CHAPTER II
SYNTHESIS TECHNIQUES AND PROPERTIES
OF GLASS

This chapter gives detailed information on Glass Melting, working and principle of various techniques used for the preparation of oxide glasses such as conventional melt-quenched technique, physical vapour deposition, thermal evaporation, sputtering, glow discharge, chemical vapour deposition, sol-gel method, applying intense shock waves mechanical alloying etc. The chapter also includes some remarkable properties of oxide glasses.

2.1. Methods for Preparation of Oxide Glasses

Oxide glasses can be prepared via various synthesis techniques for commercial and non commercial use. In commercial glasses we have to take care for the specific shapes, also the colour of the glass, some of them are discussed below.

2.1.1 Glass by melt-quenching technique

Glass Melting

Although glasses can be made by a wide variety of methods, the vast majority is still produced by melting of batch components at an elevated temperature. This procedure always involves the selection of raw materials, calculation of the relative proportions of each to use in the batch, and weighing and mixing these materials to provide a homogeneous starting material. During the initial heating process, these raw materials undergo a series of chemical and physical changes to produce the melt. Conversion of this melt to a homogeneous
liquid may require further processing, including the removal of any un-melted batch remnants, impurities and bubbles. Production of commercial products requires forming of specific shapes, as well as heat treatments to remove stresses generated during the cooling process, or to produce glasses strengthened by thermal tempering [1-3].

**Raw Materials**

In general, glasses are either produced from high quality chemically pure components or from a mixture of less pure minerals. Optical glasses used for low volume, high technology applications are produced using those chemicals, we might routinely encounter in any chemical laboratory. Bulk commercial products, on the other hand, are produced from minerals, which typically have names and compositions which are not familiar to the novice.

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: glass former, flux, property modifier, colourant and a fining agent. The same compound may be classed into different categories when used for different purposes. For example, Alumina serves as a glass former in eliminating glasses, but is considered a property modifier in most silicate glasses. The most essential component of any glass batch has been 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 of boric oxide is also
present, in addition to silica, the sample is termed a borosilicate glass. The primary
glass formers in commercial oxide glasses are silica (SiO$_2$), boric oxide (B$_2$O$_3$) and
phosphoric oxide (P$_2$O$_5$), which all readily form single component glasses. A large
number of other compounds may act as glass formers under certain circumstances,
including GeO$_2$, Bi$_2$O$_3$, As$_2$O$_3$, Sb$_2$O$_3$, TeO$_2$, Al$_2$O$_3$, Ga$_2$O$_3$, and V$_2$O$_5$. With the
exception of GeO$_2$, these oxides do not readily form glasses by themselves unless
very rapidly quenched or vapour deposited, but can serve as glass formers when
mixed with other oxides. The elements S, Se, and Te act as glass formers in
chalcogenide glasses. Although halide glasses can be made in many systems, with
many different compounds acting as glassformers, the two most common halide
glass formers are BeF$_2$ and ZrF$_2$. Although the number of possible glass
compositions is effectively unlimited, the bulk of commercial glasses are based on
silica as the glass former.

While silica itself forms an excellent glass, with a wide range of
applications, the use of pure silica glass for bottles, windows, and other bulk
commercial applications would be prohibitively expensive. Potassium oxide is also
used extensively in commercial glasses, while lithium oxide is used in a number of
commercial glass-ceramics. Rubidium and cesium oxides are frequently used in
laboratory studies of trends in behaviour due to changes in the identity of the alkali
oxide present in glasses, but are very rarely used in commercial products, due to
their high cost. PbO, which is an excellent flux, is becoming much more limited in
use due to concerns regarding toxicity of heavy metals. PbO is especially useful in
dissolving any refractory or other impurity particles which might otherwise result
in flaws in the final glass. While, addition of flux, silica lead to decreased cost of
glass formation. The addition of large amounts of alkali oxides results in a serious
degradation in many properties [4]. Colourants are used to control the colour of the final glass. In most cases, colourants are oxides of either the 3d transition metals or the 4f rare earths. Uranium oxides were once used as colourants, but their radioactivity obviously reduces their desirability for most applications. Gold and silver are also used to produce colours by formation of colloids in glasses. Colourants are only used if control of the colour 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 colourants in many products. When colourants are used to counteract the effect of other colourants to produce a slightly gray glass, they are referred to as decolourants. 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$_3$AlF$_6$ and a number of sulfates. Their presence, however, is essential in many 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 [5].

