STUDY OF OPTICAL AND STRUCTURAL PROPERTIES OF SILICA BORATE GLASSES

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Dedicated to my loving parents & wife

CERTIFICATE

This is certify that the entitled "STUDY OF OPTICAL AND STRUCTURAL PROPERTIES OF SILICA BORATE BASED GLASSES" Submitted by Mr. MANOJ KUMAR, Roll No. 600802010 *in the partial fulfillment of the requirement for award of the degree of MASTER OF TECHNOLOGY in Materials and Metallurgical Engineering from the School of Physics and Material Science, Thapar University, Patiala. It is certify that the matter embodied in this report is of the candidates own record and not submitted to any other university in any part or full form for the award of such kind of a degree.*

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ABSTRACT

Glasses find applications in various fields of Engineering and technology like optics and optoelectronics. In the present work, SiO_2-BaO-ZnO-(x) B_2O_3-(1-x)Y_2O_3 $(0\leq x \leq 10)$ glasses are synthesized by melt quenching techniques. These glasses are characterized by various techniques such as X-ray diffraction, Fourier-Transform-Infrared spectroscopy (FT-IR). U.V. Visible spectroscopy to study the effect of replacement of B_2O_3 (glasses network) by Y_2O_3 (intermediate oxides). The results are discussed in light of non-bridging oxygen (NBO), optical basicity, density and heat-treatment of glasses. The band gap has been calculated for pristine as well as heat-treated glasses. The band gap energy is found to decrease with the increasing content of Y_2O_3 in the glasses. The presence of crystalline phase in glass matrix showed remarkable effect on optical properties of glass.

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CHAPTER 1

INTRODUCTION

1.1 Background:

Glass exhibit random arrangement of atoms below its glass transition temperature, so, structurally glass is amorphous. Glass can be synthesized by quenching using sufficiently fast cooling of melt to avoid the formation of a regular crystal lattice. Amorphous solids may also be formed by methods other than melt quenching, such as vapor deposition or the sol-gel method. Silica glass may be produced by using sand as a raw material (or “quartz sand") that contains almost 100% crystalline silica in the form of quartz. The refractive, reflective and transmission properties of glass depends upon the composition and volume factors. Furthermore, the selection of composition can be selected based on the technological applications such as optics and optoelectronics. The most common method for glass pane production is using molten tin, where the molten glass floats on top of the perfectly flat molten tin, thus giving it the name "float glass". The manipulation of heated glass enables it to be shaped into different forms and the incorporation of additives at the manufacturing stage produces different colors which enable glass to be used as decorative pieces [1].

So a glass may be defined as “an amorphous solid completely lacking in long range, periodic atomic structure, and exhibiting a region of glass transformation behavior”. Any material, inorganic, organic, or metallic, formed by any technique, which exhibit glass transformation behavior is a glass [2]. For instance, the amorphous structure of glassy silica (SiO_2) is two dimensions. Without having long range order, however, there is local ordering with respect to the tetrahedral arrangement of oxygen (O) atoms around the silicon (Si) atoms.

Another definition of a glass (or vitreous solid) is a solid formed by rapid melt quenching [3]. If the cooling is sufficiently rapid (relative to the characteristic crystallization time) then crystallization is prevented and disordered atomic configuration of the super cooled liquid is frozen into the solid state at the glass transition temperature T_g. Generally, the structure of a glass exists in a metastable state with respect to its crystalline form, although in certain circumstances, for example, in a tactic polymers, there is no crystalline analogue of the amorphous phase [4]. As in other amorphous solids, the atomic structure of a glass lacks any long range translational periodicity.

1.2. Glass and their structure:

As given in previous paragraph, there are many possible definitions of glassy phase. An interesting one is that glass is a solid material with a structure similar to a liquid. This somehow reflects the practical operations necessary to obtain a glass: a glass is formed when a liquid is super cooled, in absence of enough sites of nucleation. The resulting solid structure is not completely organized, on the contrary of the crystalline structure typical of all other solids.

For this reason, glass structure is called amorphous (without a definite shape). Most of the glasses are silica-based. In a crystalline solid made of silica (e.g. quartz), SiO_4 tetrahedral are organized in a well-defined network. In amorphous silica, SiO_4 tetrahedral are still linked together, but the angle between them is not constant, and the resulting structure is not organized. Both the structure are shown in Fig.1.1.

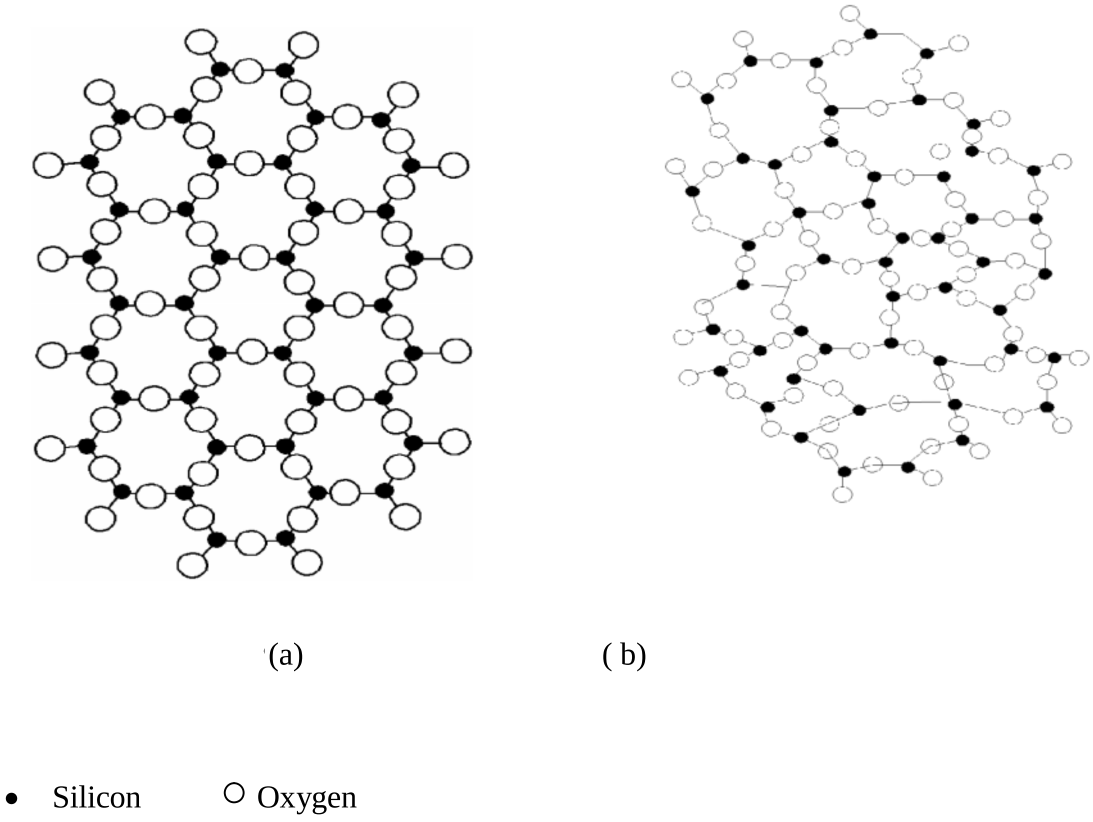


Fig. 1.1: Atomic arrangement of SiO_4 in (a) crystalline form (b) glassy form.

SiO_2 is called glass former, since glass structure is mostly kept together by SiO_4 tetrahedral. Other oxides can also be used as glass formers, such as B_2O_3 or P_2O_5. Alkaline and alkaline-earth oxides are added to glass as glass modifiers, in that they interrupt the network created by the glass former the resulting structure is called random network, and was at first hypothesized by Zachariasen [5]. Therefore to study of any type of glasses, the structure and nature of network former, network modifier and intermediate are essential because almost all the properties will decided on the bases of all these three types of materials used. The basic properties of glass network formers and network modifiers are given in Table 1.

Table 1: Some glass network formers, glass modifier and intermediate oxides with their properties.

CATIONS	IONIC RADIUS (Å)	FIELD FORCE (N/M^2)	STRUCTURAL ROLE
B^{3+}	0.23	56.7	**Network Formers**
Si^{4+}	0.42	22.7	
P^{5+}	0.57	15.9	
Al^{3+}	0.51	11.5	**Intermediate ions**
Ti^{4+}	0.68	8.7	
Zr^{4+}	0.79	6.4	
Mg^{2+}	0.66	4.6	**Network Modifiers**
Zn^{2+}	0.74	3.7	
Ca^{2+}	0.99	2	
Sr^{2+}	1.12	1.6	
Pb^{2+}	1.2	1.4	
Ba^{2+}	1.34	1.1	
Na^{+}	0.97	1.1	
K^{+}	1.33	0.6	
Li^{+}	0.68	2.2	

1.3. Constituent of the glasses:

In general, there are three classes of components for oxide glasses: network formers, intermediates, and modifiers. The network formers (silicon, boron, phosphorus) are formed a highly cross linked network of chemical bonds. The intermediates (titanium, aluminum, zirconium, beryllium, magnesium, zinc) can act as both network formers and modifiers, depending on their coordination with oxygen. The modifiers (calcium, lead, lithium, sodium, potassium) alter the network structure; they are usually present as ions, compensated by nearby non-bridging oxygen atoms, bound by one covalent bond to the glass network and holding one negative charge to compensate for the positive ion nearby. Some elements can play multiple roles; e.g. lead can act both as a network former (Pb^{4+} replacing Si^{4+}), or as a modifier. The presence of non-bridging oxygen's lowers the relative number of strong bonds in the material and disrupts the network, decreasing the viscosity of the melt and lowering the melting temperature.

