EFFECT OF DIFFERENT GLASS MODIFIERS ON STRUCTURAL, OPTICAL AND MECHANICAL PROPERTIES OF BOROSILICATE GLASSES.

Thesis submitted in partial fulfillment of the requirement for
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Masters of Physics

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Dedicated to my loving parents

CERTIFICATE

This is to certify that the thesis entitled "EFFECT OF DIFFERENT GLASS MODIFIERS ON STRUCTURAL, OPTICAL AND MECHANICAL PROPERTIES OF BOROSILICATE GLASSES" submitted by Miss Kiranpreet Kaur Gill, Roll No. 300904007 in the partial fulfillment of the requirement for award of the degree of MASTERS OF PHYSICS from the School of Physics and Material Science, Thapar University, Patiala. It is to certify that the matter embodied in this report is of the candidates own record and has not been submitted in part or full to any other university or institute for the award of any degree.

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ABSTRACT

Glasses find applications in various fields like optics and optoelectronics. In the present work, the 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 various modifiers in the glass like BaO by CaO, MgO and SrO. The results are discussed in light of non-bridging oxygen (NBO), optical basicity etc. The micro-hardness and variation of refractive index with wavelength is also considered. All the work is done with pristine glasses i.e. non heat-treated glasses.

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INTRODUCTION

1.1 HISTORICAL BACKGROUND :

No one is certain where, when or how glass originated. But the term glass is derived from a latin term “Glaseum” which means lustrous and transparent materials. It may have appeared first in the Middle Eastern regions such as Egypt and Mesopotamia around 3000 to 2000 B.C. Egyptian craftsmen developed a method for producing glass vessels around 1500 B.C. Egyptian made first synthetic glass in the form of beads sand called it “faience”. About 2000 years ago, Syrian craftsmen invented glassblowing, a skill adopted by the Romans, who carried it with them as they swept through Western Europe on their conquest. The rise of Venice to prominence in the 13th century, Venice becomes the centre of glassmaking in the western world. As the industrial revolution gathered momentum, new manufacturing technologies enabled the production of scientific glass instruments, bottles, windowpanes, and many other items. Glass beads, counters, toys, and jewelry are produced almost universally throughout Eurasia before 1850, with glass becoming substitute for precious stones. The great developers of glass vessels, vases, and containers were the Italians, Romans and later the Venetians. The reasons for the different uses of glass in different parts of the world may be largely accidental; reflecting variations in climate, drinking habits, availability of pottery, political events and many other characteristics. Intention, planning individual psychology, superior intellect or better resources seems to have little to do with it yet these accidents instigated the move of western European societies around the knowledge innovation-quantification triangle. Improvements in glassmaking and the production of more sophisticated glass instruments yielded more accurate information about the natural and physical worlds, which fed back into refinements in glass manufacture and, hence, in glass quality.

In modern age, glass plays an important and essential role in social life, science and technology. The physical, optical n other properties of glass make it suitable for different applications such as utensils, optoelectronic materials, laboratory equipments, thermal insulator (glass wool), nuclear and solar energy technologies etc. In addition to other applications, it is also being used as a decorative material [2]. Now a days, it features in almost every aspect of our lives.

1.2 INTRODUCTION TO GLASS :

Glass is a non-crystalline solid material. Glasses are typically brittle, and often optically transparent. Glass is an amorphous solid, without long range order [3].

Glasses and crystals have the same building blocks (cation polyhedra) arranged in a different patterns; e.g. glasses have broader distributions of bond angles. Glass is a super cooled liquid, meaning that it is rigid and static but does not change molecularly between melting and solidification into a desired shape. Glass is one the most versatile substances on Earth, used in many applications and in a wide variety of forms, from plain clear glass to tempered and tinted varieties, and so forth.

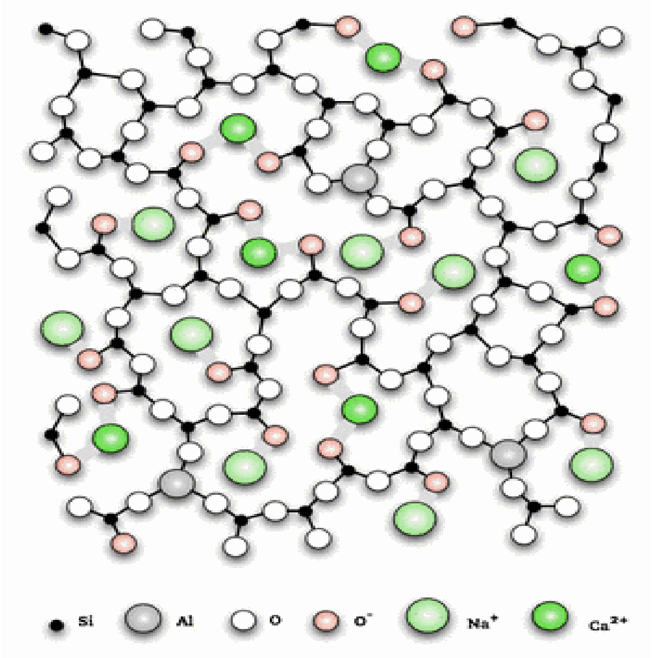


Fig.1.1- Structure of glass. [3]

The atoms in glass are arranged in the random manner of a liquid because glass is essentially a super-stiff liquid as one shown in Fig.1.1. Its atoms are jumbled together in a sloppy fashion but they can't move about to form a more orderly arrangement. Glass arrives at this peculiar amorphous state when hot liquid glass is cooled too rapidly for it to crystallize. All glasses found to share two common characteristics:

a). No glass has a long range, periodic atomic arrangement. Even more importantly, every glass exhibits time-dependent glass transformation behavior [4]. This behavior occurs over a temperature range known as the glass transformation region. A glass can thus, be defined as "an amorphous solid completely lacking in long range, periodic atomic structure and exhibiting a region of glass transformation behavior."

b). Any material; inorganic, organic, or metallic, formed by any techniques, which exhibits glass transformation behavior is a glass. [5]

1.3 ENTHALPY-TEMPERATURE DIAGRAM :

Any material, which exhibits glass transformation behavior, is a glass. Glass transformation behavior is discussed on the basis of either enthalpy or volume vs temperature diagrams, such as shown in figure 1.2; since enthalpy and volume behave in a similar fashion, the choice of the ordinate is somewhat arbitrary. In either case, we can envision a small volume of a liquid at a temperature well above the melting temperature of that substance. As we cool the liquid, the atomic structure of the melt will gradually change and will be characteristic of the exact temperature at which the melt is held. Cooling to any temperature below the melting temperature of the crystal would normally result in the conversion of the material to the crystalline state, with the formation of a long range, periodic atomic arrangement. If this occurs, the enthalpy will decrease abruptly to the value appropriate for the crystal. Continued cooling of the crystal will result in a further decrease in enthalpy due to the heat capacity of the crystal.

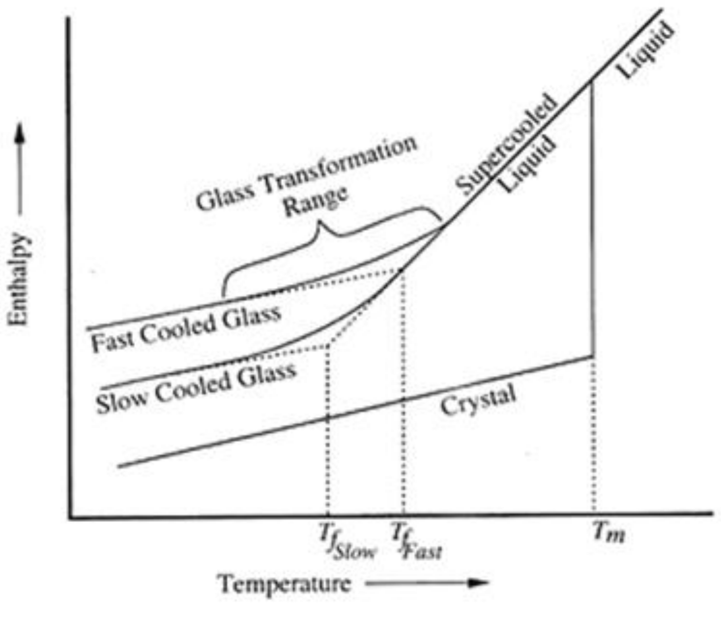


Fig. 1.2- Enthalpy- temperature diagram. [3]

If the liquid can be cooled below the melting temperature of the crystal without crystallization, a super cooled liquid is obtained. The structure of the liquid continues to rearrange as the temperature decreases, but there is no abrupt decrease in enthalpy due to discontinuous structural rearrangement. As the liquid is cooled further, the viscosity increases. This increase in viscosity eventually becomes so great that the atoms can no longer completely rearrange to the equilibrium liquid structure, during the time allowed by the experiment. The structure begins to lag behind that which would be present if sufficient time were allowed to reach equilibrium. The enthalpy begins to deviate from the equilibrium line, following a curve of gradually decreasing slope, until it eventually becomes determined by the heat capacity of the frozen liquid, i.e. , the viscosity becomes so great that the structure of liquid becomes fixed and is no longer temperature-dependent. The temperature region lying between the limits where the enthalpy is that of the equilibrium liquid and that of the frozen liquid is known as the glass transformation region. The frozen liquid is called glass or super cooled liquid.

