried out electric property studies of Li_2O-B_2O_3-Dy_2O_3 glass system for different mol% of Dy_2O_3. The addition of Dy_2O_3 was found to result in an increased rigidity of glass structure which reduced conductivity of glasses. ac conduction mechanism in this glass system followed Elliot's correlated barrier hopping model (CBH). Azizan et al. (2014) studied physical and optical properties of Li_2O-K_2O-B_2O_3 (LKB) with different concentrations of dysprosium (Dy^{3+}) ions. Analysis of FTIR spectra revealed the existence of BO_3 and BO_4 units in the glasses network and the absorption spectrum of Dy^{3+} ions produced eight optical absorption bands. The results obtained pointed to the use of these glasses in solid-state laser, optoelectronic devices and W-LEDs application. Alajerami et al. (2013) investigated the effect of TiO_2 and MgO on the thermoluminescence properties of a lithium potassium borate glass system and demonstrated their use in medical radiation therapy. Gedam and Ramteke (2012) studied the electrical properties of lithium borate glasses doped with Nd_2O_3 and reported a decrease in the conductivity and an increase in the activation energy of these glasses with the addition of Nd_2O_3.
Farouk et al. (2015) reported the optical properties of lead bismuth borate glasses doped with neodymium oxide and studied the effects of neodymium oxide addition on the optical band gap, Urbach energies and Judd–Ofelt parameters. Shanmugavelu et al. (2014) investigated the optical properties of Nd$^{3+}$ doped bismuth zinc borate glasses. Optical absorption spectra were analyzed using Judd–Ofelt theory. Yasaka et al. (2014) studied the Gamma radiation shielding and optical properties of zinc bismuth borate (ZBB) glasses and reported that glasses with Bi$_2$O$_3$ higher than 25 mol% show better shielding property compared with concretes and ZBB glasses may be developed as a lead-free radiation shielding material.

Rani et al. (2014) studied the influence of Bi$_2$O$_3$ on thermal, structural and dielectric properties of lithium zinc bismuth borate glasses. The non-linear compositional change in glass transition temperature was observed and result obtained from IR studies confirmed the dual role of Bi$_2$O$_3$ i.e. as network modifying oxide as well as network forming oxide. The dc conductivity showed a decrease with an increase in Bi$_2$O$_3$ content. Rejisha et al. (2014) performed the characterizations on strontium and barium bismuth borate glass-ceramics. XRD patterns show that presence of Bi$_{24}$B$_2$O$_{39}$ crystalline phase in the glass samples after the heat treatment. The glass ceramics prepared showed high dielectric constants and low dielectric loss.

Mahamuda et al. (2013) investigated the spectroscopic properties and luminescence behavior of Nd$^{3+}$ doped zinc alumino bismuth borate glasses. The radiative properties for the prepared glasses were calculated using JO theory. Farouk et al. (2013) studied the effect of Bi$_2$O$_3$ content on thermal stability, optical properties and structures of bismuth borate glasses containing Er$^{3+}$ ions by X-ray diffraction, infrared spectroscopy and DTA techniques. Bi$_2$O$_3$ was found to play the role of network modifier. Marzouk (2012) synthesized some rare earth ions doped bismuth borate glasses and studied the effect of gamma irradiation. The density, molar volume, ultraviolet, visible, and infrared spectroscopic and optical energy band gap of these glasses were measured to investigate their various properties. The IR spectra were slightly affected by gamma irradiation that could be due to the shielding behavior of heavy Bi$^{3+}$ ions.
Rajyasree and Rao (2011) made spectroscopic investigations on alkali earth bismuth borate glasses doped with CuO, through optical absorption, EPR, FTIR and photoluminescence (PL). Analysis of the investigations indicated a decrease in the concentration of luminescence centers of bismuth ions (Bi$^{2+}$ ions in visible region) with increasing dopant concentration. Optical and structural investigation of bismuth borate glasses doped with Dy$^{3+}$ were carried out by Insitipong et al. (2011) and they suggested the modifier role of Dy$^{3+}$ in bismuth borate glass matrix.

1.7.2. Barium titanate (BT) modified Glasses/Glass ceramics

The glasses with ferroelectric crystals embedded in them are in increasing demand, as such glasses exhibit the properties of both the constituents. Currently, many groups are working on such glasses and their glass-ceramics.