1.3.1. Glass formers:

Cations having high charges and small radiuses (and thus high field forces like boron and silicon), act as network formers. Boron is a basic component of glass yet its characteristics are so peculiar that it cannot easily be compared to other elements. Boron, like aluminum, exhibits tetrahedral coordination when forming a glass network (being in the center of a tetrahedron of oxygen ions). This is possible only when the molar alkaline percentage is less than 30-40% because above this limit boron has trigonal coordination, forming triangles. Another peculiar characteristic is that boron is not just dispersed as tetrahedrons or triangles in the network of silica tetrahedrons. Rather it forms boric groups, containing from 3 to 5 boron atoms and the groups are randomly dispersed in the glassy matrix. However single BO_3 triangles and BO_4 tetrahedrons are always present. For quenched frits the presence of these groups is likely minimal but we can presume they form again when glazes containing the frit are fired (there are experimental evidences demonstrating this). Boron oxide is an important component of low melting glasses because it increases fusibility without a proportional increase in thermal expansion. Moreover boron oxide and sodium borate, due to their low melting point, are useful during smelting of frits because they form a glassy matrix early and act as catalysts in the melting and dissolving of other materials. Which are present in glass composition.

1.3.2. Glass modifiers:

Network modifiers have small charges, large radiuses and a big coordination number for oxygen ions. While considering ions as rigid spheres is an over-simplified way to describe reality, it has still proven useful to describe characteristics of each. For instance, lithium has a ionic radius smaller than sodium and so it can locate into smaller cavities of the network former. The ionic field force of lithium is also stronger than sodium and it is essentially non-directional, thus it more easily produces crystals of a separate phase. Alkaline earth elements locate into cavities of the network as well, but they have double charges and thus act like bridges between two oxygen ions (preventing the three-dimensional network from being fully destroyed). Moreover bonds between alkaline earth ions and oxygen are stronger than alkaline so it is observed neither a rapid decrease in viscosity nor a significant increase of the thermal expansion coefficient. It is notable that for similar molar percentages, glass containing magnesium converts in crystalline form more easily than glass containing calcium.

1.3.3. Intermediate oxides:

Aluminum, titanium and zirconium are classified as intermediate oxides because they can act as a modifier or network former. Whenever these cations are connected by tetrahedrally with oxygen can acts as a glass former. However in higher coordination’s state, these cations can work as a glass modifier. In other words, the intermediate oxides may play both the roles in glasses depending upon their fraction and field strength.

1.4. Influence of modifiers on the structure of glass:

It is observed and specified that the density of glass and its counterpart (crystalline form) do not have very large difference. It is clearly indicated that the glass might be having some local structure. However, glasses exhibit different bond lengths and strengths. Due to different bonds strength in glass matrix, glasses do not have a definite melting point corresponding to a complete collapse of the entire structure. Rather a step-by-step breaking of bonds accompanies a gradual decrease on viscosity. The glassy structure described above suggests that chemical bonds among atoms must be partially covalent and partially ionic. This because covalent bonds have well defined angles and distances (incompatible with glassy structure) while ionic bonds is non-directional. In order to understand the behavior of each element and its role in the glassy network it is required consider the differences in electro negativity among different elements and oxygen.

1.5. Characteristic of glasses:

1.5.1. Glass Transition temperature (T_g):

Glasses are amorphous substances which undergo the glass transition. The most striking feature of the glass transition is the abrupt change in the properties, such as the thermal expansion coefficient (TEC) and heat capacity (cp), as it is cooled through the range of temperature where its viscosity approaches 10 gm Pa.s. In that range the characteristic time for structural relaxation is of the order of a few minutes, so the effects of structural reorganization are easily detected by scientific techniques.

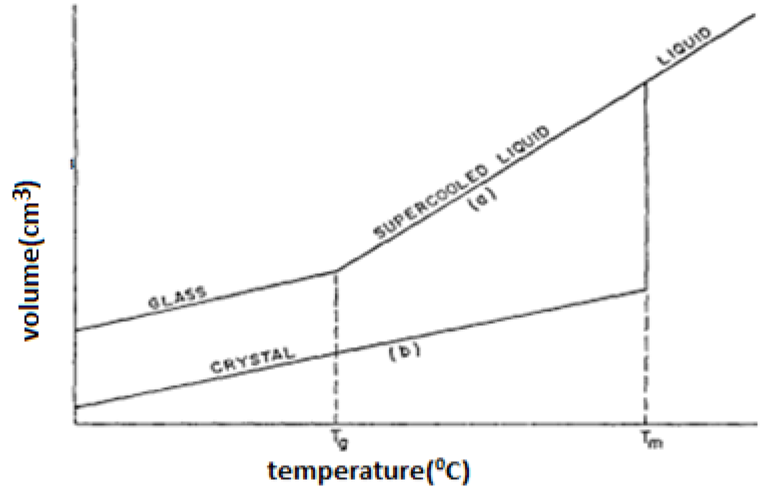


Fig. 1.2 Plot of volume vs. temperature of (a) glass (b) crystal.

If the liquid is cooled slowly it may crystallize at the melting point, T_m. If the cooling rate is fast enough to avoid crystal nucleation and growth, a super cooled liquid would be produced as shown in Fig.1.2 (path a). As the temperature drops, the time required establishing the equilibrium configuration of the liquid increases, and eventually the structural change cannot keep pace with the rate of cooling.

At that point a transition temperature, T_g, is reached below which the atoms are frozen into fixed positions (only thermal vibrations remain) and a glass is formed. Thus, glass formation from the liquid state is feasible if path (a) is followed.

1.5.2. Viscosity:

There is no clear answer to the question "Is glass solid or liquid?" In terms of molecular dynamics and thermodynamics it is possible to justify various views that it is a highly viscous liquid, an amorphous solid, or simply that glass is another state of matter that is neither liquid nor solid. In terms of its material properties, there are no clear definition of the distinction between solids and highly viscous liquids. All such phases or states of matter are idealizations of real material properties. Nevertheless, from a more common sense point of view, glass should be considered a solid since it is rigid according to everyday experience. The use of the term "super cooled liquid" to describe glass still persists, but is considered by many to be an unfortunate misnomer that should be avoided. In any case, claims that glass panes in old windows have deformed due to glass flow have never been substantiated. Examples of Roman glassware and calculation based on measurements of glass visco-properties indicate that these claims cannot be true.

1.5.3. Glass versus a super cooled liquid:

Glass is generally classed as an amorphous solid rather than a liquid. Glass displays all the mechanical properties of a solid. The notion that glass flows to an appreciable extent over extended periods of time is not supported by empirical research or theoretical analysis (see viscosity of amorphous materials). From a more commonsense point of view, glass should be considered a solid since it is rigid according to everyday experience [6].

Some people consider glass to be a liquid due to its lack of a first-order phase transition [7], where certain thermodynamic variables such as volume, entropy and enthalpy are continuous through the glass transition range. However, the glass transition may be described as analogous to a second-order phase transition where the intensive thermodynamic variables such as the thermal expansivity and heat capacity are discontinuous [8]. Despite this, the equilibrium theory of phase transformations in solids does not entirely hold for glass, and hence the glass transition cannot be classed as one of the classical equilibrium phase transformations in solids [9]. Although the atomic structure of glass shares characteristics of the structure in a super cooled liquid, glass tends to behave as a solid below its glass transition temperature [10].

A super cooled liquid behaves as a liquid, but it is below the freezing point of the material, and will crystallize almost instantly if a crystal is added as a core. The change in heat capacity at a glass transition and a melting temperature of comparable materials are typically of the same order of magnitude, indicating that the change in active degrees of freedom is comparable as well. Both in a glass and in a crystal it is mostly only the vibrational degrees of freedom that remain active, whereas rotational and translational motion is arrested. This helps to explain why both crystalline and non-crystalline solids exhibit rigidity on most experimental time scales. A glass is an inorganic product of melting that has been cooled to a solid state without crystallization. For normal glasses and frits, solidification to the amorphous state is effected by rapid rising of the viscosity of the melt during cooling. When the viscosity is high enough, elements are forced to assume an irregular three-dimensional network. This is true even for opaque and matt frits, the rapid quenching in water freezes the structure of molten batch. Basically all the elements could not form the glass even very fast cooling rate. The elements are categorized in three category, these are as follows;

Group 1: Elements having higher electro-negativity, their oxides form glasses when melted alone.

Group 2: Elements are not able to form a glass when melted alone, but they will when melted with elements of group 1.

Group 3: These elements are not able to form a glassy structure.

While the quality of bonds and electro-negativity are good predictors of the behavior of elements in forming a glassy structure, there are other aspects not to be ignored. For instance, the strength of the bonds and the number of electrons in the external shells of atoms (presenting the possibility of different coordination status) deserve consideration. In addition, oxides normally forming glasses can form crystalline structures if cooled too slowly, thus those prone to crystal formation can only be frozen to a glassy state if cooled more quickly. This kinetic aspect isn't important for the glass making process because the melts are quenched in water; however when glass are subjected to thermal treatment as glaze materials glass bonds can break and be rebuilt to crystal phases.

1.6. Properties of glasses:

Some properties of glasses can be related to liquid like structure. The property of transparency is a character of liquids than that of solid state. Glasses are isotropic and lack internal grain boundaries lying in specific orientation [11].

1.6.1. Physical properties:

Density of the glass is his strong function of its composition and most important measure of the glass. It also stands on its own as an intrinsic property of casting Light on short range structure. The addition of network modifier component increases the density as the network modifier ions attempt to occupy the interstices within the network [12].