Since the temperature where the enthalpy departs from the equilibrium, the viscosity of the liquid controls curve. i.e., by kinetic factors, use of a slower cooling rate will allow the enthalpy to follow the equilibrium curve to a lower temperature. The glass transformation region will shift to lower temperatures and the formation of a completely frozen liquid, or glass, will not occur until a lower temperature. The glass obtained will have a lower enthalpy than that obtained using a faster cooling rate. The atomic arrangement will be that characteristic of the equilibrium liquid at a lower temperature than that of the more rapidly cooled glass.

As indicated above, the glass transformation occurs over a range of temperatures and cannot be characterized by any single temperature. It is, however, convenient to be able to use just such a single temperature as an indication of the onset of the glass transformation region during heating of a glass. This temperature, which is termed either the glass transformation temperature, or the glass transition temperature, (T_g), is rather vaguely defined by changes in either thermal analysis curves or thermal expansion curves. The values obtained from these two methods, while similar, are not identical. The values obtained from T is also a function of the heating rate used to produce these curves. Since Tg is a function of both the experimental method used for the measurement and the heating rate used in that measurement, it cannot be considered to be a true property of the glass. However, Tg is a useful indicator of the approximate temperature where the super cooled liquid converts to a solid on cooling, or, conversely, of which the solid begins to behave as a visco-elastic solid on heating.

1.4 CONSTITUENTS OF GLASSES:

In general, glasses are either produced from high quality, chemically pure components, or from a mixture of far less pure minerals. Regardless of the source of the components used to produce a specific glass, the batch materials can be divided into five categories on the basis of their role in the process are:

1.4.1 Glass former: The same compound may be classed into different categories when used for different purposes. Alumina, for example, serves as a glass former in aluminate glasses, but is considered a property modifier in most silicate glasses [3]. The most essential component of any glass batch is always the glass former. Every glass contains one or more components which serve as the primary source of the structure. While these components are commonly designated as glass formers, they are also called network formers, or glass forming oxides in many oxide glasses. The identity of these components usually serves as the basis for the generic name used for the glass. If most of the glass former present in a specific sample is silica, for example, that glass is called a silicate. If a significant amount if boric oxide is also present, in addition to silica, the sample is termed borosilicate glass. The primary glass formers in commercial oxide glasses are silica (SiO_2), boric oxide (B_2O_3) and phosphoric oxide (P_2O_5), which all readily form single component glasses. A large number of other compounds may act as glass formers under certain circumstances, including GeO, Bi_2O_3, As_2O_3, Sb_2O_3, TeO_2, Al_2O_3, Ga_2O_3 and V_2O_5 etc. The glass former bond strength lies in the range 60-80 kcal/mol.

1.4.2 Glass modifier: Adding certain other materials can do the alteration in the properties of glass forming material which are known as property modifier such as alkaline earth and transitional metal oxide, and most importantly alkali oxides. Alkali metal oxides are termed network modifiers, because these ions take up random positions in the glass network and thus modify or change the structure of glass network. The network modifier bond strength usually lies in the range 10-40 kcal/mol. Similarly, alkaline earth elements locate into cavities of the glass network. However, bonds between alkaline earth ions and oxygen are stronger than alkali metals so neither a rapid decrease in viscosity nor a significant increase of the thermal expansion coefficient of the glasses is observed in alkaline earth based glasses.

1.4.3 Glass Intermediates : Some oxides can either work as a network former or network modifier which depends on their chemical nature. Aluminium, titanium and zirconium oxides are classified as intermediate oxides in glass when they form other than tetrahedron due to their higher coordination state in glass. They modify the glass network. The bond strength of these oxides usually lies in the range between 50 to 60 k cal/ mol.

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	

1.4.4. **Colorant**: Colorants are used to control the color of the final glass. In most cases, colorants are oxides of either the 3d transition metals or the 4f rare earth elements. Uranium oxides were once used as colorants, but their radioactivity, obviously, reduces their desirability for most applications. Gold and silver are also used to produce colors by formation of colloids in glasses. Colorants are only used if control of the color of the glass is desired, and are usually present in small quantities. Iron oxides, which are common impurities in the sands used to produce commercial silicate glasses, act as unintentional colorants in many products. When colorants are used to counteract the effect of other colorants to produce a slightly gray glass, they are referred to as decolorants.

1.4.5 Fining agent: Finally, fining agents are added to glass forming batches to promote the removal of bubbles from the melt. Fining agents include the arsenic and antimony oxides, potassium and sodium nitrates, NaCl, fluorides such as CaF_2, NaF, and Na_3AlF_6 and a number of sulfates. These materials are usually present in very small quantities (<1 wt %), and are usually treated as if they have only minor effects on the properties of commercial glasses, which would be prohibitively expensive to produce without the aid of fining agents in reducing the content of unwanted bubbles in the final product.

1.5 CLASSIFICATION OF GLASSES

Depending upon chemical composition, a large number of glasses with different chemical and physical properties can be prepared. Chemical composition is chosen depending upon the required application of prepared glass. Oxide glasses have considerable potential advantages over the non-oxide materials because non-oxides readily react with water and atmospheric oxygen to form oxides. On the basis of chemical compositions, glasses can be divided into following categories:-

1.5.1 Silicate glasses : Most of the commercially made glasses are based on silica (SiO_2). Besides silica, glasses also contain other oxides like CaO, Na_2O, K_2O and Al_2O_3, which influence their properties. Among various types of silicates, 'glasses vitreous silica' is the most refractory glass in commercial use. It has high chemical resistance to corrosion, a very low electrical conductivity, a near zero coefficient of thermal expansion and good ultra violet (UV) transparency. On the other side, it has high cost of manufacture and uses are limited to astronomical mirrors, optical fibers and crucibles for melting. Soda-lime glasses are the most common form of commercial silicate glass and least expensive. These usually contain 60-70 mainly used for windows because they transmit a high percentage of visible light. They are also used as glass containers as they are virtually inert hence can't contaminate the inside % silica (SiO_2), 12-18 % soda (Na_2O) and 5-10 % lime (CaO). Soda-lime glasses are components. The main disadvantage of these glasses is that they have high value of thermal expansion. Soda-lime silicate glasses have received lots of attention for medical application as bioactive glasses.

Small amount of alkali added to silica and boron make a family of borosilicate glasses having low thermal expansion and high resistance to chemical attack. They are mainly used in pipelines, light bulbs, sealed-beam headlights, laboratory and cooking. The silicate glasses containing PbO and SiO_2 as the principal components with small amount of soda are termed as lead silicate glasses. These glasses are utilized in microelectronics for their high degree of brilliance, large working range and high electrical resistivity. Aluminosilicate glasses contain an average of 20 % Al_2O_3 in addition to other oxides like magnesium oxide, boric oxide, calcium oxide and soda. Their softening point is higher (915° C) than other oxide glasses; so they are used in high temperature applications. Compared to borosilicate, aluminosilicates are more difficult to fabricate due to high melting point of constituents. They are also used in applications, where chemical resistance is important. These glasses are very expensive. A major commercial use of this system is high efficiency lamps inside an automobile halogen headlamp where the glass can be sealed directly to molybdenum electrical leads.

1.5.2 Metallic glasses : Metallic glasses are non-crystalline materials composed of either pure metals or combination of metal and metalloids. These glasses have electrical, optical and magnetic properties like metals. Glasses are made in the form of thin tapes or fibers using very high speed quenching techniques and are used inside thermonuclear reactors because of their amorphous nature makes them less susceptible to radiation damage.