**Compositional Nomenclature**

The terminology used to describe the composition of a given glass can be quite confusing. No single system exists for designating the composition of inorganic glasses. Not only different systems are used for oxide, halide, and chalcogenide glasses, but a number of different systems are used for oxide glasses alone. The compositions may be expressed in terms of molar, weight, or atomic fractions or percentages. Historically, oxide glass compositions were expressed in terms of weight percentages of the oxidized components. While use of a weight
fraction basis simplifies preparation of batches and is very useful in commercial production, it does little to aid in understanding the relative effect of various components of glass or melts properties. On the other hand, use of a molar fraction or percentage basis, while very useful in understanding compositional effects and currently used in most of the literature, complicates batch preparation [6].

**Batch Calculations**

Glass batch calculations can range from very simple to very complex, as a function of the complexity of the composition and the raw materials used to prepare the mixture. Batches containing only oxides in their exact state as expressed by the glass formula, for example, involve very simple calculations, while batches using a number of different minerals, where a glass component may be present in two or more raw materials, require much more complicated calculation. All batch calculations follow the same procedure. First, determine the weight fraction of each component required to produce the desired molar composition.

Begin by multiplying the mole fraction of each component of the molecular weight of that component. Next, total these contributions to determine the molecular weight of the glass, and then divide each individual contribution by the molecular weight of the glass to determine the weight fraction of each component. Finally, multiply the weight fraction of each component by the mole of glass to be produced. The batch weight of any component which decomposes during melting is adjusted by multiplying the weight fraction of that component by the appropriate gravimetric factor for the raw material actually used in the batch. Use of raw materials which supply more than one batch component requires additional calculations [7].
Mechanisms of Batch Melting

A large number of steps occur during the conversion of a batch to a melt. While the details will be strongly dependent upon the specific batch materials used and the type of glass produced, these numbers of steps occur in most batches. The steps which occur during the formation of a soda-lime-silicate melt will be used as an example of the processes which may occur during melt formation.

Release of Gases

The initial heating of a glass forming batch usually results in the release of some moisture, which may have been absorbed on the particles or combined as water of hydration or as hydroxyl [8].

Formation of Liquid Phases

Liquid phases are formed by the direct melting of batch components, by melting of decomposition products, and by melting of eutectic mixtures formed from the batch components [9].

Melting Accelerants

A number of methods can be used to decrease the batch-free time. The most important methods for accelerating the melting process are based on changes in batch raw materials. Replacement of a small portion of sodium carbonate by sodium sulfate, for example, speeds the dissolution of sand by forming additional, lower melting eutectic mixtures.

Volatilization of Components from Melts

A large number of the components of glasses are quite volatile at elevated temperatures. Loss of these components can significantly alter the composition of the glass obtained after prolonged melting, as compared to that obtained for short
melting times. Volatilization losses are particularly significant for alkali oxides, lead, boron, phosphorus, halides, and other components which have high vapour pressures at high temperatures. The rate of loss of alkali increases rapidly in the order of \( \text{Li} < \text{Na} < \text{K} < \text{Rb} < \text{Cs} \). The loss of a component can be reduced by increasing the concentration of that component in the atmosphere above the melt. Covering the melt will force the partial pressure of the volatile components to increase directly above the melt, establishing a dynamic equilibrium between the dissolved and vaporized species, and prevent significant loss of those components. These losses can usually be reduced dramatically by lowering the melt temperature.

**Fining of Melts**

The terms fining and refining refer to the removal of gaseous inclusions or bubbles, from the melt. Although the presence of bubbles in a glass sample is not necessarily determine for many scientific studies, bubbles are definitely undesirable in most commercial glasses. Bubbles in commercial products are almost always considered flaws and result in rejection of the product. Fining of a melt begins during the melting process, but typically extends to times well after the complete disappearance of residual batch.

**Sources of Bubbles**

The bubbles can be formed by the physical trapping of atmospheric gases during the initial phase of batch melting or by the decomposition of batch components. The gases in the interstices between batch particles may be trapped as the particles begin to soften and form a viscous liquid. As the viscosity decreases with increasing temperature, these interstices become fully surrounded by liquid. Surface forces then cause these interstices to assume the spherical shape of
bubbles. These bubbles contain gases characteristic of the melting atmosphere, which may be air, combustion gases or some gas deliberately introduced to control chemical reactions with the batch. Prevention of the formation of these bubbles involves elimination of gas from the interstices of the batch [10].