1.6.2. Mechanical properties:

Glasses are brittle materials as a result fracture behavior is usually determined by environmental factors and not by the inherent strength of the bonds forming the vitreous network. The glasses are also susceptible to failure due to thermal shock. The fracture strength of the glasses varies with prior surface treatment, inherent stress etc. Other mechanical properties of glasses are inherent to the material. The hardness of glasses is a function of the strength of individual bonds and density of packing of the atoms in the localized structure [13].

1.6.3. Thermal properties:

When a glass is heated it expands and if the temperature over the body is uniform and body is not restrained then there will be no stress formation in the body. If there is non-uniform heating of the body, then different layers of glasses will attempt to expand differently and stress develop. The magnitude of glass generated is related to thermal expansion. Thermal expansion of glasses is increased with increasing temperature. In gener-al, glass ceramics shows higher TEC as compared to the glasses. It may be described due to presence of different crystalline phases and their volume factors. Basically, TEC is a function of bond strengths and temperature. The strong bonded materials exhibit lower TEC.

1.6.4. Electrical properties:

The electrical conductivity of glasses changes due to the presence of network modifiers. Glass which does not contain any modifier possesses a very low conductivity as compared to crystalline counterpart. The strength of bond of the ions in the network and their size influence the electrical properties. On the basis of electrical properties glasses can be categorized as follows:

1. Glasses with very small conductivity (high resistivity), for example high contained SiO_2 glasses.
2. Glasses with high ionic conductivity and low electronic conductivity. The example of this category is alkaline earth based glasses.
3. Glasses with electronic conductivity only. Generally, these glasses exhibit PbO, Bi_2O_3 etc, and intermediate oxides in their compositions.

1.6.5. Chemical properties:

Glass is more corrosion resistant than any other materials. Glass is indestructible by chemical attack, under certain conditions it will corrode, even dissolves in acid and alkali solution. Alkali attacks the silica directly whereas acids attack the alkali in the glass. Corrosion by water is similar to acid corrosion in alkali and is removed from the glass surface. The properties of glass can be varied and regulated over an extensive range by modifying the composition, production techniques or both. Due to all of these properties a lot of applications of glasses are now a days, some of them is discussed in the next article. In any glass mechanical, chemical, thermal properties cannot be occur separately.

1.7. Applications of glasses:

1.7.1. Toughened glass:

For many applications such as buildings requiring large spans of glass, toughened glass is the only acceptable alternative. These glasses have exceptional good strengths compared to standard annealed float glasses. These improved properties are a result of the stress profile that is induced in the glass by the toughening heat treatment process. When performed correctly, the glass surface is in compression, while the centre is in tension. This stress profile in the glass is successful as most failures start at the surface from tensile loads as shown in Fig 1.3. In toughened glass, the applied tensile load must overcome the compressive stress at the surface before the surface can go into tension and fail.

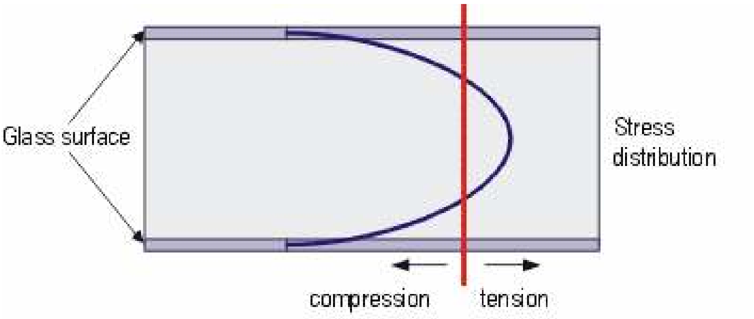


Fig. 1.3 Schematic representation of the stress profile in toughened glass.

The heat treatment process involves heating annealed (stress free) glass up to a temperature between its glass transition temperature and its softening point and then rapidly cooling the surface. This is usually achieved using air jets. This process freezes the surface, while the interior may still be molten and consequently there is a temperature differential across the thickness of the glass. The hotter core section then contracts at a faster rate compared to the outside until an isothermal state is reached. Initially the rapid cooling of the surface tends to induce a tensile stress in the surface. This is reversed in the latter stages of cooling, resulting in compressive stresses in the surface.

Nevertheless, evacuated glazing is still as insulative as much thicker conventional double glazing and tends to be stronger, since the two constituent glass sheets are pressed together by the atmosphere, and hence react practically as one thick sheet to bending forces. Evacuated glazing also offers very good sound insulation in comparison with other popular types of window glazing [13].

1.7.2. Chemically strengthened glass:

When broken it still shatters in long pointed splinters similar to float (annealed) glass. For this reason, it is not considered a safety glass and must be laminated if a safety glass is required. Chemically strengthened glass is typically six to eight times higher the strength than annealed glass. The glass is chemically strengthened by submersing the glass in a bath containing a potassium salt at 450°C. This causes sodium ions in the glass surface to be replaced by potassium ions from the bath solution Chemical strengthening results in a strengthening similar to toughened glass, however the process does not use extreme variations of temperature and therefore chemically strengthened glass has little or no bow or warp, optical distortion or strain pattern. This differs from toughened glass, in which slender pieces can often be significantly bowed. Chemically strengthened glass was used on some fighter aircraft canopies.

1.7.3. Window glasses:

Qualified windows can save energy and money, and increase home comfort. Low-priced windows are a bad choice. Qualified windows provide savings, last long, and cost less in the long term. Old conventional windows lose large amounts of heat to the outside during the heating season and gain too unwanted heat during the cooling season. According to some experts over 25% of the heating and cooling energy bills in a typical home are due to inefficient windows. The glass is particularly important in terms of the energy-efficiency of windows, but the frame and sashes and the materials they are made from are also important. The hollow sections of the frame and sash should be filled with foam insulation to increase the energy efficiency of the window.

Low-E coating glass is the most common type of glass for boosting the energy efficiency of windows in cold climates. They allow lower values of the U-factor, that is, heat losses will be minimized. Low E2 glasses, also called solar low-E, or spectrally selective glass, are crucial in hot climates. They block unwanted solar gains and contribute to smaller air conditioning bills in summer and hot days. Controlling glare is also important, in some cases. To control that glare and also the heat, a glass with a low visible transmission (VT) and a low SHGC. Besides E-low glass and Low E2 glasses, there are also impact-resistant glasses (to improve the safety in areas prone to flying debris or high winds), tinted glasses (to improve privacy or control solar heat gains…) and hydrophilic glass exterior coatings to reduce the frequency of cleaning.

1.7.4. Optoelectric glasses:

Chalcogenide glasses, especially sulphide glasses, are becoming increasingly important for the fabrication of optoelectronic devices, in part because of their high nonlinearity, strong photosensitivity and other unique properties [14]. The conventional method of fabricating a chalcogenide glass is sealed ampoule melting. In this process the raw materials are placed in a quartz tube, which is then evacuated to a low pressure and sealed by melting and fusing the open end. The tube is placed in a furnace that typically rocks or oscillates the sealed ampoule in order to homogenize the melt.

The ampoule is then cooled and the glass annealed finally to yield an ingot of raw, unshaped glass. Further processing is then required to form, for example, thin films, optical fiber and optoelectronic devices. Sealed ampoule melting has a number of disadvantages, in particular it is a closed system and any impurities within the starting materials are trapped in the sealed system and incorporated into the glass. In particular oxygen impurities, carbon and hydrogen resulting from the use of organic compounds and transition metal ions all introduce undesirable absorption bands in the transmission spectrum of the glass [15]. Most of the optoelectronic device is synthesized by their film technology in which glass substitute is used to deposit the film. For this purpose, various glass are being used depend on the refractive index and properties of the glasses.

CHAPTER 2

LITRATURE REVIEW

Many researchers have been reported that borates and borosilicate glasses containing boron oxide can be used for optical lenses with high refractive index and low dispersion characteristics [16]. $ZnO–PbO–B_2O_3$ glasses have been characterized for a strong tendency for phase separation and may be used in glass solders for sealing CTV bulbs, IC packages, glass discharge tubes etc [17]. The structural and physical properties of PbO glasses is summarized by many researchers [18,19]. PbO and ZnO can enter in glass network both as a network former and as a network modifier. At lower concentrations, PbO modifies the network through forming BO4 tetrahedral at the rate of two BO4 groups per PbO molecule and, at higher concentrations; PbO can partly play the role of a glass-forming oxide in the form of PbO4 pyramids with Pb2+ at the apex of the pyramid [20,21].

Bi_2O_3-based glasses, which contain none of the conventional network formers such as B_2O_3, P_2O_5 and SiO_2 attract much attention for the optical transmission applications due to their long infrared cutoff. Their nonlinearity makes them an appealing material for ultrafast optical witches [22]. In Bi_2O_3-containing glasses, it is assumed that Bi_2O_3 exists mostly as BiO_6 octahedral [23]. The glass-forming ability of Bi^{3+} ions in the presence of alkali ions is an interesting aspect for the glass structure. However, these glasses, if formed, will be useful materials for spectral devices and optical switches [24].

Phosphates glasses with various compositions are of exceptional importance due to their interesting linear and nonlinear optical properties [25]. Combining bismuth oxide (Bi_2O_3)

and lead oxide (PbO) with phosphorus pent oxide allows one to tune the optical properties in a wide range depending on the glass composition.