1.5.3 Phosphate glasses: Phosphate glass has been researched for over one hundred and fifty years [6], however, despite P_2O_5 being one of the four classic Zachariasen glass forming oxides (along with SiO_2, B_2O_3 and GeO_2), the nature of the glass, its applications, research and development have been limited due to its hygroscopic nature. It was not until the addition of at least 30 mol. % of metal oxides was found to improve the durability of the glass significantly and its possible applications were actively pursued after that. These glasses have a very large transmission in the ultraviolet region, low thermo-optical coefficient and large emission compared to silicate glasses [7]. So, these are suitable materials for high power laser. Phosphate glasses are also attractive as glass-metal seals due to their low melting temperature, low viscosity and their high thermal expansion coefficients. The lack of durability of some phosphate glasses was utilized to find elemental deficiencies in cattle and sheep [8].

1.5.4 Borate glasses: In borate systems, melts of composition that are rich in B_2O_3 show a high viscosity and a marked tendency to glass formation. It allows the preparation of glasses that may possess interesting physical properties for optical applications. Addition of heavy metal oxides (HMO) increase density of glass system and find applications in scintillator materials for high energy particle and medical imaging, poled second order nonlinear optoelectronics such as laser host fibers for communication and photonic switches, third order harmonic light generation and glazes. In recent time, researchers [9] have demonstrated that silica free alkali-calcium borate glasses also exhibit bioactive behavior, and it can be used as a possible alternative for some of biomedical applications.

1.6 PROPERTIES OF GLASSES:

The special properties of glasses are related to their 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 or structural elements lying in specific orientations [10]. Some of the special properties of glasses are as follows:

1.6.1 Optical properties:

The major technological developments that have added to the comfort of living are glass lenses as an aid to failing vision, glass windows to bring daylight into housing structure while providing protection from the harsh elements of nature, glass in the light bulb to provide light in dark and glass fibers for enhanced communication. The glass fiber communication is based upon the refractive index, optical dispersion and transmission properties in infrared region of spectrum. Silicate glasses have relatively small index of refraction due to absence of non-bridging oxygen atoms. In case of alkali silicate glasses, non-bridging oxygen ions with higher polarizability are present, which results an increase in the index of refraction with rising alkali content. An increase in the refractive index has also been observed with increase in the compositions of oxides like CaO, MgO, ZnO, PbO and B_2O_3 . Besides composition, the refractive index of a glass also depends upon the rate of cooling. A glass cooled at higher rate will have high index of refraction than a well-annealed glass at room temperature.

1.6.2 Physical properties:

Density of a glass is a strong function of its composition and most important measure of a glass. It also stands on its own as an intrinsic property capable 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 [11]. The addition of alkalis to SiO_2 results in an increase in density.

1.6.3 Electrical properties:

Electrical properties of glasses are most important to be studied for their applications in electrical and electronic industries. A substance is said to be electrically conducting when free electrons or ions within make the flow of current possible. This property is characterized by the parameter called electrical conductivity, which is reciprocal of resistivity. The electrical conductivity of a glass changes due to the presence of network modifiers. Glass, which does not contain any modifier posses a very less conductivity as compared to the crystalline counterpart. Vitreous silica and pure B_2O_3 glasses fall under this category. The strength of the bond of the ions in the network and their size influences the electrical properties. On the basis of electrical properties [3], glasses can be categorized as follows:

1. Glasses with very small conductivity (high resistivity).
2. Glasses with very high ionic conductivity and low electronic conductivity.
3. Glasses with electronic conductivity only.

Glasses with very high resistivity are generally used as an insulator. The glasses of this type are free from network modifiers. Glasses having high ionic conductivity can be prepared by the use of network modifiers, which generally have a small ion radius. The composition of the glass also plays an important role for such type of glasses. When the oxygen ions are replaced by sulphide ions, then the prepared glass contains open structure and hence an improvement in the ionic conductivity are obtained by the proper choice of the elements and are called semi-conducting glasses. They contain large amount of transition elements that can occur in several valences like Fe, Co, Mn, V etc. For example V can occur as (V^{5+}) ion as well as (V^{4+}) ion. The electronic conductivity is obtained by the transition of an electron from (V^{4+}) ion to an adjacent (V^{5+}) ion. Besides these glasses, Chalcogenide glasses also show semi-conducting properties than mainly contain elements like S, Se and Te.

1.6.4 Mechanical properties:

Glasses are brittle as a result fracture behavior is usually determined by environment factors and not by the inherent strength of the bonds forming the vitreous network. The fracture strength of glasses varies with prior surface treatment, chemical environment and inherent stress etc. The glasses are also quit susceptible to failure due to thermal shock. Other mechanical properties of glasses are inherent to the material. The elastic modulus is determined by the individual bounds in the material and by the structure of the network. The hardness of glasses is a function of the bonds strength and density of packing of the atoms in the localized structure [12].

1.6.5 Thermal properties*:*

The expansion and the contraction due to thermal energy is an important consideration for product design. When a glass is heated it expands. If the temperature over the body of glass is equal everywhere and body is not restrained then there will be no development of stress in the body. On the other hand if there is non -uniform heating of the body, then the different layers of glass will attempt to expand differently and consequently stress developed. The magnitude of stress so generated is related to thermal expansion. Thermal expansion of glasses with few exceptions increases with increase in temperature range over 227-727° C [3]. The negative thermal expansion coefficients are believed to result from the ability of the network to absorb lattice expansion through bending of bonds into empty interstices of the structure. The addition of alkali to silica network breaks up the oxygen bridges, resulting in monotonically increasing thermal expansion coefficient. Addition of modifier ions to glass network prevents bond bending and hence thermal expansion coefficient. The large thermal expansion coefficient of vitreous boric oxide is due to two dimensional nature of the structure of glass and weak bonding in their dimensions. Addition of alkali oxides to borate network shows borate anomaly.

1.6.6 Chemical properties:

Glass is much more resistant to corrosion than other materials, so much so that it is easy to think of it as corrosion-proof. Glass windows after several years of exposure to sunlight and atmosphere remain clear and apparently unaffected. Glass bottles hold wide range of liquids that would dissolve other materials. In the laboratory, reactions are carried out in the glass beakers and flasks without damage to the beaker or contamination of the solution reacting. But, in spite of these indications that glass is indestructible by chemical attack, under certain conditions it will corrode, even dissolves. In these cases, it is important to choose the right type of glass, since some are more corrosion resistant than others. Only a few chemical aggressively attack glass, i.e. hydrofluoric acid, concentrated phosphoric acid (when hot, or when contains fluorides), hot concentrated alkali solutions and superheated water. Hydrofluoric acid is the most powerful of this group: it attacks any type of silicate glass. Other acids only slightly: the degree of attack can be measured in laboratory tests but such corrosion is rarely significant for acids other than hydrofluoric and phosphoric. Acids and alkali solution attack glass in different way. Alkali attacks the silica directly while acids attack the alkali in the glass. Corrosion by water is similar to acid corrosion in that alkali is removed from the glass surface. Water corrosion acts at a much slower rate. At high temperatures, however, water corrosion can be become significant. Many factors influence the rate of corrosion and no laboratory test is capable of predicting behavior under all conditions.

Corrosion plays an important role in characterizing the glasses as it helps in determining the bioactive properties of the glasses. The properties in glass can be varied and regulated over an extensive range by modifying the composition, production techniques or both. In any glass the mechanical, chemical, optical, and thermal properties cannot occur separately. Instead, any glass represents a combination of properties. It is the art of the glass scientist to produce the most favorable combination of properties.

1.6.7 Viscosity:

The kinetic model of glass formation indicates that the temperature dependence of the viscosity plays a major role in determining the ease of glass formation for any melt. Glasses are most easily formed if either (a) the viscosity is very high at the melting temperature of the crystalline phase which would form melt or (b) the viscosity increases very rapidly with deceasing temperature. In either case, crystallization is impeded by the kinetic barrier to atomic arrangement which results from a high viscosity. Viscosity is also very important in determining the melting condition to form a bubble-free, homogenous melt, the temperature of annealing to remove internal stress and the temperature range used to form commercial products. The range of viscosity is very wide and it is not possible to make measurements over the whole range by any one method. At transition temperature (Tg) the viscosity of the glass melt is high as 10^{23} Poise. Viscosity of a glass is affected due to the presence of a modifier. The polarizability or ionic field strength of a modifier affects the viscosity of a glass at high temperature. Low field strength modifies decrease the viscosity. At low temperature, the coordination number of a modifier also affects the viscosity.

1.7. ZACHARIASEN’S RANDOM NETWORK THEORY OF GLASS FORMATION:

Before Zachariasen, glass structures were considered to be comprised of nanocrystals- ~20Å size- estimated from broadening of diffraction patterns: $b = 0.9\lambda/(t \cos \theta)$, where λ is the x-ray wavelength, t is the particle size, θ is the Bragg angle. Bragg's Law describes the conditions for constructive interference, and so the angle of incident x-rays that will produce intense diffraction peaks. Other diffraction angles will lead to the destructive interference. The angle is related to the wavelength of the incident x-rays (λ) and the lattice spacings.