**Removal of Bubbles by Buoyancy Effects**

The bubbles can be removed from melting either by physically rising to the surface or by chemical dissolution of the gas into the surrounding melt. Since the density of a bubble is less than that of the surrounding liquid, a bubble will automatically rise to the surface and burst unless prevented from doing so by some external agent [11].

**Fining Agents**

Chemical methods for removal of bubbles from melts depend upon the addition of batch components collectively termed fining agents. Fining agents release large quantities of gases, which form large bubbles which rapidly rise to the surface of the melt. These large bubbles tend to carry smaller bubbles and seed to the surface as well. In addition, some fining agents cause the absorption of O$_2$ from bubbles at lower temperatures, thus reducing the size of seed due to diffusion from the bubble into the melt. The seed eventually shrinks to below the critical radius, where the surface energy causes the complete disappearance of the bubble [12].

**Homogenizing of Melts**

The fluid produced during the initial batch decomposition process is very heterogeneous. This heterogeneity is gradually reduced by the stirring action of rising bubbles during the fining process. Production of an acceptably homogeneous glass, however, usually requires additional time for diffusion processes to improve the homogeneity of the melt. Homogeneity is normally described in a negative
sense: a homogeneous melt is free from significant heterogeneities; perfectly acceptable level of homogeneity for a window glass might be completely unacceptable for a glass used as an optical lens [13-16].

**Specialized Melting Methods**

Many glass forming melts require special techniques which do not apply to the melting of more common compositions. Toxicity may require processing in glove boxes to protect workers from dangerous fumes or powders. Volatility of the components may require processing in sealed containers to obtain the desired composition of the final glass. Special atmospheres may be needed to prevent contamination of non-oxide glasses.

Formation of chalcogenide glasses provides an excellent example of the complexity encountered in melting unusual glasses. Not only are the components of these glasses toxic and highly volatile, but contamination by very small quantities of oxygen will destroy the infrared transmission of the glass. These melts are usually prepared by weighing and mixing the components in an inert atmosphere dry box, placing the mixture of powders in a vitreous silica tube, and then sealing the tube at both ends under a vacuum. The tube is placed in a furnace, heated to the desired temperature, and then quenched to allow the melt to form a glass. Since homogeneity of the melt is difficult to attain under these conditions, the ampoules are often heated in a rocking furnace to aid in stirring of the melt.

Heavy metal halide glasses also require melting in an oxygen-free atmosphere to preserve their optical properties. These glasses are often melted under a reactive atmosphere, such as CC1 or SF6 which due to decomposition of the atmospheric gas, contains free halide. The atmosphere acts as both a greater for oxygen and as a source of the halide to replace volatilization losses and maintain
the stoichiometry of the melt. This melting procedure is termed reactive melt processing, usually designated as RAP. The melt-quenching technique was the only method for the developments of chemical vapour deposition and sol-gel processes, by which bulk glasses of acceptable size could be obtained. Even at present, glasses are engendered by the melt-quenching technique make up more than 99% of practical glasses in both volume and number of types. The process, which is predicated on the fusion of crystalline raw materials into a viscous liquid followed by composing it into a shape and quenching to a glass [17], is distinguished from other methods of glass preparation in many aspects including the available systems, size and shape of the products, etc.

A coalescence prepared by felicitous amounts of crushed crystalline raw materials to procure the desired property is placed in a muffle furnace composed of firebrick or into a crucible, platinum, alumina, etc. to be fused into a liquid at high temperature. When glass which has a special property is required in an inhabited amount, the melting of coalescence is made utilizing a crucible with an externally supplied heat source such as the combustion of fossil fuel. Depending on the application, the melt is sometimes cooled very gradually to a rigid condition within crucible so that only the highly homogeneous part is utilized. Generally the molten glass is kept at the temperature 1400‒1500 °C more than 10 h in order to abstract minuscule bubbles and to enhance the homogenization of the melt through convection and the inter diffusion of the constituent atoms. The formation of a melt into a desired shape is carried out at a temperature corresponding to 900‒1100 °C for most commercial glasses, by utilizing sundry synthesis methods of glass such as casting into a mold, blowing, up-drawing, down-drawing, pressing, rolling out, floating, and sundry amalgamations [18].
Most of the prepared glasses are customarily annealed in a temperature range that is scarcely higher than the glass transition temperature to abstract any thermal stress, which developed during the composing and subsequent cooling due to the low thermal conductivity of a glass.