Nano particle silica-gel derived glasses is an attractive amorphous material, that is applied, as a wave-guide, chemical gas sensor [26] and so on[27,28]. Mollei and jinga[29] suggest that it can be prepared by sol-gel method, which is being actively studied in leading laboratories all over the world. The advantage of this process is to avoid generation of dangerous dust, as would be produced in conventional ceramics processing. Moreover it is low temperature nature. One of the major advantages of the sol-gel process is the possibility to prepare multi-component systems with ease.

The glasses in the system SiO_2-Nd_2O_3 posses many favorable properties as thermo-stable medium for optical performance. Mollei-Jinga's coworkers [30] successfully obtained neodymium doped silica glass containing up to 20 wt % Nd_2O_3 using the sol-gel process. They have suggested that coordination number of Nd cations is hexavalent. Although the sol-gel process allows the preparation of glasses with much higher concentrations of neodymium however, microscopic clustering is possible when other appropriated components are added. Therefore, it is important to understand more fully the local environment of neodymium in silica matrix.

Rare earth ions are used as do pants in glasses mainly for two reasons. The first one is their well defined and sharp energy levels, which may serve as structural probes for the environment of the do pants, and the other one is the modifications of the energy level structure of the rare earth ions caused by the glassy environment may lead to interesting applications, e.g., solid state lasers [31] The glass compositions are more favorable for high-density memory devices, because the inhomogeneous widths of the transition between the energy levels are much broader than those of crystals. In addition, the high transparency and easy mass production are also particularly promising for practical application in optical device [32]. In their work, nano-structure monolithic silica gel derived glasses pure and doped with Nd^{3+} ion using two different precursor materials TMOS and TEOS, were successfully prepared by a simple sol-gel method. The effect of increasing the heat-treatment temperature on the microstructure of the prepared samples was reported by Medda et. al.[33].

El-Adawy and Moustafa[34] have described that the effect of small metal particles, such as Au, Ag and Cu, embedded in oxide glasses can be used as resonant-type nonlinear optical materials for photonic devices. Size, shape, concentration and spatial distribution of the do pant particles within the composite determine these peculiar optical properties. Ion-implantation and ion-exchange techniques are usually used to introduce metal ions into a glass network. The subsequent thermal treatment of samples results in the formation of metallic atoms and colloidal particles. Their presence can strongly affect the optical properties of such composites the color of which originates from the surface plasmon resonance [35]. Phosphorus pent oxide (P_2O_5) acts as one of the most important glass former and flux materials.

Phosphate glasses exhibit very important physical properties such as low melting temperature, high thermal expansion coefficient, low glass transition temperature, low softening temperature and high ultraviolet (UV) transmission. Despite their solubility, the low processing temperature has led these glasses to be used in applications such as glass to metal seals, low temperature enamels for metals and as a optical elements [35,36]. Many researchers have been carried out the research on phosphate based glasses, especially concerning an optimization of glass preparation, investigation of their properties and information about the glass structure. Tellurium oxide (TeO_2)-based glasses are of scientific and technical interest on account of their various unique properties, and have been considered as promising materials for use in optical amplifiers because of their low phonon energy or nonlinear optical devices because of their large third-order nonlinear susceptibility [37]. Recently, optically transparent TeO_2 based glass-ceramics exhibit some interesting properties and investigated by chaudhary et al [38]. It is known that a pure TeO_2 does not form a glass under usual quenching conditions. The addition of other elements is needed to form TeO_2-based bulk glasses.

Glasses are also being used as a shielding materials especially rare earth doped glasses. The detrimental consequences of high energy radiation, referred to as radiation damage, bring about extensive changes to a variety of material properties including chemical, electrical, magnetic, mechanical, optical, and so on. Radiation effects are conveniently grouped into two quite distinct categories, namely, ionization effects and displacement effects. In a good conductor, the ionization effects will disappear very quickly and will only contribute to the heating of the material. In an insulator, however, the electrons liberated by ionization may be trapped at various lattice imperfections resulting in more or less permanent changes in the glasses. Exposure of glasses to ionizing radiation (x-rays, γ -rays, ultraviolet light) causes essential changes in their optical and structural characteristics with profound optical absorption bands in the visible and ultraviolet parts of the spectrum. The most fundamental radiation-induced defects (or color centers) in silicate glasses are the non bridging oxygen hole centers (NBOHCs) (NBOHC :≡ Si–O), the E –

centre (≡Si), the proxy radical (POR :≡ Si–O–O) and the trapped electrons (TE) where the notation ≡ represents three bonds with other oxygen in the glass network and denotes an unpaired electron[39].

In general, NBOHC has an optical absorption around 620 and 440 nm, the *E*_ centre has an absorption band at about 215 nm and POR has an absorption band near 260 nm. Radiation induces the generation of free charge carriers in the glass matrix. The passage of energetic photons through an insulating solid cause's extensive ionization and electronic excitations leading to the production of the above-mentioned color centers, luminescence and other related phenomena. Copper-doped phosphate glasses have interesting electrical and optical properties that make them suitable for use as super ionic conductors, solid state lasers, color filters, and nonlinear optics [40]. Glasses containing transition metal ions, such as Fe, Co, Cu, Mo, W, etc., are known to be electronically semiconductors. the existence of relative proportions of the ions in different valiancy states (such as Cu^{+} and Cu^{2+} in copper oxide glasses) has been used to explain electronic conduction. Phosphate glasses have a range of compositional and structural possibilities (ultra, meta, pyro, and ortho) [41]. In amorphous P2O5, the glass structure is composed of three bridging oxygen and one P=O that is called ultra phosphate. With addition of modifier oxides, the structure is conversed to meta phosphate that is composed of two bridging oxygen and two terminal oxygen's. The study of oxide glasses has received considerable attention due to their structural peculiarities [42]. These glasses have wide applications in the fields of electronics, nuclear and solar energy technologies and acoustic-optic devices [43].

CHAPTER 3

Experimental Techniques

3.1. Raw Material:

In the present study, raw materials used for preparing the samples were SiO_2 (99%, CDH), ZnO (99.5%, Sdfine), B_2O_3 (99%, Sdfine), BaO (99.9%, CDH), and Y_2O_3 (99.995%, Sigma Aldrich). All these materials were used without any further purification.

3.1.1. Sample preparation:

Glass samples were prepared by grinding the raw materials using conventional techniques followed by melting. Each batch was prepared by taking an appropriate mole fraction of well-desired initial ingredients and grinding them in mortar and pestle. Sample compositions with their label are given in table 2. The following process for making of sample is shown in Fig. 3.1.

Table 2: Glass composition with sample labels

Sample Name	SiO_2	BaO	ZnO	B_2O_3	Y_2O_3
BY1	40	30	20	10	0
BY2	40	30	20	7.5	2.5
BY3	40	30	20	5	5
BY4	40	30	20	2.5	7.5
BY5	40	30	20	0	10

Fig. 3.1 Process of pouring the glass in graphite mould at 1550°C.

For each system, required amount of raw materials as per the stoichiometric ratio were taken. The mixture was grinded to break agglomerate particles. After grinding the mixture was further transformed to ball mill and grinded for two hours in a ball mill in wet medium (acetone). The ball milling was done using porcelain balls in porcelain jar (Retsch, Germany, Model S 1000). The mass to ball ratio for each system was 1:2 which was kept constant for each milling. The resulting mixture was dried in air. The mixed dried powder of the homogenous mass was transformed in recrystallized alumina crucible and heated in an atomized Molybdenum Disilicide ($MoSi_2$) electric high resistance furnace in oxidizing atmosphere. The powder of the samples were initially heated to achieve a temperature of 1000 ºC in 2 hrs i.e. at a heating rate of 8K/min. The temperature was maintained at 1000 °C for 45 minutes to facilitate the calcinations. During heating process moisture is released and the calcinations occur. After that the temperature was increased up to 1200 °C at a rate of 3K/min and kept at this temperature for 30 minutes to facilitate the fusion and melting process.

Then, system was reheated at 1550 ºC by keeping constant heating rate and kept at this temperature for 1 hour 45 minutes in order to achieve the homogeneous molten glass. The schedule followed for sample melting is also shown in Fig.3.2. The molten mass was poured in a preheated graphite mold. The remaining melt was poured on the flat copper plate and quenched by other copper plate in air to obtain flakes. All the samples were prepared using the same route as described above. Before melting, the furnace was calibrated and in hot zone fluctuation in temperature was within ± 2 °C. In order to check the percentage weight loss of volatile substances

(B_2O_3, ZnO) after the formation of glass, glass compositions are studied by AAS (atomic absorption spectroscopy) and wet chemical analysis and results obtained by them is given in next chapter. The details of the sample preparation and other relevant information about preparation and characterization are summarized in the Fig.3.3.