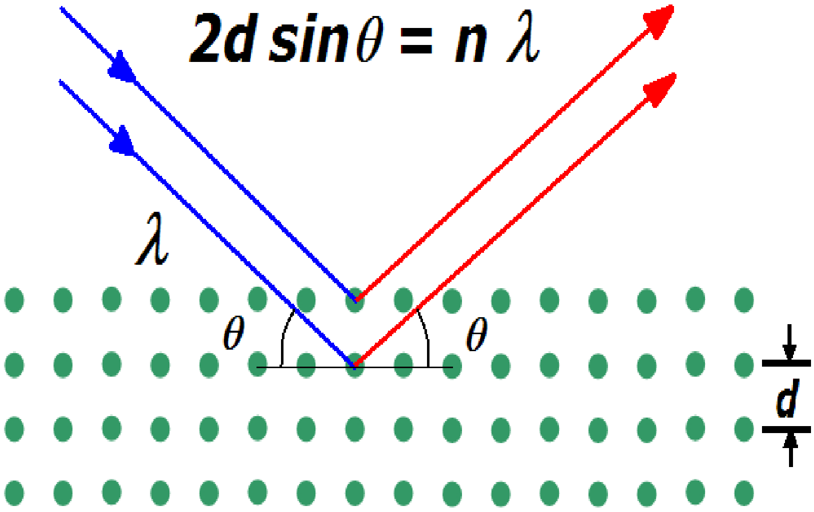


Fig.1.3- Bragg’s law depiction.

Zachariasen (crystallographer) [13] noted similar mechanical properties (elastic modulus, etc.) between glasses and crystals and so expected similar structural energies →similar underlying atomistic building blocks (cation polyhedra). Certain polyhedra are more likely to form the disordered networks particular to a glass: Glasses have greater structural energies/amorphous structures. Glasses lack the periodic (long range) order of a crystal. Infinite unit cell (no repeating large scale structures). 3D network lacking symmetry and periodicity and same average packing and properties in all directions.

Zachariasen's Rules for Glass Formation: Zachariasen gave the following rules of glass formation:-

1. No oxygen atom may be linked to more than two cations.

2. The cation coordination number is small: 3 or 4.

3. Oxygen polyhedra share corners, not edges or faces.

4. For 3D networks, at least three corners must be shared. In general, all four rules should be satisfied for glass formation to occur.

CHAPTER 2

LITERATURE REVIEW

Amorphous, polycrystalline, and single crystal are three general types of solids. In amorphous materials, to provide the glass network, we can use one or more glass former such as P_2O_5, B_2O_3 or Si_2O. Also, some of transition metal oxides can be as a glass former, such as V_2O_5 and MoO_3 [14, 15]. Phosphate glasses have some physical properties better than other glasses (e.g., silicate and borate) such as high thermal expansion coefficients, low melting and softening temperatures, high electrical conductivity, UV transmission, and optical characteristics [16]. The main advantage of a phosphate glasses comparing to other oxide glasses are their ability to accommodate high concentrations of transition metal ions and remain amorphous [17]. 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 [17]. 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 valency states (such as Cu^+ and Cu^{2+} in copper oxide glasses) has been used to explain electronic conduction [18]. Phosphate glasses have a range of compositional and structural possibilities (ultra, meta, pyro, and ortho) [17].

Glasses have many technological applications due to their electrical and optical properties. Vanadium doped glasses are known to demonstrate semiconductor properties. Borate glasses are the focus of interest due to their structures and properties that are quite different from silica glasses. Many researchers like Gokhan et al, have studied B_2O_3 intensively in recent years [19]. Borate glasses are used as electro-optic switches, electro-optic modulators, solid-state laser materials and non-linear optical parametric converters [20-22]. In addition, they are often used as dielectric and insulating materials and it is known that borate glass constitutes a good shield against IR radiation [23]. Studies on glasses containing relatively low concentration of V_2O_5 in presence of B_2O_3 are very few [24]. Semiconducting transition metal oxide (such as V_2O_5) based glasses have gained much interest in solid-state chemistry and materials science with regard to their possible applications as memory and switching devices [25-29]. Vanadium-containing oxide glasses are known to be semiconductors and the transport mechanism involves the exchange of electrons between vanadium (IV) and vanadium (V) centers [30].

Borates and silicate glasses containing boron oxide have been widely used for optical lenses with high refractive index and low dispersion characteristics [31]. Alkali borate glasses are of great technological interest especially lithium borates as solid electrolytes because of their fast ionic conduction. El-Alaily N.A. et al studied the optical properties including infrared and refractive index and density of lithium borate glass as a base glass. The effect of the presence of either aluminum or lead oxide, or the presence of one of the following transition metal, Fe_2O_3, TiO_2 or V_2O_5 was investigated. The effect of exposing the glass to either gamma, or fast neutron irradiation on the last properties was also studied. The results showed that three main bands appeared due to bending vibration or stretching of either, tetrahedral or triagonal borate units. The addition of alkalies causes only a shift of the bands either to higher or lower wavelength. Glass containing lead oxide had the highest refractive index and density, also the presence of any of the transition metal oxide lowering the average coordination number of oxygen which causes a compaction of the structure [32] hence an increase in the values of density and refractive index. Since irradiation of glass causes compaction of B_2O_3 by breaking the bonds between triagonal elements, the average ring size becomes smaller which leads to an increase in density and refractive index [33] too.

Nanoparticle silica-gel derived glasses is an attractive amorphous material, that is applied, as a wave-guide [34], chemical gas sensor [35] and so on. Mollei and Jinga suggested that it can be prepared by sol-gel method, which is being actively studied in leading laboratories all over the world [36]. The advantage of this process is to avoid generation of dangerous dust, as would be produced in conventional ceramics processing. The primary attention was paid to its low temperature nature [37-44]. 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 [42] successfully obtained neodymium doped silica glass containing up to 20 wt % Nd_2O_3 using the sol-gel process. They suggested oxygen coordination number to be 6 around neodymium. Although the sol-gel process allows the preparation of glasses with much higher concentrations of neodymium however, the problem of microscopic clustering remains even if some 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 dopants 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 dopants, 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 [45]. 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 [46]. 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.

El- Adawy and Moustafa 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 dopant particles within the composite determine these peculiar optical properties [47]. 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 [48]. Phosphorous pent oxide (P2O5) acts as one of the most important glass former and flux materials.

The study of oxide glasses has received considerable attention due to their structural peculiarities [49, 50]. These glasses have wide applications in the fields of electronics, nuclear and solar energy technologies and acoustic-optic devices [51-55].

ZnO–PbO– B_2O_3 glasses have been characterized for a strong tendency for phase separation and are used in glass solders for sealing CTV bulbs, IC packages, glass discharge tubes etc [56, 57]. PbO and ZnO can enter a glass network both as a network former and as a network modifier [58]. PbO modifies the network through forming BO_4 tetrahedra at the rate of two BO_4 groups per PbO molecule [59] and, at higher concentrations, PbO can partly play the role of a glass-forming oxide in the form of PbO_4 pyramids with Pb^{2+} at the apex of the pyramid [60].

Silica based glasses are used as nuclear shielding materials. The effect of radiation on these glasses varies [61] as per the constituents used in these glasses. Glasses of different composition of SiO_2 –Na_2OMgO-Al_2O_3 were made by melt casting techniques by A.K. Sandhu et al. These glasses were irradiated with neutrons of different affluences. Optical absorption measurements of neutron-irradiated silica based glasses were performed at room temperature (RT) to detect and characterize the induced radiation damage in these materials. The absorption band found for neutron-irradiated glasses are induced by hole type color centers related to non-bridging oxygen ions (NBO) located in different surroundings of glass matrix. Decrease in the transmittance indicates the formation of color-center defects. Values for band gap energy and the width of the energy tail above the mobility gap have been measured before and after irradiation. The band gap energy has been found to decrease with increasing affluence while the Urbach energy shows an increase [62].

Phosphorus pentoxide (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 [63, 64]. 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 for optical elements [65]. On phosphate-based glasses, several workers like Sidek et al has worked out, especially concerning an optimization of glass preparation, investigation of their properties and information about the glass structure. Phosphates glasses with various compositions are of exceptional importance due to their interesting linear and nonlinear optical properties [66-68].