**Advantages of melt-quenching method**

• The high flexibility of the geometry of a glass and particularly the advantage in obtaining materials of large size in comparison with a single crystal or polycrystalline ceramics is as important as the structural and thermodynamic features when considering the preparation of glasses with special properties. Examples of the products based on this feature are the giant pulse laser, Faraday rotator, etc. whose total performance is dependent on the size of material.

• In the melt-quenching method there is large flexibility of composition as compared with other methods. Since simple quenching of a melt does not require stoichiometry among constituents, the preparation of glasses with a wide variety of compositions, consisting of sometimes up to ten kinds of constituents at various ratios from a few to several tens of percent, is possible. The doping or co-doping of active ions such as rare-earth or transition metal at a level of a few percent or less is also made relatively easily, which is quite important for the production of glasses with special properties. Most of the important industrial glasses are based on this advantage of flexibility of composition.

• The important fact that should be stressed about the melt-quenching technique is that most of the above-mentioned features are true not only for the familiar silicate, borate, vanadium and phosphate systems, but also for the many exotic glasses of the oxide system as well as non-oxide glasses such as those of the fluoride and metal alloy systems [19].
Disadvantages in the melt-quenching technique compared with other processes.

- The melt-quenching technique which uses crystalline raw materials has disadvantages for the preparation of glasses of ultra-high purity such as those used for optical communication in comparison with the chemical vapour deposition and sol-gel processes that use liquid raw materials.

- The difficulty of maintaining high purity is also attributed to possible contamination by the crucible or furnace materials which often react with the glass melt under high temperature. In order to minimize the contamination, crucibles made of noble metal such as platinum and its alloys are often used for the preparation of special glasses.

- Another disadvantage of the melt-quenching technique that should be noted is that it is extremely difficult to prepare glasses containing a large amount of refractory material represented by SiO$_2$, TiO$_2$, Al$_2$O$_3$, ZrO$_2$ etc. with this technique, because of the requirement for an extremely high temperature for melting. The production of the binary or ternary glasses containing these components, as well as silica glass of ultra-high purity, are therefore made by either chemical vapour deposition or the sol-gel process[20].

Keeping in the mind the above advantages and disadvantages of the melt-quenching technique was used for preparation of the (10-x)BaO-xFe$_2$O$_5$ and (10-x)SrO-xFe$_2$O$_5$ systems.

2.1.2 Thermal evaporation

This is one of the most widely used methods for producing amorphous thin films of semiconductors and chalcogenide glasses. Thin amorphous films of amorphous semiconductors like Si, Ge, Ga, As, chalcogenide compounds like
As$_2$S$_3$, As$_2$Se$_3$ etc. are prepared by this method. In this method, the starting material is vaporized and is collected on a substrate [21]. The thermal evaporation technique is performed in a vacuum to reduce contamination and to avoid the effect due to scattering. The evaporating material, placed in a boat crucible, is heated either resistively using electron beam and the vapours are collected on a cold substrate. Due to the lower temperature of the substrate, the mobility of the atoms, reaching the surface of the substrate randomly, is frozen resulting in the formation of an amorphous thin film the essential feature of thermal evaporation is that atomic surface mobility is greatly diminished because of the cold substrate, causing the atom to be frozen in the random positions at which they arrive. The principal advantage of thermal evaporation as a preparative technique lies in the variability in the purity and composition of the films. The quality of the resulting film developed by this method depends on the substrate temperature, distance between the source and substrate and their orientation pressure in the chamber and the filament temperature.

2.1.3 Sputtering

Besides the rapid liquid quenching, the most commonly used technique for the preparation of glassy semiconductors and metals is sputtering. Sputtering method involves the bombardment of a source of energetic ions obtained from low-pressure plasma resulting in the removal of atoms or cluster of atoms from the source material and its subsequent deposition as a film on the substrate. Sputtering method is more flexible compared to the thermal evaporation method reasonably homogeneous and uniformly thick deposits can be produced. The nature of sputtering gas and its pressure, ratio of partial pressure of reactive gas to inert gas, power applied to target, bias voltage of target of substrate etc. Further, the process
of sputtering does not degrade the properties of the substrate. The simplest way to induce sputtering is to apply a high negative voltage to the target surface, thereby attracting positive ions from the plasma [22].