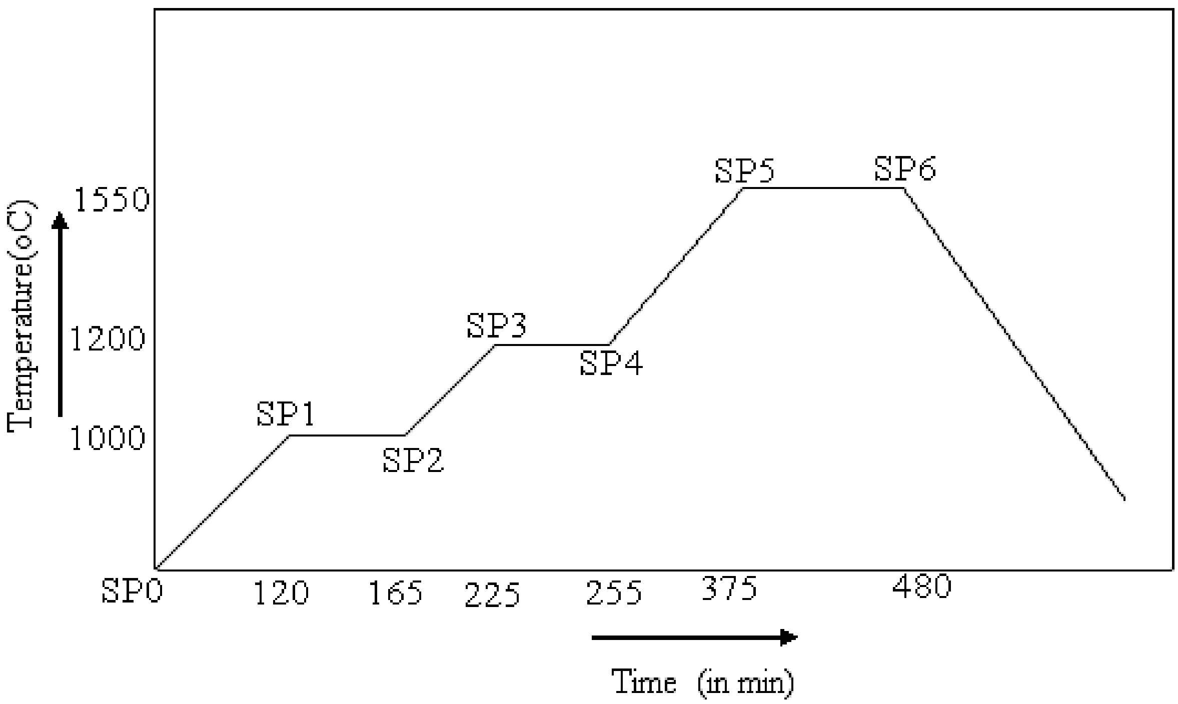


Fig. 3.2 Typical schedule followed for the melting of the glass samples.

3.1.2. Annealing:

The obtained frits were annealed at 500 ^{O}C (below T_g, glass transition temperature) for 10 hours in air in a calibrated resistance heating furnace. The annealing process is done to remove the internal stresses generated during quenching process.

3.2. Characterization of Material:

The materials obtained following the above procedure is then characterized to know the initial structure and transformation during various heat-treatments. Different transition temperatures (T_g, T_c), percentage change in length with respect to temperature and conductivity measurement were also done. For the analysis of above parameters, the obtained glass samples were characterized through X-ray diffraction (XRD), Fourier transform, U.V spectroscopy, density measurement by Arkemedies principle. The details of these techniques are given below:

3.2.1. X-Ray Diffraction:

X-ray diffraction (XRD) is a versatile, non-destructive technique that reveals detailed information about the chemical composition and crystallographic structure of natural and manufactured materials. X-ray powder diffractrogram was recorded at room temperature by Philips Xpert Powder diffractometer using monochromatic CuK_α

radiation (λ = 1.5418 Å) at a scan speed of 1^{o}/minutes. Monochromatic X-rays are used

to determine the inter planar spacing of the unknown samples. Samples are analyzed as powders with grains in random orientations to insure that all crystallographic directions are sampled by the beam. When X-rays are scattered from a crystal lattice (fig. 3.4), peaks of scattered intensity are observed which correspond to the following conditions:

1. The angle of incidence = angle of scattering.

2. The path length difference is equal to an integer number of wavelengths.

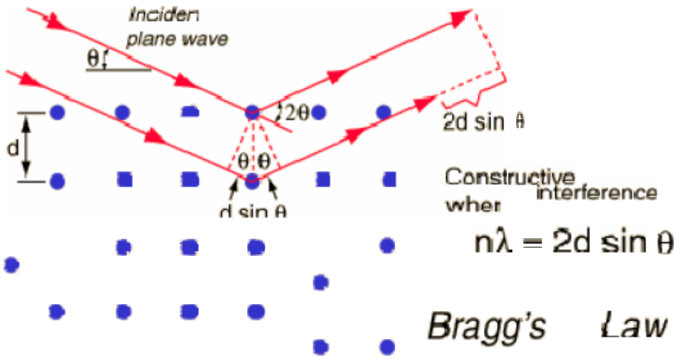


Figure 3.4 Geometric derivation of Bragg’s law

The condition for maximum intensity contained in Bragg's law above allow us to calculate details about the crystal structure, or if the crystal structure is known, to determine the wavelength of the x-rays incident upon the crystal.

3.2.2. UV-Visible Spectroscopy:

Ultraviolet-visible spectroscopy (UV/ VIS) involves the spectroscopy of photons in the UV- visible region. It uses light in the visible and adjacent near ultraviolet (UV) and near infrared (NIR) ranges. In this region of the electromagnetic spectrum, molecules undergo electronic transitions.

This technique is complementary to fluorescence spectroscopy, in that fluorescence deals with transitions from the excited state to the ground state, while absorption measures transitions from the ground state to the excited state.

Fig 3.5 Diagram of UV Spectrometer

UV-visible spectroscopy is the reliable and accurate procedure for analysis of samples. UV measures the absorption, transmission and emission of ultraviolet and visible wavelength by matter. UV Spectroscopy measures absorption and transmission of electromagnetic radiations by atoms or molecules. Here we are calculating the band gap of the samples to know the effect of different compositions of Y_2O_3 on the energy band gap of without heat treated and heat treated samples. Absorption is the powerful tool for measuring the band gap of the glass samples. Let the photon beam intensity I_O is incident the sample of the thickness t and intensity of light transmitted is I_t ,

then

$$I_t = I_O e^{-\alpha t} \tag{1}$$

α = absorption coefficient

This varies with photon wavelength and also with material to material. For direct transition

$$\alpha h\nu = A(h\nu - E_g)^n \tag{2}$$

3.2.3. Fourier transform infrared spectrometer (FT-IR):

FT-IR is an effective analytical tool for identification of unknowns, sample screening and profiling samples. FT-IR absorption spectra were recorded at room temperature in the 400–4000 cm^{-1} range using a spectrometer of type Shimadzu (Japan) FT-IR-8700. The spectra obtained were used to analyze the structure of glasses before and after heat treatment of the sample. In sample prepration for FT-IR , glass sample is grinded by motor-pacer to obtained sample in powder form. Now abour 4.0 mg of each sample were used for recording the absorption spectra. The FT-IR analysis after heat treatment of the sample is also completed by similar process as in without heat treated sample.

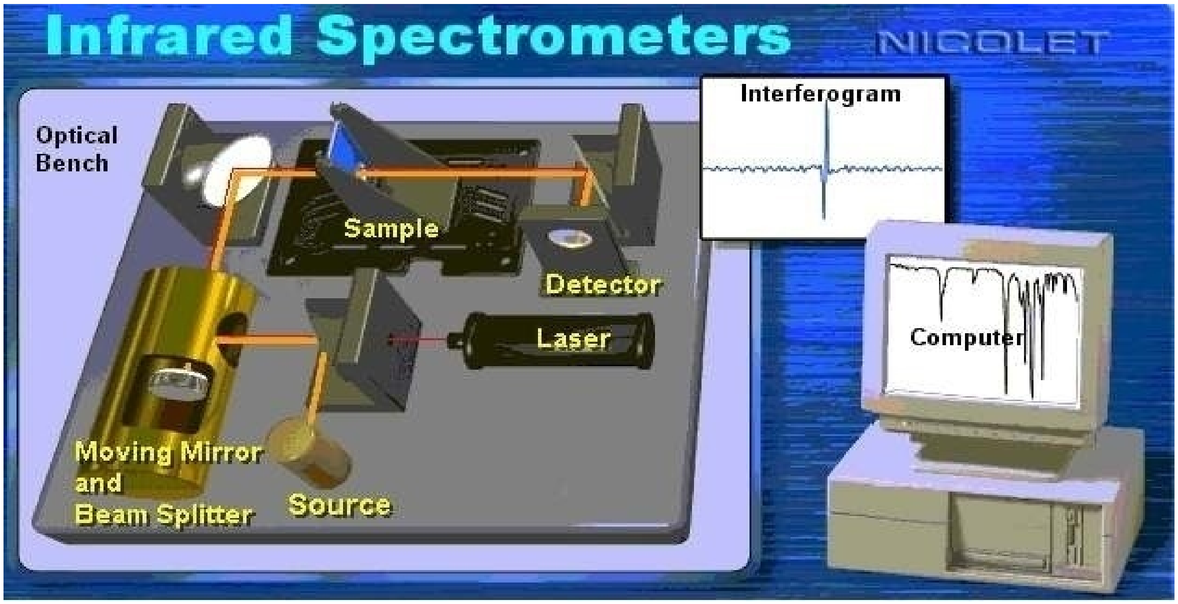
FT-IR stands for Fourier Transform Infrared, the preferred method of infrared spectroscopy. In infrared spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). The resulting Spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. Like a fingerprint no two unique molecular structures produce the same Infrared spectrum. This makes infrared spectroscopy useful for several types of analysis. FTI-R is used to analysis the bonding of the samples [45].

FTIR is most useful for identifying chemicals that are either organic or inorganic. It can be utilized to quantitative some components of an unknown mixture. It can be applied to the analysis of solids, liquids, and gasses. The term Fourier transform infrared spectroscopy (FTIR) refers to a fairly recent development in the manner in which the data is collected and converted from an interference pattern to a spectrum. FTIR can be used to identify chemicals from spills, paints, polymers, coatings, drugs, and contaminants. FTIR is perhaps the most powerful tool for identifying types of chemical bonds (functional groups). The wavelength of light absorbed is characteristic of the chemical bond as can be seen in this annotated spectrum [46]. In table 3 band assignment of FTIR spectra is given.