Tellurite glasses have been intensive studied because of their technological and scientific importance. Such amorphous materials are candidates for new optical materials because of their superior properties, such as high refractive index, high dielectric constants, a wide band infrared transmittance and large third order non-linear optical susceptibility [69,70]. Moreover they possess relatively low transformation temperatures, high densities and non- hygroscopic properties, which limit the application of phosphate and borate glasses [71,72]. Therefore these glasses are suitable as host for active element doping, represent the main justification for their continuous technological interest in areas of optoelectronics such as laser technology, optical fibers, non-linear optical devices and sensor systems [69-73]. The increase of refractive index of the TeO_2-ZnO glasses with the addition of ZnO was best explained by Sidek et al [74] in terms of either electron density or polarizability of the ions. The absorption edge shift to higher energy (shorter wavelength) with increasing ZnO content was observed in this glass. The optical band gap (Eopt) of zinc tellurite glass decreases with increasing of ZnO content probably due to the increment of Non-Bridging Oxygen (NBO) ion contents which eventually shifted the band edge to lower energies. The physical and optical properties of zinc tellurite glasses were found generally affected by the changes in the glass composition. FTIR spectra of zinc tellurite glass revealed broad, weak and strong absorption bands in the investigated range of wave numbers from 4000-400 cm^{-1} which associated with their corresponding bond modes of vibration and the glass structure. The addition of ZnO into TeO2 glass network shifted the major band.

Gamma and neutron irradiation affect the structure of the glass matrix, resulting in changes in the optical, physical and electrical properties [75-79]. Defect centers induced by ionizing radiation in glasses are described by microscopic models constructed on the basis of local information obtained from studies using several spectroscopic techniques, such as optical absorption, infrared or Raman spectroscopy [80]. A.K. Sandhu et al studied the effect of thermal neutron irradiation on the optical and structural properties of the quaternary silicate glasses of varying compositions. Experimental results reveal [81] the formation of color centers in the visible region of the optical spectra. The optical energy gap and the width of the energy tail above the mobility gap have been measured before and after irradiation. The optical energy gap has been found to decrease with increase in neutron affluence. The decrease in the energy gap with the decrease in silica content of the glass was also observed. The change in glass network structure as revealed by the formation of non-bridging silicon–oxygen (Si–O–NBO) groups has been observed and explained in terms of radiation induced structural defects and composition of the glass.

Data on the individual IR band parameters of glasses are of special interest because they allow for (i) estimating changes in band parameters when passing from crystal to glass and, if possible, relating these to underlying changes in structure, (ii) refining and/or correcting the structural interpretation of the spectra based on the consideration of band frequency versus composition or band intensity versus composition plots, and (iii) calculating glass properties in frequency ranges other than those investigated spectroscopically, including the 'static' dielectric constant. These data can be best obtained with the dispersion analysis method using a specific analytical model for the complex dielectric constant of glasses [82]. Moreover, results obtained with this analytical model for the complex dielectric constant indicate a way for developing a new approach to the semi-empirical calculation of the IR spectrum of glass that involves the construction of the phonon intensity distribution over the frequency range under study for various possible models of glass structure with the periodic boundary conditions.

Infrared (IR) spectroscopy is one of the most common spectroscopic techniques used by organic and inorganic chemists [83]. Simply, it is the absorption measurement of different IR frequencies by a sample positioned in the path of an IR beam. The main goal of IR spectroscopic analysis is to determine the chemical functional groups in the sample. Different functional groups absorb characteristic frequencies of IR radiation. Using various sampling accessories, IR spectrometers can accept a wide range of sample types such as gases, liquids, and solids. Thus, IR spectroscopy is an important and popular tool for structural elucidation and compound identification.

CHAPTER 3

EXPERIMENTAL TECHNIQUES

3.1 GLASS SAMPLE PREPERATION:

For each system, required amount of raw materials as per the stoichiometry ratio were taken as given in table 2. The mixture was ground to break agglomerate particles. After grinding the mixture was further transferred to ball mill and ground for two hours in wet medium (acetone). The ball milling was done using porcelain balls in porcelain jar (Retsch, Germany, Model S 1000). The powder to ball ratio for each system was 1:2 which was kept constant for each milling. The resulting mixture was dried in air. The ground powder was transferred in recrystallized alumina crucible and melted in an atomized Molybdenum Disilicide ($MoSi_2$) high temperature furnace in oxidizing atmosphere. The powders of the samples were initially heated at 1000° C for 2 hours to facilitate the calcination. During calcination process moisture is released. After that the temperature was increased to 1200° C and kept at this temperature for 0.5 hours to facilitate the fusion and melting process. Then, system was reheated at 1550° C and kept at this temperature for 1.5 h to achieve homogeneous molten materials. 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 the temperature fluctuation in hot zone was 2° C.

Table 2: Compositions of Glass samples

ML	30 MgO	40 SiO_2	20 B_2O_3	10 La_2O_3
CL	30 CaO	40 SiO_2	20 B_2O_3	10 La_2O_3
SL	30 SrO	40 SiO_2	20 B_2O_3	10 La_2O_3
BL	30 BaO	40 SiO_2	20 B_2O_3	10 La_2O_3

3.2 DETAILS OF CHARACTERIZATION TECHNIQUES :

The glass samples are characterized using various techniques to check their optical, structural and mechanical properties. The samples are then characterized to know the initial structure and transformation during various heat-treatments. The X-ray diffraction techniques were used for structural characterization of glass and glass ceramics. The obtained glass samples were characterized through X-ray diffraction (XRD), Fourier transform infrared spectrometer (FTIR), UV spectroscopy etc.

3.2.1 : X-Ray diffraction (XRD) :

Fig 3.1 X-ray diffractometer.

X-ray diffraction (XRD) is a versatile, non-destructive technique that reveals detailed qualitative and quantitative information about the crystalline phases, chemical composition and crystallographic structure of natural and synthetic materials. X-ray powder diffraction pattern were recorded at room temperature by PAN analytical diffractogram with CuK_α radiation ($\lambda = 1.5418$ A°) obtained from a copper target using an inbuilt Ni filter. The XRD pattern was taken generally in the range of $10° \leq 2\theta \leq 80°$ for most of the samples. Samples are analyzed as powders with grains in random orientations to insure that all crystallographic directions are exposed by the beam. Monochromatic X-rays are used to determine the interplanar spacing of the unknown samples using Bragg's law.

$$2d\text{Sin}\theta = n\,\lambda \qquad (1)$$

Where d = interplanar spacing, λ= wavelength of incident X-ray, θ=diffraction angle, n=integer.

When X-rays are scattered from a crystal lattice, 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.

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. The data obtained from XRD is indexed by standard powder diffraction files provided by International Centre for Diffraction Data (ICDD).

3.2.2 Fourier transform infrared spectrometer (FT-IR):

Fig.3.3 – FTIR spectrometer

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 preparation for FT-IR, glass sample is grinded by motor-pastel to obtained sample in powder form. Now, about 4.0 mg of each sample were used for recording the absorption spectra. The FTIR analysis after heat treatment of the sample is also completed by similar process as in without heat treated sample.

FTIR 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 the infrared spectroscopy useful for several types of analysis. FTIR is used to analysis the bonding of the samples [84].

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 [85].

3.2.3 UV- Visible Spectroscopy :

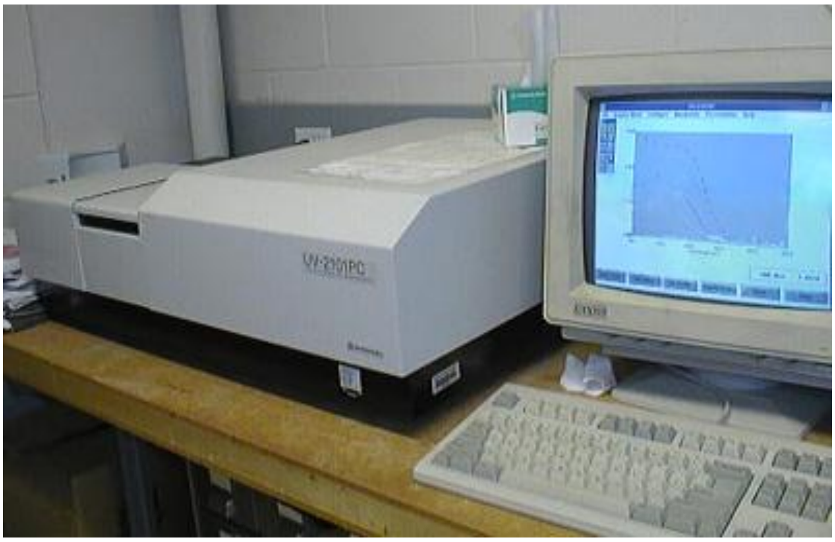


Fig.3.2- UV spectrometer.