2.1.4 R F Glows charge

This method is also used to prepare amorphous solids of semiconductors in the form of thin films. The glow discharge method is similar to sputtering process. In this process, instead of plasma ejecting the material from the target, a chemical reaction is initiated in the gas phase by creating in r. f. glow discharge of the reactant gases, leading to the deposition of a material on the substrate placed inside a chamber [23]. The discharge can be produced either in the pure reactant gas or in a mixture of reactant gases and a carrier gas like argon. By using a combination of reactant gases, films of different materials can be prepared. It is difficult to control parameters precisely in this method as compared to earlier methods.

2.1.5 Glass by chemical vapour deposition

This method is used to prepare amorphous solids of polycrystalline materials. Chemical vapour deposition is similar to the glow discharge method in that both depend on the decomposition of vapour species. In this CVD method, chemical decomposition of a vapour takes place leading to deposition of a solid film on a substrate placed in the plasma. The chemical vapour deposition method in principle is similar to the glow discharge method, but the decomposition of the reactant gas is achieved by thermal energy, for which temperature of the order of 1000 K, is commonly used [24].

2.1.6 Glass by sol-gel process

The sol-gel process begins with the formation of a sol consisting of colloids dispersed in a liquid medium. A sol turns into a porous gel by the coagulation of
these colloids while standing in a mold or on a substrate which is used as a coating film, etc. [25]. The gel thus obtained is dried and sintered into a pore-free dense glass or glass film, etc. at a temperature slightly above the glass transition temperature of the eventual glass [26].

There are various ways of preparing a sol which depend on the material to be made. In the case of the formation of bulk glass, the most widely used methods is the hydrolysis and polycondensation of silicon alkoxide or its mixture with the alkoxides of Ti, Al, Zr, Ge, etc. [27]. An alternative way is to disperse fine particles of sub-micron size obtained by flame hydrolysis of SiCl\textsubscript{4} in chloroform using n-propanol as dispersing agent [28].

Initially 1 mole of TMOS is dissolved in about 5 moles of methanol contained in a flask under stirring and then 4 moles of water are added to the solution under vigorous stirring. The role of the methanol is to form a homogeneous solution as the mutual solvent of two immiscible liquids, TMOS and water. The clear silicate solution is cast in a cylindrical plastic mold and left in an oven at a temperature that is below the boiling point of methanol. Slow drying is necessary to avoid fracture of the gel due to a capillary force induced by the evaporation of the liquid. The dried silica gel is, then, subjected to heat treatment under vacuum at a temperature about 1000 °C for densification into a pore-free glass. The treatment under vacuum is to enhance the removal of water that was generated by the dehydration of silanols covering the surface of the silica particles [29].

Since most alkoxide precursors are in a liquid state and are easily purified by repeating distillation, and since there is no possibility of contamination from a container because this is a crucible less process, it is also possible to obtain glasses
of very high purity such as those used for fabrication of optical fiber [30].

The advantage of this technique is that, it is a low temperature glass preparation method. The method for producing amorphous materials via sol-gel method has considerable technological promises. The sol-gel method has its greatest usefulness for those systems which give rise to very viscous melts near the melting point, or alternatively which have extremely high. Melting points and hence possesses considerable technical problems in actually being able to make glass by melting quenching. Also, there are some disadvantages compared with the other processes discussed above. The biggest drawback of the sol-gel process is the large amount of shrinkage of a wet gel upon drying, which often leads to a fracture [31].

2.1.7 Electrolytic deposition

Amorphous layers of a metal oxide can be grown on the metal surface by using it as an anode in an electrolytic cell having a variety of aqueous electrolytes. When DC voltage is applied between the electrodes, the cation migrates towards the cathode and the anions, which include $\text{O}^2-$, migrate towards the anode. At the anode, under sufficient over voltage, $\text{O}^2-$ reacts with the metal producing the glassy layer of the oxide having thickness up to several thousands of angstroms [32].