Yadav et al. (2016) investigated the effect of donor and acceptor dopants on crystallization and dielectric behaviors of barium strontium titanate glass ceramics. XRD studies confirmed the presence of $\text{Ba}_{1.91}\text{Sr}_{0.09}\text{TiO}_4$ and $\text{Ba}_2\text{TiSi}_2\text{O}_8$ crystalline phases in the heat treated samples. Harizanova et al. (2016) studied the phase composition identification and microstructure of sodium-aluminoborosilicate glass-ceramics containing $\text{BaTiO}_3$. The phase composition of the glass-ceramics was studied by X-ray diffraction and it revealed the formation of cubic $\text{BaTiO}_3$ which was also confirmed by temperature dependent Raman spectroscopy. Microstructures of all annealed samples were found to be consisting of globular interconnected particles in which nanosized $\text{BaTiO}_3$ crystals grow randomly.

Szreder et al. (2014) reported the ac and dc electrical conductivity of barium titanate doped bismuth-vanadate as-quenched and heat-treated materials in the frequency range from 1 mHz to 1 MHz and in the temperature range from 153 K to 423 K. The heat treatment was found to have a great impact on the conduction process in investigated materials. The as-quenched samples showed one relaxation process which was due to the overlapping polaron hopping whereas heat-treated samples were found to exhibit two different conduction mechanisms. Abdel-Khalek and Ali (2014) substituted $\text{BaTiO}_3$ into vando-tellurite glasses and reported their structural, dielectric and ac conductivity properties and reported an increase in $T_g$ with increase in $\text{BaTiO}_3$. FTIR study showed the presence of various structural units present in the system and
confirmed the presence of BaTiO$_3$. They also reported a decrease in $\sigma_{ac}$ with the increase in BaTiO$_3$ concentration up to 10 mol% and then an increase for further doping of BaTiO$_3$ content. The decreased in the AC conductivity was attributed to the increase of BaTiO$_3$ which has heavy atomic masses, hinders the electronic motion whereas the increase in ac conductivity from $x = 10$ up to 15 mol% was considered to be due to the nanocrystalline BaTiO$_3$ dispersed in the glass matrix.

Al-Syadi et al. (2013) studied the impedance spectroscopy of V$_2$O$_5$-Bi$_2$O$_3$-BaTiO$_3$ glass- ceramics. XRD studies showed the presence of BaTi$_4$O$_9$ and Ba$_3$TiV$_4$O$_{15}$ nanoparticles in the synthesized glass ceramics. The relaxation properties of the investigated samples, presented in the electric modulus formalism, showed a slight deviation from ideal Debye relaxation and also found to be temperature independent. Bahgat et al. (2013) investigated the enhancement of electric conductivity in transparent glass-ceramic nanocomposites of Bi$_2$O$_3$-BaTiO$_3$ glasses. FTIR analysis showed the presence of BiO$_6$, BiO$_3$ and TiO$_6$ structural units. Electrical conductivity was found to be enhanced by $10^2$ to $10^3$ times in the transparent glass ceramic nanocomposite phase as compared to that of glassy phase.

Yadav et al. (2013) carried out investigations on the crystallization kinematics and dielectric behavior of (Ba,Sr)TiO$_3$ borosilicate glass ceramics and showed the behavior of $\varepsilon'$ and Tan$\delta$. Chen et al. (2010) also studied the crystallization kinetics and dielectric properties of barium strontium titanate based glass-ceramics. The crystallization of BST, from aluminosilicate glass was studied using isothermal method, and interpreted the kinetic parameters associated with the crystallization.