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. 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 oxides on the energy band gap of pristine samples. Absorption is the powerful tool for measuring the band gap of the glass samples. Let the photon beam intensity I_0 is incident on the sample of the thickness t and intensity of light transmitted is I_t , then

$$I_t = I_0 e^{-\alpha t} \qquad (2)$$

Here α = absorption coefficient.

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

$$\alpha h\nu = A (h\nu - E_g)^n \qquad (3)$$

3.2.4 Vicker's Hardness

Micro hardness testing of metals, ceramics and composites is useful for a variety of applications for which 'macro' hardness measurements are unsuitable: testing very thin materials like foils, measuring individual microstructures within a larger matrix, or measuring the hardness gradients of a part along the cross section. Micro hardness testing per ASTM E-384 gives an allowable range of loads for testing with a diamond indenter; the resulting indentation is measured and converted to a hardness value. The actual indenters used are Vickers (more common; a square base diamond pyramid with an apical angle of 136°) or Knoop (a narrow rhombus shaped indenter).

Figure 4.5 : Micro hardness testing machine.

The result for either Vickers or Knoop micro hardness is reported in kg/cm^2 and is proportional to the load divided by the square of the diagonal of the indentation measured from the test. Vickers micro hardness tester (Mitutoyo, Japan) is used for measuring micro hardness of the composites.

$$HV = F/A \approx 1.8544F/d^2 \qquad (4)$$

where F is kgf and d is millimetres

CHAPTER 4

RESULTS AND DISCUSSION

4.1 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 [86]. 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 [87] :

$$x_o - x_m = \sqrt{[(Q+1.13)/2b]} \qquad (5)$$

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 as in Table 3:

Table 3: The electronegativity of metals and oxygen ions with γ_m (basicity moderating parameter).

Oxides	x_m	x_o	γ_m
MgO	1.2	3.12	1.28
CaO	1	2.96	1
SrO	0.95	2.86	0.91
BaO	0.9	2.75	0.87
B_2O_3	2	3.66	2.36
SiO_2	1.8	3.51	2.08
La_2O_3	1.1	2.71	1.13

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

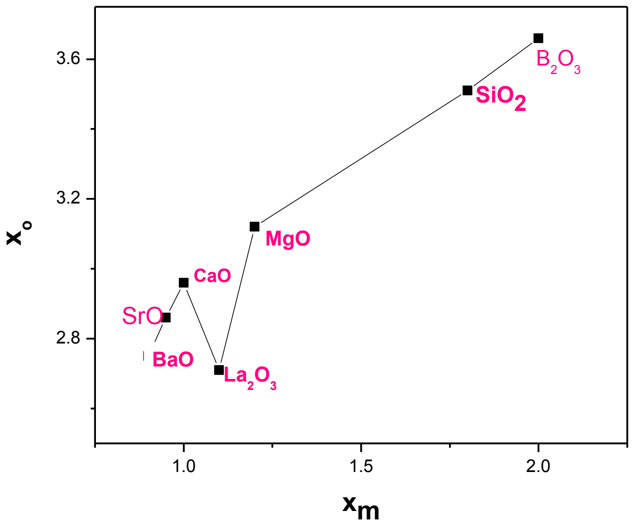


Fig.4.1 Variation of metal-ion electronegativity and oxygen electronegativity of constituents of glasses.

The optical basicity can be calculated from chemical composition using following relation [88]:

$$\Lambda_m = \Sigma\ O_i/O\gamma_m \qquad (6)$$

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 optical basicity of the glass samples are summarized in table 4:

Table 4: The optical basicity of glass samples

Glass samples	Optical basicity (Λ_m)
BL	0.6245
SL	0.6169
CL	0.6021
ML	0.5690

BL samples has higher values of optical basicity due to higher number of NBO's in this glass. The reason being having the smallest field strength. The field strength (charge/radius ratio) associated with divalent alkaline-earth metal ions Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} varies as 0.45 , 0.33, 0.30 and 0.24, respectively. It strengthens the network via bonding to neighbouring oxygen. The Ba^{2+} having the highest cationic radius (corresponding to smallest field strength), experiences less attraction from the non-bridging oxygen. Although Ba^{2+} forms more co-ordinate links, it does not sufficiently reinforce the structure due to its linkage with the non-bridging oxygen. Therefore, BaO has the largest NBO's and hence BL samples having BaO as modifier has higher values of optical basicity.

The increasing thermodynamic stability is associated with increasing charge on oxygen atoms. 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 non-bridging as well as the co-ordination 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:

$$\sigma = 1 - [\ (z_a r_a/2)\ (\ 1-1/\gamma_a) + (z_b r_b/2)\ (1-1/\gamma_b) + \ldots.] \qquad (7)$$

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:

$$\sigma = 1- (3r_a/2)\ (1-1/2.36) =1- 0.864\ r_a \qquad (8)$$

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

$$\sigma = 1-(2r_a)\ (1-1/2.08) = 1-1.038\ r_a. \qquad (9)$$

Table 5: Microscopic optical basicities for bridging as well as non-bridging oxides of silicon and boron.

Coordination →	Non-bridging (σ)		Bridging (σ)		
	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 5 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.

4.2 X-Ray Diffraction (XRD) :

X- ray diffraction studies of the glass (fig.4.2) reveal no diffraction peaks or lines, indicating no crystalline phases. This clearly emphasizes the fact that the studied glasses (ML / CL / BL / SL) are completely amorphous. A broad diffuse scattering at low angles observed for the as-prepared samples is the indication of long range structural disorder. All the glasses exhibit broad halo around 30°.

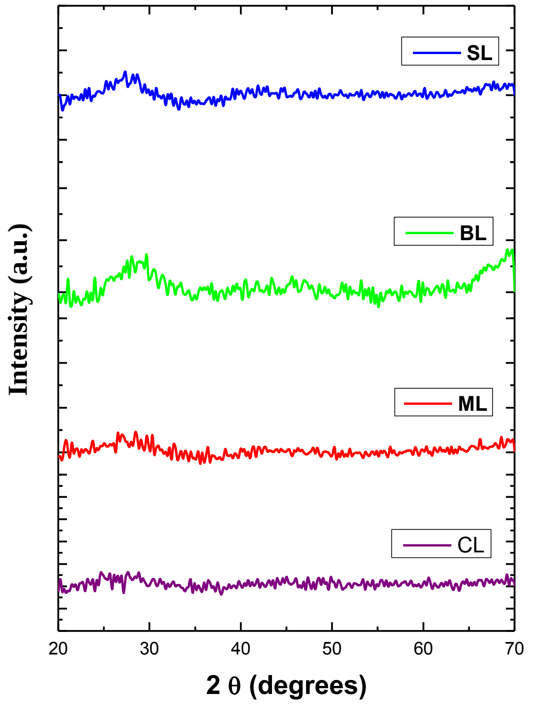


Fig. 4.2 The XRD diffractogram of CL, ML, BL and SL glasses.

4.3 Fourier Transform Infrared analysis :

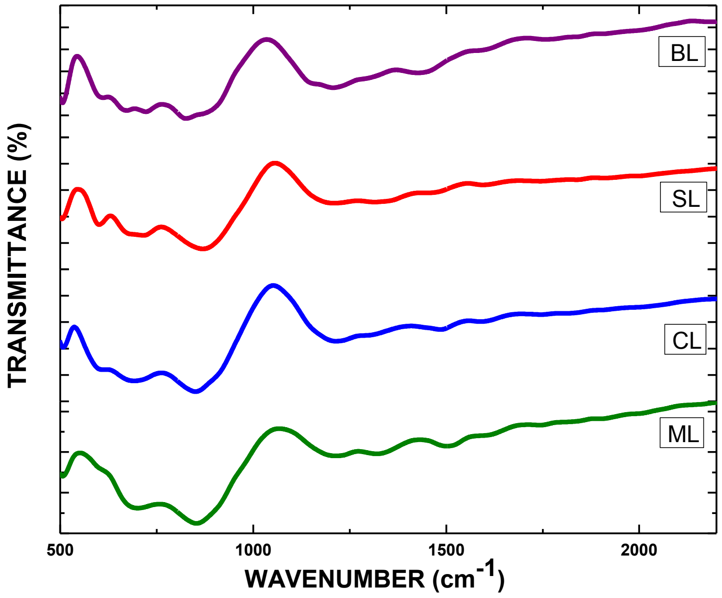


Fig.4.3 - FTIR spectra of various glass samples.