Wave number (cm^{-1})	**Vibrational mode**
750-820	Si-O-Si symmetric stretching of bridging oxygen
694.33	Atoms oxygen bridges between trigonal atoms (BO_4 stretching)
1394.44, 1417.58, 1419.51, 1515.94	B-O vibrations of various borate groups (BO_3 stretching)
1548.73, 1539.09	B-O bonds vibration (BO_3 stretching)

Table 3 FTIR band assignment

Fig 3.6 Diagram of FT-IR



CHAPTER 4:

RESULTS AND DISCUSSION

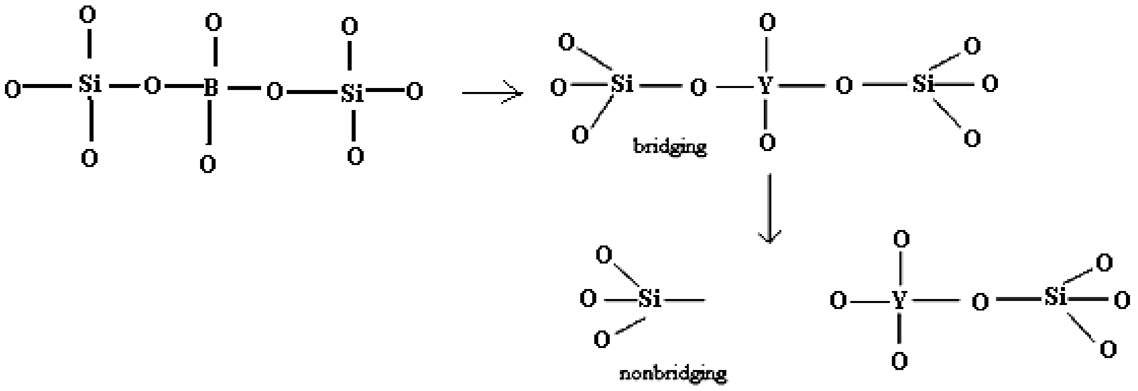
4.1. Density and molar volume:

The density, molar volume and excess molar volume of glass samples are given in table 4.

Table 4: Densities, molar volume, excess molar volume and optical basicity of the glasses.

Sample	Optical basicity(Λ_m)	Density(ρ) (g/cc)	Molar volume(V_m) (cm^3/mol)	Excess molar volume(V_o)
BY1	0.48	3.653	29.8	5.27
BY2	0.50	2.111	49.64	25.57
BY3	0.51	3.185	31.67	7.29
BY4	0.53	2.868	33.79	10.64
BY5	0.55	3.929	23.66	11.10

It is observed that none of these parameters are following a particular trend. However, BY5 and BY1 glasses exhibit higher density and lower molar volume followed by BY3 glasses. It indicates that glass structure became more compact where higher Y_2O_3 or B_2O_3 content is present in the glass. The lower values of molar volume in these glass samples can be explained on the basis of smaller bond length or inter-atomic spacing between the cations and oxygens. In other words it may be attributed due to increase in force constants of bonds inside the glass network [47] . The basicity calculations showed the highest basicity values of BY5 glass indicating the breakage of glass network which further leads to the formation of non-bridging oxygens. In other words, BY5 glass exhibit lower cross-linking which further enhances the closer packing of the structural units. This may be the reason to get highest density in this glass [48]. Basically, the creation of NBO's alter the glass structure in such a way that the modifier cation Y^{3+} attempt to occupy the interstices within the network, hence altering the cross-linking as well as coordination number within glass. The creation of NBO's can be proposed as follows:



Contrary to this, BY1 glass exhibit lower density than BY5 glass. Moreover, BY1 glass does not have intermediate oxide (Y_2O_3). In addition to this, the field strength of B^{3+} cation is more than Y^{3+} cation. This could be attributed to the lower atomic weight of boron as compared to yttrium. The density of multicomponent glasses depends indispensably on its constituents. On the other hand BY2, BY3 and BY4 glasses show lower density as well as lower molar volume than BY1 and BY5 glasses. In these systems, competition between B^{3+} and Y^{3+} ions leads to open glass structure. Initially when the Y_2O_3 content is lower, then it is working as a network former. But as the concentration of Y_2O_3 becomes higher, it acts as network modifier. Apart from this, it is well reported in literature that an intermediate oxide can act as either a network former or network modifier depending upon its coordination as well as concentration in the glass [49].

4.2 Optical Basicity Calculations:

In the glass system, the tendency to form the structural units of oxide atoms can be estimated by optical basicity. In general this tendency increases with increasing NBO's in glass system [50]. The cause of negative charge borne by an ion arises from unequal sharing of electrons in a compound which can also be termed as resonance between covalent and ionic structures. According to Duffy [51]:

$$x_o - x_m = \sqrt{[(Q+1.13)/2b]} \qquad (4)$$

where 2b is the number of bonds, Q is the heat of formation (in kJ/mol), x_o and x_m are the electronegativity values of oxygen ion and metal ions, respectively. These values are summarized in table 5.

Table 5 : The electronic negativity of metals and oxygen ions with γ_m basicity moderating parameter.

Oxide	x_m	x_0	γ_m	Λ_0(oxides)
SiO_2	1.8	3.51	2.08	0.48
BaO	0.9	2.75	0.87	1.15
ZnO	1.65	3.19	1.87	0.53
B_2O_3	2	3.66	2.36	0.42
Y_2O_3	1.22	3.42	1.29	0.78

The variation of x_o with respect to x_m is also shown in fig 4.1.

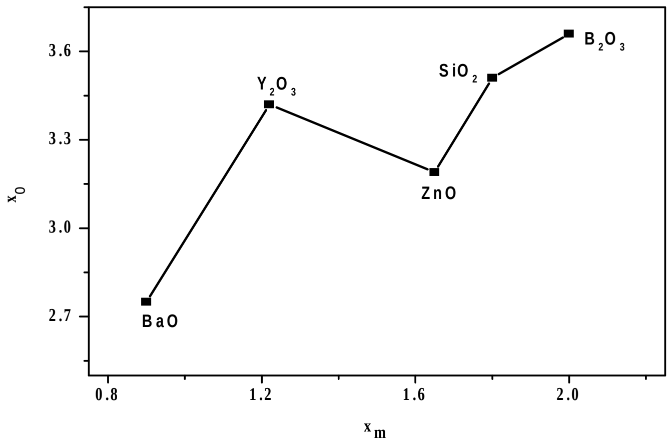


Fig.4.1. Variation of metal-ion electronegativity and oxygen electronegativity of constituents of glasses.

The optical basicity can be calculated from chemical composition using following relation [52]:

$$\Lambda_m = \sum \frac{O_i}{O\,\gamma_m} \qquad (5)$$

O is the total number of oxygen atoms present, γ_m is the basicity moderating parameter and O_i is number of atoms in individual oxides. Basicity moderating parameter is almost similar to electronegativity as both parameters measure the attraction of electrons for chemical bonding. The variation of optical basicity with the increasing concentration of Y_2O_3 is shown in fig.4.2.

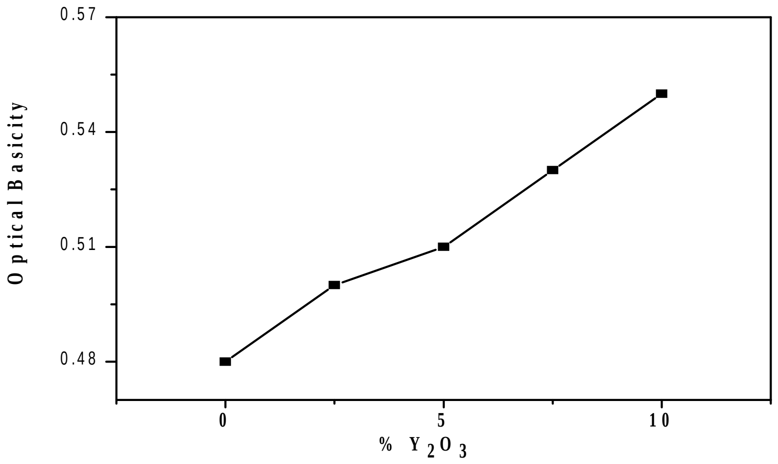


Fig.4.2 Optical basicity with respect to Y_2O_3 (mol%).

As indicated from table 5, BY5 glass has higher values of optical basicity due to higher number of NBO's in this glass. The increasing thermodynamic stability is associated with increasing charge on oxygen atoms. When the glass is heated then the increasing vibrations of boron/silicon and oxygen atoms introduce large scale disruption in the network via the conversion of bridging oxygen to non- bridging oxygen. The distribution of bulk optical density Λ_m in the glass changes as the network disrupts. It depends on whether the oxide is bridging or nonbridging as well as the co-ordination number of Si or B. Therefore, microscopic optical basicities (σ) are assigned to the individual oxides although the bulk optical density Λ_m remains unchanged. The general equation for the calculation of σ of an oxide medium is given by :

$$\sigma = 1- [(z_a r_a/2)(1-1/\gamma_a) + (z_b r_b/2)(1-1/\gamma_b) + \ldots\ldots] \qquad (6)$$

where z_a , z_b are the oxidation numbers, γ_a and γ_b are basicity moderating parameters, r_a and r_b are the ratios of cations w.r.t. total number of oxides. To calculate the microscopic optical basicity of single oxide for borate glass, we can employ following relation:

$$\sigma = 1- (3r_a/2)(1-1/2.36) = 1- 0.864r_a \qquad (7)$$

r_a depends upon coordination of boron. Similarly, for silicate system we can imply the following relation:

$$\sigma = 1- (2r_a)(1-1/2.08) = 1 – 1.038\, r_a \qquad (8)$$

Table 6: Microscopic optical basicities for bridging as well as non-bridging oxides of silicon and boron.