It has been demonstrated that glassy films of oxides of Al, Zr, Nb, Ta etc. can be easily prepared by this method. In addition to this, any other methods have been reported to produce amorphous materials which are specific for certain systems, such as high pressure shock waves, slow mechanical grinding, explosive compaction, radiation damage, etc. It has also been reported that amorphous intermetallic compounds can be made by hydrogen absorption [33].
2.2 Properties of Glasses

The liquid like structure of being the special property of glass. Transparency is character of liquid and also characteristic of the glass, but in solid state. Glasses are isotropic and lack internal grain boundaries or structural elements lying in a specific orientation [34]. Some properties of glasses are explained below.

2.2.1 Physical Properties of glasses

Density of glass is a strong function of its composition and most important measure of glass. It also stands on its own as an intrinsic property capable of casting light on the short range structure. The addition of network modifier components increases the density as network modifier ions use to obtain the interstitials within the network. In some glasses the addition of network modifier in the glass former results in an increase in density [35].

2.2.2 Chemical Properties

Glass is much more resistant to corrosion than other materials, so that it is easy to think of it as corrosion-proof. Glassy materials after several years of exposure to sunlight and atmosphere remain clear and apparently unaffected. Glass wares hold a wide range of liquids that would dissolve other materials. In the laboratory, most of the reactions are carried out in glass beakers and flasks without damage to the beaker or contamination of the solution reacting. But, in spite of these indications that glass is imperishable by chemical attack, under certain conditions it will destroy, 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 chemicals 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 attack 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 ways. 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 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 of glass can be modified 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. Selecting an individual glass for an application, it is initial constituents that it important. Usually, one property cannot be changed without causing a change in the other properties. It is the art of the glass scientist to produce the most favorable combination of properties [36, 37].

2.2.3 Thermal Properties

The expansion/contraction due to thermal energy is significant attention to product design. The glass expands when it is heated, if the temperature over the body of the 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 the body, then the different layer of glass attempt to expand differently and consequently stress develop[38]. The magnitude of stress so generated is
related to thermal expansion. The addition of modifier in glass increases the bond bending which automatically increase the thermal expansion. Thermal expansion of glasses with few exceptions increases with increase in temperature. The negative thermal expansion coefficients are believed to result from ability of network to absorb lattice expansion through bending of bonds into the empty interstices of the structure. The addition of alkali increases the thermal expansion. Thermal expansion is a volume averaged function of contribution of each of the phases present in a sample, formation of crystal with the thermal expansion coefficient which are very different from initial glass can radically alter the thermal expansion coefficient of the composite. Formation of crystal can also change the value of the Tg and crystallization temperature (Tc) by changing the composition of residual glass [39].

2.2.4 Optical Properties

Glasses are among the few solids which transmit light in the visible region of the spectrum, most of the glasses transmit light in the visible region of the spectrum. Many applications of glasses are based on the combination of a wide range of optical properties with ease of fabrication of glass specimens in simple and complex shapes. Optical properties of glasses influence their applications from transport containers up to high technology areas such as telecommunications and optical computers. The range of optical properties is very wide and glasses are considered to be leaders in the area of high technology materials.

The major technological development that have added to comfort of living are glass lenses as an aid to failing vision, glass window to bring daylight into the housing structure while providing protection from harsh particle, dust particles etc. Glass in the light bulb provides light in the dark and glass fiber in enhanced
Optical properties of glasses are subdivided into three categories first many applications based on bulk optical properties such as refractive index and optical dispersion. Other property, including colour based on optical property which is a strong function of wavelength and last is nontraditional optical effect.

**Bulk optical properties:**

Development of early telescope and microscope is a search of new optical glasses with appropriate refractive index and optical dispersion. Refractive index remains the most measured optical properties of glass and most basic optical property for determination of appropriate glass. The refractive index is defined as ratio of the velocity of light in a vacuum divided by the velocity of light in the medium. This ratio can be measured by Snell’s law [41].

\[
\frac{\text{Index}}{} = \frac{\text{sin } \theta_i}{\text{sin } \theta_r} \quad \ldots \quad \ldots \quad (1)
\]

Where, \( n = \text{refractive index} \), \( \theta_i = \text{angle of incident} \) and \( \theta_r = \text{angle of refractive} \) The variation in index with wavelength is called optical dispersion. Dispersion is defined by an entire curve of refractive index with respect to wavelength.