The IR spectra of glass samples exhibit a very small absorption band at 650-780 cm^{-1} which can be assigned to Si-O-Si symmetric stretching of bridging oxygen between tetrahedra. Additionally, strong absorption band appeared at 888 cm^{-1} which can be attributed to $Si-O^-$ stretching with two non-bridging oxygen. Apart from these bands, FTIR spectra also exhibit two weak band variations at 1250 cm^{-1} and 1604 cm^{-1}. These variations can be assigned to boroxyl rings and H_2O molecular vibrations, respectively. The kink at 770 cm^{-1} can be attributed to tri, tetra and pentaborate O bridges between tetra and trigonal boron atoms oxygen bridges between trigonal atoms. The small kinks at 1198 cm^{-1} can be assigned to Si-O-Si asymmetric stretching of bridging oxygen. The small kinks at 1426 , 1487 and 1507 cm^{-1} are observed which can be due to BO vibrations of various borate groups [89].

The sharper peaks of glass samples 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 glasses as the modifier is changed. 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 [90]. It is well established that addition of heavy cations in glass shifts the peaks to lower wave numbers smally. With the introduction of more heavy cation, 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 736 cm^{-1} is getting broadened indicating the scission of Si-O-Si chain in the glass network. The bands centered at 873 and 896 cm^{-1} is assigned to the $Si-O^-$ stretching with two non-bridging oxygen per SiO_4 tetrahedron. These bands are becoming stronger with the replacement of heavy modifier as it is breaking the network structure of glass former, thus producing NBO's with the gradual incorporation of ions in the glass structure. When alkaline earth metal ions occupy interstitial position, then it can introduce coordinated defects known as dangling (broken bonds) [91].

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, 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 :

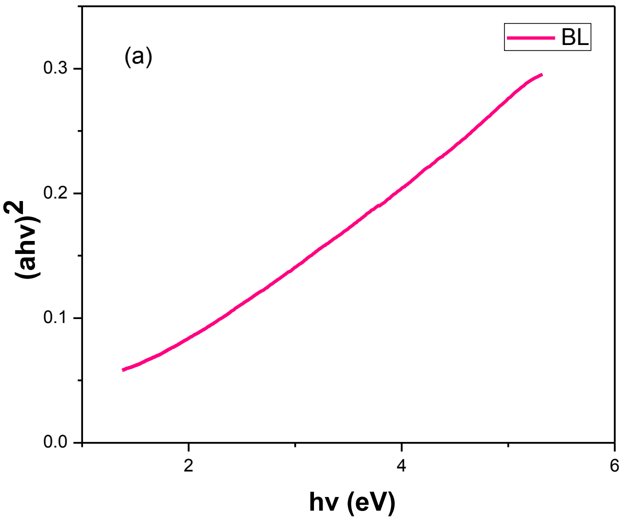
$$2BO_{3/2} + O^{2-} \rightarrow 2\,[\,BO_{4/2}]^{-} \qquad (10)$$

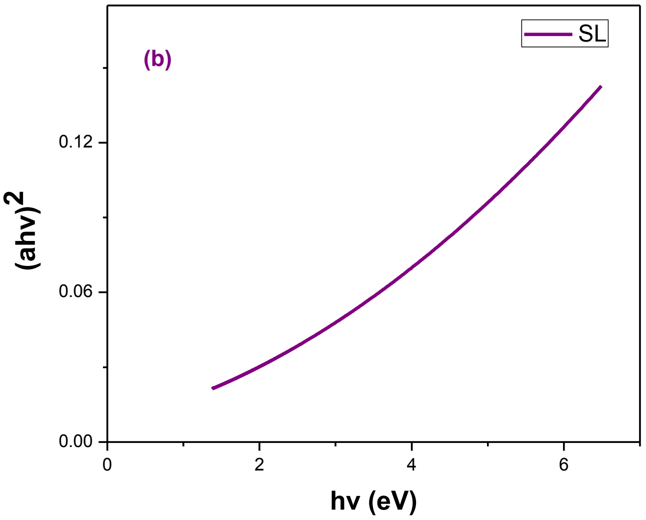
4.4 UV-VIS Spectroscopy:

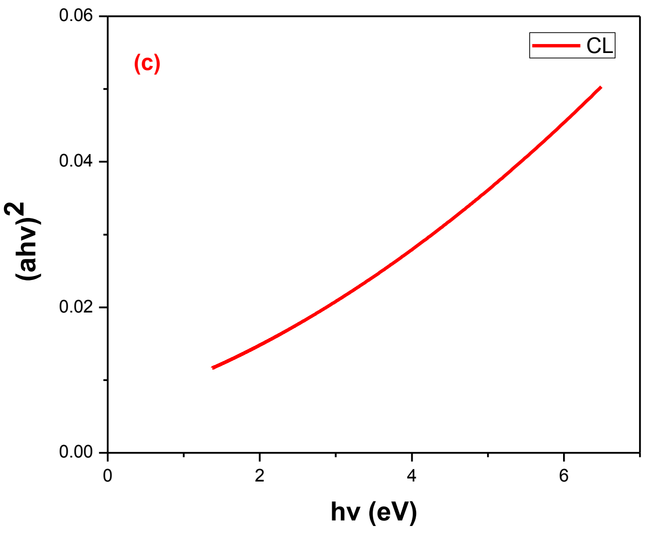
According to Tauc, in many amorphous materials the variation of absorption coefficient with photon energy shows three regions. The first region which is also known as 'Tauc region' corresponds to high absorption from which optical energy band can be calculated. This region is associated with inter band transitions i.e. it may correspond to transition of an electron belonging to an oxygen ion in an excited state [92]. As a consequence of this, a marked sharp increase in the absorption coefficient $\alpha(\nu)$ will result. The more weakly these electrons are bound, the more easily absorption occurs. For Tauc's region, the absorption coefficient is given in quadratic form which is discussed by Mott and Davis [93] in more general form :

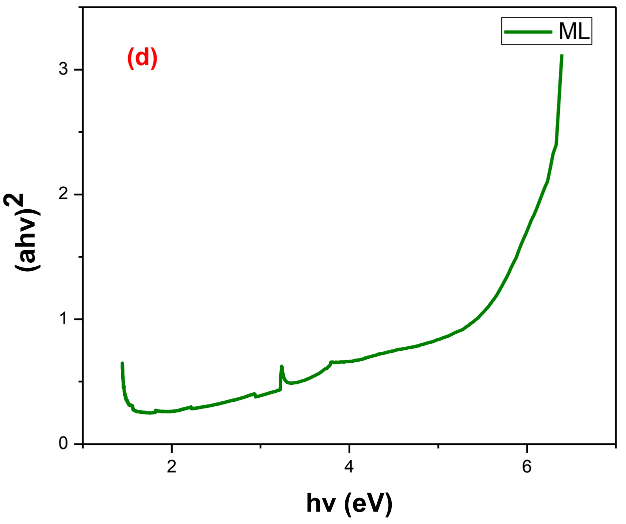
$$\alpha h\nu = \text{const}\,[\,(h\nu - E_{opt})^{n}/h\nu] \qquad (11)$$

where $h\nu$ is the photon energy and E_{opt} is the optical band. Here, n is an index that have different values depending on 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 $(\alpha h\nu)^{1/2} = 0$.


(a)
BL
(ahv)^2
0.0
0.1
0.2
0.3
2
4
6
hv (eV)


(b)
SL
(ahv)^2
0.00
0.06
0.12
0
2
4
6
hv (eV)





Figs. 4.4 Variation of $(\alpha h\nu)^2$ with hν of glass samples (a) BL, (b) SL, (c) CL, (d) ML is changed.

Determination of optical band gap :

The optical absorption coefficient, α, of a material can be evaluated from the optical transmittance and reflectance using the relation,

$$\alpha = 1/d \ln (1-R)/T \qquad (12)$$

where d is the thickness of the sample, while the absorption coefficient $\alpha(\nu)$, as a function of photon energy ($h\nu$), for direct and indirect optical transitions, according to Pankove, is given by:

$$\alpha h\nu = A_0 (h\nu - E_g^{opt})^p \qquad (13)$$

For amorphous materials, indirect transitions are valid according to the Tauc relations, i.e. the power part p = 2; so, the values of indirect optical band gap energy E_g^{opt} can be obtained from Eq. above by extrapolating the absorption coefficient to zero absorption in the $(\alpha h\nu)^{1/}2$ hν plot. The respective values of E_g^{opt} are obtained by extrapolating to $(\alpha h\nu)^{1/2} = 0$ for the indirect transitions. The values of E_{opt} are listed in table 6 as:

Table 6 : Values of optical band gap (E_{opt}) and Urbach energy (E_u)

Glass Sample	E_{opt} (eV)	E_u
ML	4.8	0.34
CL	2.8	0.39
SL	2.2	0.43
BL	1.5	0.47

It can be seen that the band gap decreases from 4.8 to 1.5 eV as the modifier is changed. 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 higher 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 [94]. It is reported that the introduction of heavy metals like barium in glass decrease the optical band gap [95]. The change in optical band gap is attributed to the structural changes due to the different sites occupancies by cations.