	Non-bridging (σ)		Bridging(σ)		
coordination→	threefold	fourfold	Threefold	fourfold	Threefold & fourfold
Boron	0.71	0.78	0.42	0.57	0.50
Silicon	0.65	0.74	0.31	0.48	0.39

It is observed from table 6 that the σ are higher for non-bridging oxides. This clearly implies that non-bridging oxides are much more basic than bridging oxides. This further leads to the formation of basic sites inside the structure.

4.3 X-ray diffraction:

The glass samples were subjected to heat treatment at 900°C for 5h to understand the nucleation kinetics of different crystalline phases and their effect on the optical band gap. The selection of heat-treatment temperature was based on thermal analysis of these glasses [53]. The XRD pattern of BY4 glasses exhibit the Y_2SiO_5 crystalline phase whereas BY5 glass exhibit both Y_2SiO_5 and $Y_2Si_2O_7$ phase as shown in fig.4.3.

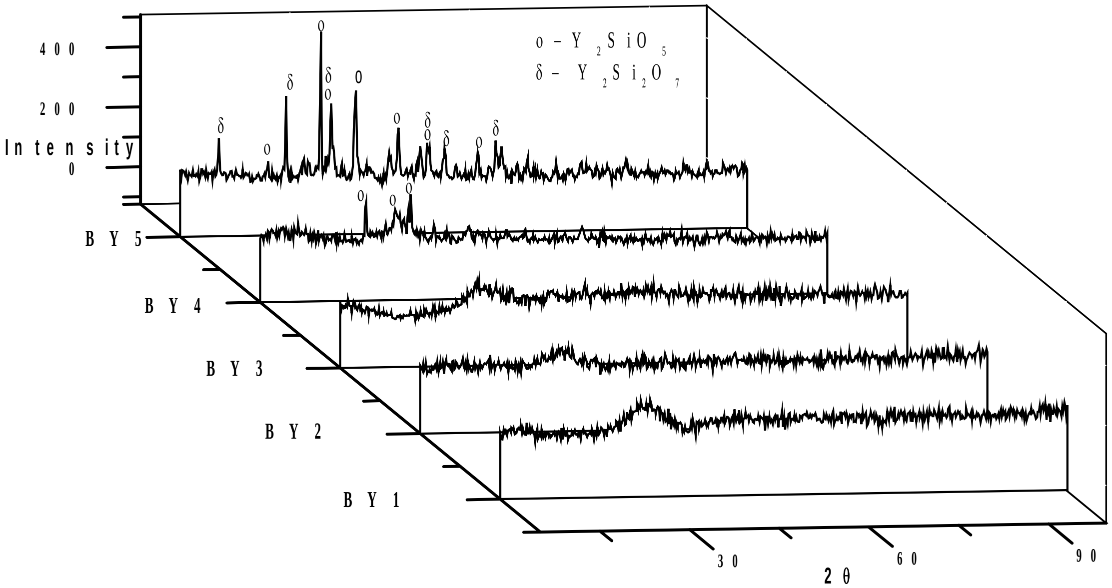


Fig.4.3 The XRD diffractogram for heat-treated glass samples.

It is observed that by increasing the Y_2O_3 content, the intensity of peak increases while broadening decreases indicating enhancement of crystallinity in both the glasses. Structurally Y_2SiO_5 and $Y_2Si_2O_7$ phases are cubic and orthorhombic respectively. Among both phases, $Y_2Si_2O_7$ phase exhibits higher stability and symmetry thanY_2SiO_5 phase. During the initial stages of heat-treatment, silica rich solid solution might have formed and during the later stage Y^{3+} may get incorporated into the SiO_2 rich solid solution. The Y^{3+} ions are larger than Si^{4+} ions and they must have been responsible for the enhancement of lattice parameters which leads to slight peak shifting as observed in XRD pattern of BY4 and BY5 glass. Contrary to BY4 and BY5 glasses, the other three glasses exhibit broad halo around 30^o. It indicates that BY1, BY2 and BY3 glass samples still contain glassy phase even after heat-treatment. Conclusively, higher content of Y_2O_3 in glass leads to weakening of the glass network and promotes crystallization after heat treatment. Thus, the XRD results are consistent with the results obtained from density and molar volume. The segregation of silica rich phases in the present glass also indicate that the addition of Y_2O_3 at the cost of B_2O_3 in glasses is breaking the network of silicon.

4.4 Fourier Transform Infra-Red analysis:

The IR spectra of pristine and heat-treated glasses are given in figs.4.4 and fig.4.5 respectively.

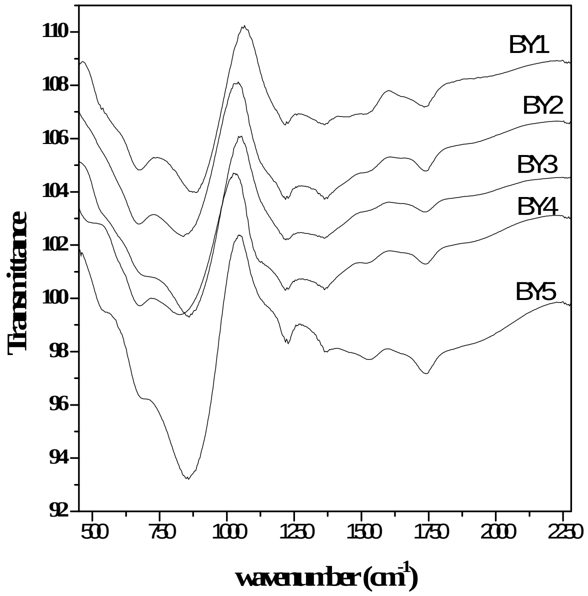


Fig.4.4 FTIR spectra of heat-treated samples.

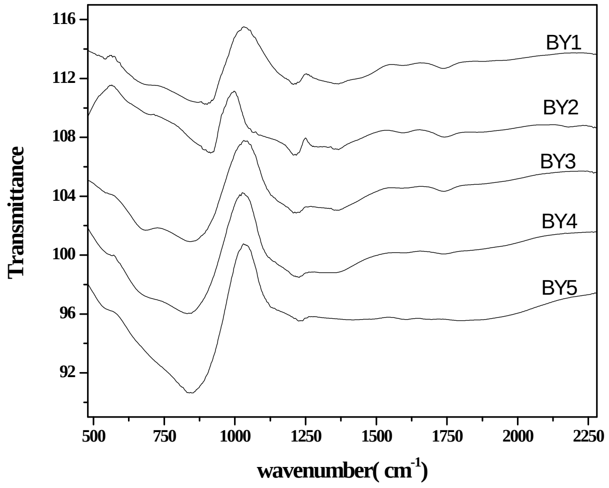


Fig.4.5 FTIR spectra of non heat treated sample.

The IR spectra of pristine glasses exhibit a very small absorption band at 650-780 cm^{-1} which can be assigned to Si-O-Si streching of bridging oxygen between tetrahedra. Additionally, strong absorption band appeared at 880 cm^{-1} which can be attributed to $Si-O^-$ stretching with two non-bridging oxygens. Apart from these bands, FTIR spectra also exhibit two weak band inflections at 1250 cm^{-1} and 1600 cm^{-1}. These inflections can be assigned to boroxyl rings and H_2O molecular vibrations, respectively. The heat-treated glasses show remarkable change in FTIR spectra. The sharpness of the bands increases in comparison to pristine glasses. Moreover, small kinks at 1300 cm^{-1} to 1520 cm^{-1} are observed which can be due to BO vibrations of various borate groups [54].

The sharper peaks of heat treated glasses can be due to strong vibrational frequency of the various groups present in glasses. The shifting of FTIR peaks to the lower wavelength side is clearly seen in the glasses with higher yetteria content. According to Cental Force Model, the shifting of Si-O-Si stretching vibrational frequency can be due to the structural changes which are associated with variation of intertetrahedral Si-O-Si bond angles [55]. It is well established that addition of heavy cations in glass shifts the peaks to lower wave numbers. With the introduction of more yetteria, the structural rearrangement can take place in Si-O-Si environment leading to strained network and hence resulting in net decrease of local symmetry. The band at 750 cm^{-1} is getting broadened indicating the scission of Si-O-Si chain in the glass network. The bands centered at 850 cm^{-1} is assigned to the Si-O- stretching with two non-bridging oxygen (Si-O-2NBO) per SiO_4 tetrahedron (Q^2 group). These bands are becoming stronger with the addition of Y_2O_3. The reason being increasing concentration of Y_2O_3 is breaking the network structure of glass former, thus producing NBO’s with the gradual incorporation of ions in the glass structure. When Y^{3+} ions occupy interstitial position, then it can introduce coordinated defects known as dangling (broken bonds) [56]. The IR results are supported by the optical basicity calculations and other physical parameters as given in table 4,5 and 6, respectively.