**Ultra violet absorption:**

Even transparent colorless glasses cannot transmit radiation at wavelength beyond their inherent ultraviolet edge. This frequency is due to the transition of valance electrons to the excited state. Conversion of bridging state of oxygen to non-bridging state of oxygen will lower the energy required for electronic excitation and shift the ultraviolet edge to lower frequency. Addition of alkali oxides to silica result in shift of ultraviolet edge toward the visible region.
**Infrared absorption:**
Absorption of light in the ultraviolet and visible region is due to electronic transition. While there is a lower energy electronic transition in the infrared region of the spectrum, most optical absorptions in this region are due to vibrational transition. These absorptions are due to impurity absorption due to gases and the fundamental structural vibration. The glasses are very interesting materials with useful properties such as glasses form the basic elements of virtually all optical systems, Glasses are among the few solids that transmit visible light, World-wide telecommunications by optical fibers, High refractive index [42].

**2.2.5 Electrical Properties**

In semiconductor the electrical property lies in between conductor and insulator. Semiconducting glasses show lowest thermal conductivities, lowest electrical conductivity and low mobility. Glass is an electrical insulator, but however, glass can be given a metallic oxide coating that conducts electricity. Rare earth metal oxide glasses and transition metal oxide glasses show semi conductivity due to mixed valence state. Semi conductivity arises due to hopping of electron from higher valence state to lower valance state [43, 44]. Over the past decades, a considerable number of studies have been made in the conduction process or the glass network structure of vanadium-based glasses. Depending on the type of glass the temperature of the glass and the surface conditions its passes electricity. The electrical properties and especially the key role of dopants are also very much influenced by chemical equilibrium involving electron donors and acceptors, as well as defects in the glass structure. In effect, there is a growing tendency for theoretical discussions in the fields of ionic and electronic conductivity to converge on problems in glass chemistry. However, historically
there has been some tendency for ionic and electronic processes to be treated as distinct phenomena, with chemists concentrating largely on ionic and physicists on electronic systems [45].

Although most glasses contain charged metallic ions capable of carrying an electric current, the high viscosity of glass impedes their movements and electrical activity. Thus, glass is an efficient electrical insulator, though this property varies with viscosity, which in turn is a function of temperature. Indeed, the electrical conductivity of glass increases rapidly with temperature. Since univalent alkali ions have the greatest mobility through the glass structure, they are the primary charge carriers of a glass and therefore determine its electrical conductivity. In general, the higher the concentration of alkali metals, the higher the electrical conductivity [46]. It is important to study the electrical properties of glasses for their potential applications in electrical and electronic industries. A substance is said to be electrically conducting when free electrons or ions within it make the flow of current possible. In most oxide glasses, the electrical conductivity results from ionic motion. In certain spatial composition containing multivalent oxides, such as vanadium pentoxide or iron oxide the conduction is electronic.

This property is characterized by electrical conductivity, which is reciprocal of resistivity. The electrical conductivity of a glass can be modified due to the presence of network modifiers. Glass, which does not contain any modifier, possesses a very less conductivity as compared to the crystalline materials. The strength of the bond of the ions in the network and their size influences the electrical properties. On the basis of electrical properties [47],

Glasses can be categorized in three main parts, namely, Glasses with very small conductivity, Glass with very high ionic conductivity and low electronic
conductivity, 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 a 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 [48].

2.2.6 Dielectric properties

The dielectric properties of the solids are related to their structures, therefore a change in the behaviour of a solid under alternating field is important. Generally dielectrics are classified into three categories, namely non-polar substance showing optical polarization only, a polar substance showing optical as well as infrared polarization and dipolar substance which in addition show polarization due to dipolar orientation. In the first type, an electric field produces elastic displacement of electrons only. This type contains all dielectrics consisting of a single type of atoms, second one includes substances consisting of molecules whose total dipole moment vanishes through they containing dipolar groups of atoms and the third one includes all materials consisting of dipolar molecules [49, 50].

2.2.7 Mechanical Properties

Glasses are breakable materials; the structure of glass and the strength of bonds forming the glass network determine the hardness of the glass, the fracture strength of glasses varies with prior surface treatment, chemical environment and inherent stress etc. The glasses 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 strength of
individual bonds and density of packing of the atoms in the localized structure. Fracture in glasses can be caused by thermal stresses which may be temporary or permanent. Annealing process can be used to remove thermal stresses [51, 52].
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