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 ($\alpha < 10^{-4}$ cm^{-1}), there is usually an Urbach tail where $\alpha(\nu)$ depends exponentially on the photon energy hν as follows :

$$\alpha(\nu) = \alpha_0 \exp (h\nu/E_u) \qquad (14)$$

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.

The exponential dependence of $\alpha(\nu)$ on photon energy depicts that the material obeys Urbach rule. Dow and Redfield described the cause of Urbach energy as the random internal electric field associated with the structural disorder which broadens the excitons line [96]. Tauc and Menth [97] have reported that disordering can arise from transitions between the localized states in the 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 replacement of modifier is again suggesting an increase in amorphousity as well as open structure of the glass due to the formation of non-bridging oxygen. The third region is the weak absorption tail produced from defects and impurities in UV spectra.

4.5 Micro hardness testing :

It can be observed from the table 7 that ML samples have maximum hardness in them and the BL has minimum. The reason can be attributed to the Bond strength as the pattern varies as MgO > CaO > SrO > BaO. Therefore, ML samples has greater bond strengths and hence, much attraction between bonds, not easy to break bonds as comparison to BL.

Table 7: Micro hardness of ML, CL, SL and BL glasses.

Glass samples	Hardness (GPa)
ML	5.214
CL	4.541
SL	4.107
BL	3.646

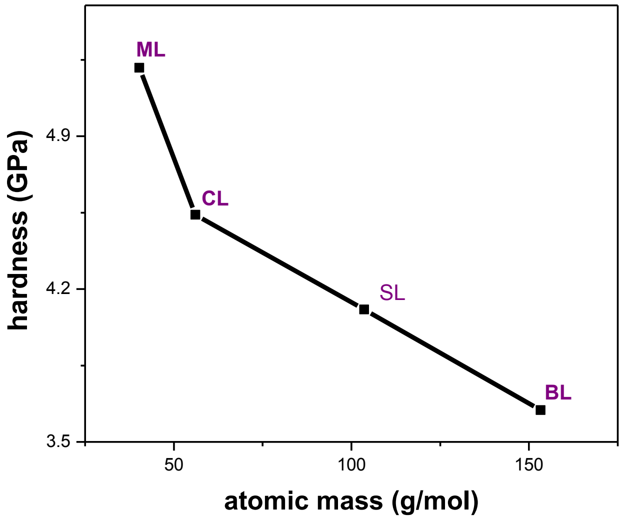


Fig.4.6 : Variation of hardness with atomic masses of different glasses.

4.6 Determination of the refractive index:

According to the theory of reflectivity of light, the refractive index n as a function of the reflectance R and the extinction coefficient k can be determined by the quadratic equation:

$$R = [(1-n)^2 + k^2]/ [(1+n)^2 + k^2] \qquad (15)$$

The extinction coefficient can be computed based on the wavelength λ and the calculated values of α according to the relation:

$$\alpha = 4\pi k/\lambda \qquad (16)$$

It is clear from the figure (4.7) that the refractive index decreases with an increase in the wavelength of the incident photon. It can be assigned that with the addition of modifier BaO, one has maximum refractive index and the replacement of modifier as MgO gives the minimum refractive index. An increase in the oxide ion polarizability, along with an increase in the refractive index, can be attributed to an increase in the molar refraction, which gives rise to an increase in the measured refractive indices on increasing the electronic polarizability of ion oxide.

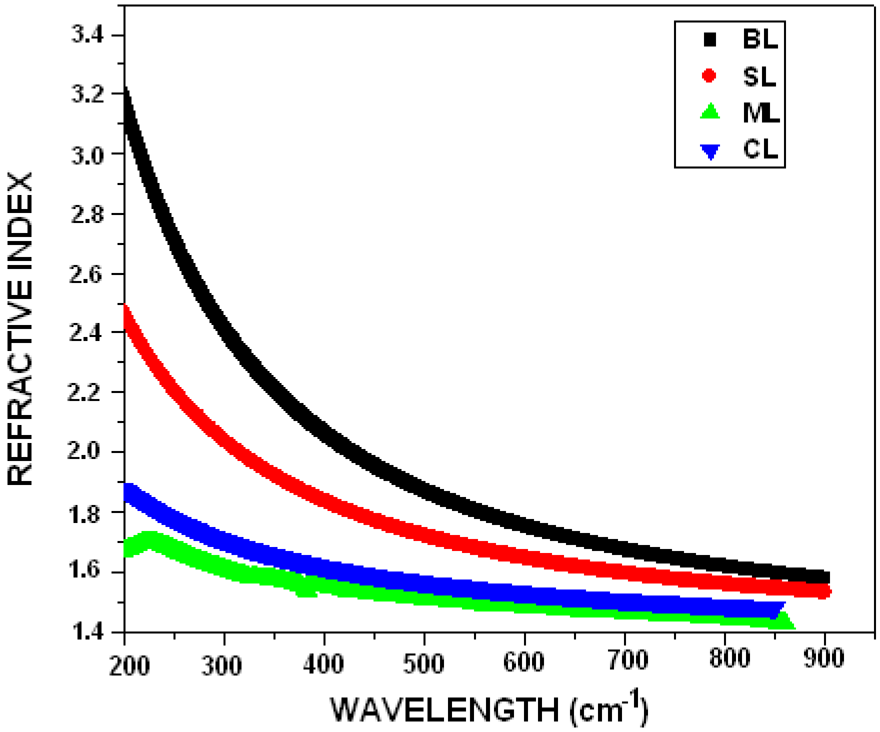


Fig 4.7: Variation of refractive index with wavelength of various glass samples.

CHAPTER 5

CONCLUSIONS AND FUTURE SCOPE

5.1 Conclusions:

The replacement of modifier alkaline earth metals in glass samples, exhibit marked effect on their structural, optical, mechanical and physical properties. With the replacement of modifier in a glass, the E_{opt} (optical energy band gap) show a considerable decrease, due to increase in number of non-bridging oxygen. It is concluded that, with the introduction of heavy metals like barium in glass, decreases the optical band gap. 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. The change in optical band gap is attributed to the structural changes due to the different sites occupancies by cations. Consequently, the width of tails of the localized states in the band gap is observed to increase (E_u) indicating more disorder in glass structure. The increase in Urbach energy with the replacement of modifier is suggesting an increase in amorphousity as well as open structure of the glass due to the formation of non-bridging oxygen. X- ray diffraction studies of the glass reveal no diffraction peaks or lines, indicating no crystalline phases. This clearly emphasizes the fact that the studied glasses are completely amorphous. A broad diffuse scattering at low angles observed for the as-prepared samples is the indication of long range structural disorder. All the glasses exhibit broad halo around 30̊. In FTIR spectra, bands are shifted to lower wave number slightly, with the addition of heavy cations like Ba^{2+} in glass. With the introduction of more heavy cation, the structural rearrangement can take place in Si-O-Si environment leading to strained network and hence resulting in net decrease of local symmetry. Optical basicity calculations clearly depicted the increase of ionicity with the increasing number of NBO’s in the glass. BL samples has higher values of optical basicity due to higher number of

NBO's in this glass. The reason being having the smallest field strength. It strengthens the network via bonding to neighbouring oxygen. The Ba^{2+} having the highest cationic radius (corresponding to smallest field strength), experiences less attraction from the non-bridging oxygen. The increasing thermodynamic stability is associated with increasing charge on oxygen atoms. 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 non-bridging as well as the co- ordination of Si or B. The Micro-hardness calculations shows that higher the bond strength of the modifier oxide, increases the hardness of glass. The refractive index showed a decreasing trend with an increase in the wavelength of incident photon.

5.2 Future Scope :

Elastic properties of borate glasses through ultrasound velocity measurements is one of the important techniques to elucidate the structure of glasses, since their properties have direct bearing on the bonding and interatomic forces. Sound velocity measurement at ultrasonic frequencies is used to determine the mechanical properties of glasses which can be directly related to the interatomic potential in the system. The measurement of ultrasonic parameters such as velocity and attenuation as a function of composition, temperature and frequency is of great interest in glasses. These ultrasonic parameters besides density and molar volume are sensitive and informative about the changes occurring in the structure of glass network.

Recent interest extends to fast ion conductors, lasers and non-linear optical materials. Synthesis and study of lanthanum borate, aluminum borate whiskers and borate glasses, inparticular, have become subjects of great interest due to their structural peculiarities.

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