The bands at 1250 cm^{-1} are due to the boroxyl rings. Pure B_2O_3 glass structure is two dimensional structure comprising of boroxyl rings with three coordinated $BO_{3/2}$. With the addition of modifier Y_2O_3 the structure becomes three dimensional due to conversion of three coordinated boron to form four coordinated $BO_{4/2}$. This can be proposed as follows :

$$2\,BO_{3/2} + O^{2-} \longrightarrow 2[\,BO_{4/2}]^{-} \qquad (9)$$

Interestingly with increasing content of Y_2O_3 in glass, the intensity of these bands is increasing due to more concentration of boroxyl rings. Because of this, the B-O vibrations at 1300- 1520 cm^{-1} are becoming more prominent. However, in BY5 sample, it is totally suppressed.

4.5 UV-VIS Spectroscopy:

According to Tauc, in many amorphous materials the variation of absorption coefficient with photon energy shows three regions. The first region which is also known as ‘Tauc region’ corresponds to high absorption from which optical energy gap can be calculated. This region is associated with inter band transitions i.e. it may correspond to transition of an electron belonging to an oxygen ion in an excited state [57]. As a consequence of this, a marked sharp increase in the absorption coefficient α(ν) will result. The more weakly these electrons are bound, the more easily absorption occurs. For Tauc’s region, absorption coefficient is given in quadratic form which is discussed by Mott and Davis [58] in more general form :

$$\alpha h\nu = \text{const}\left[\frac{(h\nu - E_{opt})^n}{h\nu}\right] \qquad (10)$$

where hν is the photon energy and E_{opt} is the optical band gap. Here, n is an index that have different values depending upon the mechanism of inter band transitions i.e. 2, 3, 1/2 , 1/3 values corresponding to indirect allowed, indirect forbidden, direct allowed and direct forbidden. E_{opt} values are determined from the curves representing $(\alpha h\nu)^2$ as a function of extrapolation of linear region of the plots of $(\alpha h\nu)^{1/2} = 0$ and the values of E_{opt} are listed in table 7.

Table 7: Optical band gap (E_{opt}) and Urbach energy (E_u) for all the pristine as well as heat-treated glasses.

Glass	Non- heat treated glass		Heat treated glass	
	E_{opt} (eV)	E_u	E_{opt} (eV)	E_u
BY1	5.5	0.47	2.9	0.26
BY2	5.3	0.52	2.7	0.38
BY3	5.2	0.58	2.6	0.42
BY4	4.9	0.69	2.4	0.49
BY5	3.5	0.78	2.0	0.55

It can be seen that the band gap decreases from 5.3 to 3.5 eV with increasing content of Y_2O_3. Its introduction will cause the Si-O-Si bonds breakage and appearance of non- bridging oxygens (NBO) in the network. Shift of energy gap to lower energies can be due to the formation of NBO’s. Moreover, the negative charge on NBO’s has larger magnitude than on the BO. When the ionicity of oxygen atoms is increased by converting them from bridging to non-bridging, then the top of valence band is raised resulting in reduced energy gap [59]. Sarita et.al [60] have reported that the introduction of heavy metals (Bi_2O_3) in ZnO-Bi_2O_3-B_2O_3 glass decrease the optical band gap. The change in optical band gap is attributed to the structural changes due to the different site occupancies by cations. Interestingly, XRD of heat-treated BY1, BY2 and BY3 glasses (fig.4.3) have not shown the formation of any crystalline phase. It indicates that even in these glasses some relaxation or ordering might have taken place during the process of heat-treatment. Some researchers have reported that the change of coordination of various cations in glasses after their heat-treatment leads to change in absorption spectra [61]. Fig.4.6 shows the variation of band gap with the concentration of Y_2O_3 for non-heat treated samples and heat treated samples .

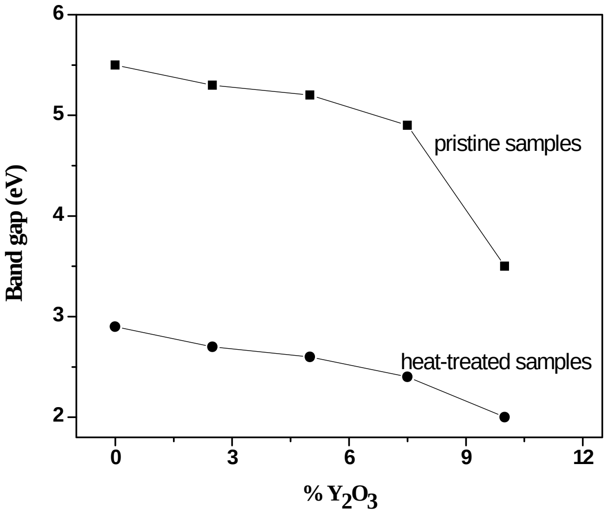


Fig.4.6 The band gap trend with increasing Y_2O_3 for heat-treated as well as non heat-treated samples.

With the increase in crystallinity of glass, the forbidden band gap decreases from 2.9 to 2 eV as the absorption can occur at lower frequencies. The band gap in case of heat treated samples is very less as compared with non heat-treated samples.

The second region known as ‘Urbach region’ is exponential region due to the structural disorientations and randomness of the system. Disordered materials produce localized states in the band gap which results from exponential absorption tail. For small absorption coefficients ($\alpha < 10^{-4}\ \mathrm{cm}^{-1}$), there is usually an Urbach tail where α (ν) depends exponentially on the photon energy hν as follows:

$$\alpha(\nu) = \alpha_o \exp(h\nu/E_u) \qquad (11)$$

where α_o is the constant and E_u is Urbach energy which is the width of the tails of localized states in the band gap representing degree of disorder in amorphous materials. E_u values are calculated from slopes of linear portion of the curve between ln(α) against hν as shown in the inset of fig.4.7.

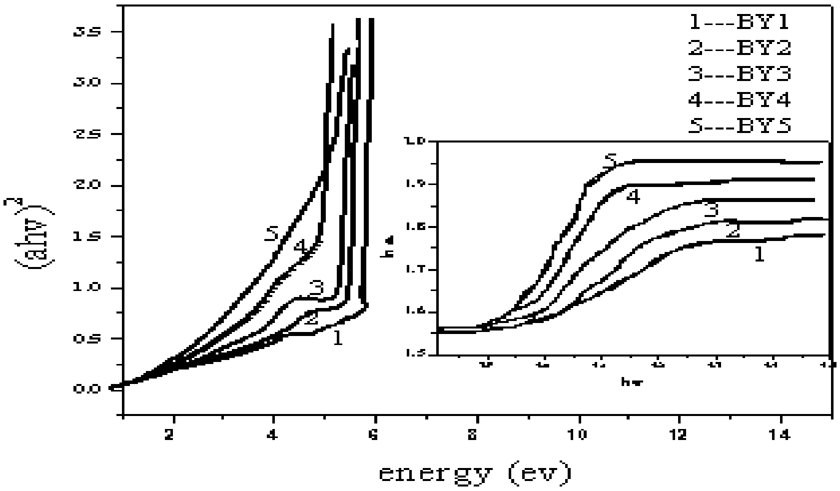


Fig.4.7 Tauc’s plot for all the samples before heat-treatment. The inset shows the variation of ln α Vs. hν for calculating the Urbach energy.

The exponential dependence of α(v) on photon energy depicts that the material obeys Urbach rule. Dow and Redfield described the cause of Urbach energy as the random internal electrical field associated with the structural disorder which broadens the exciton line [62].

Tauc and Menth [63] have reported that disordering can arise from transitions between the localized states in band edge tails where the density is assumed to fall exponentially. Many factors like dislocations, thermal vibrations and electric field of defects etc. can cause the tailing of energy states in the forbidden gap. The increase in Urbach energy with the increase of Y_2O_3 content is again suggesting an increase in amorphousity as well as open structure of the glass due to the formation of non-bridging oxygens. In case of heat- treated glasses the Urbach energy is even lower compared to non heat-treated samples indicating the increase in crystallinity which is consistent with the results obtained from E_{opt} calculations. Third region is the weak absorption tail produced from defects and impurities in UV spectra.

CHAPTER 5

CONCLUSIONS AND FUTURE SCOPE

5.1. Conclusions:

The addition of Y_2O_3 in SiO_2 –BaO – ZnO – xB_2O_3 - $(1-x)Y_2O_3$, $(0 \leq x \leq 10)$ glasses exhibit marked effect on their structural, optical and physical properties. The E_{opt} show a considerable decrease with increase of Y_2O_3 content due to increase in number of non-bridging oxygen. Consequently, the width of tails of the localized states in the band gap is observed to increase (E_u) indicating more disorder in the glass structure. These glasses are heat treated at 950 ^{0}C for 5h. Higher Y2O3 contained glasses exhibit crystalline phases. The band gap and Urbach energy is lower for heat-treated samples as compared to non heat-treated samples due to increase in crystalanity and homogeneity. In FT-IR spectra, bands are shifted to lower wave number with addition of Y_2O_3 in glasses. Optical basicity calculations clearly depicted the increase of ionicity with increasing Y_2O_3 content. The controlled heat-treatment of glasses can influence their various properties especially optical properties which can further be exploited according to the required application. Density(ρ)(g/cc) remains between the range 3.92 to 2.11, means there is not much more variation on the density after changing the composition of Y_2O_3. It is also observed that there is a competition between B_2O_3 and Y_2O_3, B_2O_3 always tries to give the ordered structure but Y_2O_3 always tries to destroy it.

5.2. Future Scope:

In the present samples, the effect of Y_2O_3 and heat treatment was observed. The heat treated samples exhibit lower optical band gap with sharp bands of FT-IR spectra. These samples must be heat treated for longer duration at higher temperature so that the effect of segregated various crystalline phase can be investigated. For better understanding and correlation between structural and other prospectus it will be essentials to do the Scanning electrons microscope (SEM)

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