Al-Assiri et al. (2009) studied the nanostructural behavior and transport properties of BaTiO$_3$ doped vanadate glasses and glass–ceramics dispersed with ferroelectric nanocrystals. $T_g$ of the samples was found to increase with increase in BaTiO$_3$ content. The value of dielectric permittivity ($\varepsilon$) of these glasses was also found to be very high compared to familiar vanadium containing glasses, which is considered to be due to the presence of nanocrystalline BaTiO$_3$ in the glass matrix. They also showed that the conductivity of the nanocrystalline glass–ceramics was higher than that of the corresponding glassy phase.
1.8 Motivation and Objectives of the work

In recent years, there has been an increasing interest in glasses and glass–ceramics having nano/micro crystallites of a ferroelectric compound embedded in them. The advantage of such materials is that they exhibit the properties of both the constituents i.e. of the mother glass matrix and the added ferroelectric ceramic material, due to which they can be employed in various technological applications (Chen et al. 2010). Barium titanate (BT) is one of the best known perovskite ferroelectric compounds which has a very large non-linear optical and electro-optic coefficient, making it attractive in designing non-linear optical devices (Abdel-Khalek and Ali 2014). Due to its high dielectric constant and low losses, barium titanate finds extensive usage in electronic industry such as in capacitors, ultrasonic transducers, radio communication filters, electroluminescent panels, and piezoelectric devices (Hu and Krupanidhi 1993; Haertling 1999; Wan et al. 2008; Chen et al. 2010; Ferreira et al. 2013; Bahgat et al. 2013). Owing to its outstanding applications, BT modified glasses are of significant interest. In the last few years, there has been an increasing interest in the study of BaTiO$_3$ in a glassy matrix or glass ceramics, which are attractive in electro-optic based devices. Moreover, BaTiO$_3$ based glass ceramics have found to be potential candidates in electronic applications (Al-Assiri 2009). BaTiO$_3$ (BT) glass ceramics are also considered to be the promising candidate for making capacitor due to its high dielectric constant (Yadav and Gautam 2014).

Harizanova et al. (2016) studied the phase composition identification and microstructure of sodium-aluminoborosilicate glass-ceramics containing BaTiO$_3$. Szreder et al. (2014) reported the nanostructural and dielectric behavior of vanadate glasses containing BaTiO$_3$. Electric conductivity in transparent glass-ceramic nanocomposites of Bi$_2$O$_3$-BaTiO$_3$ was studied by Bahgat et al. (2013). Yadav et al. (2013) investigated the crystallization kinematics and dielectric behavior of (Ba,Sr)TiO$_3$ in borosilicate glass ceramics and showed the behavior of $\varepsilon'$ and $\tan\delta$.

From the review of various available studies on BT modified glasses it is quite clear that most of the studies on these glasses are devoted to the crystallization kinetics and dielectric studies. Very few reports related to a detailed spectroscopic studies such
as FTIR, Raman and optical studies have been found in literature. The structural studies such as FTIR and Raman spectroscopies are an important tool to reveal the local arrangements in the glass network. Optical studies are important as it is one of the fundamental properties of the glasses and are helpful in gaining the information of optical band gap energy etc. Also, there is a lot of scope to continue the studies on the dielectric properties of BT modified glasses/glass ceramics and to throw more light on the conduction mechanism in these glasses. Since, in order to develop new electronic materials for device applications a good understanding of charge carrier transport and electrical conduction is an essential task.

This thesis achieved the goal and contributes the insight understandings of some glasses and glass ceramics in terms of their synthesis, structural, optical and electrical transport properties. In order to achieve the aim, the following objectives have been set:

✓ To prepare the transparent glass samples with composition (70B$_2$O$_3$-29Li$_2$O-1Dy$_2$O$_3$)-$_x$BT and (70B$_2$O$_3$-29Bi$_2$O$_3$-1Dy$_2$O$_3$)-$_x$BT, where BT corresponds to barium titanate, by melt quench technique.

✓ To convert these glass samples into glass ceramics by applying suitable heat treatment.

✓ To characterize the glass samples and their glass ceramics for understanding the structural and thermal behavior and its modification with addition of BT using X-Ray Diffraction (XRD), Differential Scanning Calorimetry (DSC), Fourier Transform Infra Red (FTIR) and Raman spectroscopic studies.

✓ To perform the optical studies on these prepared samples using UV-Visible spectroscopy in order to observe the variation in band gap energy with introduction of BT into the host glass matrix.

✓ To study the electrical transport characteristics of (70B$_2$O$_3$-29Li$_2$O-1Dy$_2$O$_3$)-$_x$BT glasses and glass ceramics using modulus formulation and ac conductivity formalism with a view to have a broad understanding over the conduction mechanism in the glass. Such studies are likely to be helpful for examining the suitability of these materials for applications in electronic devices.