Chapter 1

Introduction

In this chapter, the history of glass and the fabrication of glasses in the laboratory is incorporated to consolidate the concepts of the glass. This comprising of the selection of raw materials, batch calculations, weighing and mixing these materials, melting of batch components at an elevated temperature etc. This procedure always involves calculation of the relative proportions of each to use in the batch and therefore, synthesis, melting and processing techniques are also included in this chapter. In order to know fundamental glass types, three different types of glasses have been studied, viz Fused silica, Soda lime and borosilicate glass. These glasses are produced for specialized applications. Moreover, radiation sources, characterization techniques for glass materials and interaction of radiation with glass materials have been discussed in more detail. It also gives a general back ground to the topic of research work carried out in the thesis.
1.1 Background and objective of the thesis

Glass is one of the most widely studied material and is often considered as an archetype for amorphous solid. It is judged to be an ideal for many applications like lamp envelopes, glass ceramics, surface strengthen glass, glass lasers, fibre glass, radiation harden glass etc. and being employed in optical systems such as space optics and lithography. The invention of glass is in 700 B.C, but advent of the age of technology created many new opportunities for the researchers to work into various areas of the glass[1].

In this advance world, the glass is used in optical communications, display technology, biomedical engineering and many more. It is now challenge to design new glasses with improved properties for optical waveguides and fiber-lasers, thin film glass, micro sheet for electronics, integrated optics etc. At the same time, there is an ever-expanding global market for nanoparticle diffused glasses as an active optical components. Therefore, challenge before us is to improve the efficiency, mechanical reliability and environmental impact of more traditional glass products. In all cases, understanding the composition, their processing, effects under radiation environment are the main fundamental issues for further studies of design and applications[2].

Due to the introduction of optical fiber technology in space applications, nuclear industry, high-energy physics experiments, it has become essential to investigate the influence of different kinds of radiations on the characteristics of many glass materials. In the last decades, the study has been focused on the effects of different radiations on the various types of glasses, fiber optics and studied the bulk properties such as attenuation, luminescence and refractive index.[3]

Radiation can induce numerous changes in the properties of glass. Radiation causes the displacement of lattice atoms or causes electron defects that involve changes in the valence state of lattice or impure atoms. Radiation effects are grouped into two distinct categories, namely, ionisation effects and displacement effects[4]. The ionizing radiation produces electron–hole pairs which individually become trapped at various defect sites in the glass structure. In a good conductor, the ionisation effects will disappear very quickly and will only contribute to the heating
of the material. However, in case of an insulator, electrons liberated by ionisation may trapped at various lattice imperfections resulting in more or less permanent changes in the substance [5]. Radiation induces the generation of free charge carriers in the glass matrix. For example, the energetic photons such as gamma rays create extensive ionisation and electronic excitation through the indirect interaction process of photoelectric effect, Compton effect and pair production for the production of point defects, luminescence which is then turned into the structural modifications. The same way the electron can interact with the glass and induce the defects which further modifies the glass structure[6]. Moreover, high energy swift heavy ion (SHI) makes elastic collisions with atoms of the solid and loses its energy through electronic processes called electronic energy loss (S_e), and nuclear processes called nuclear energy loss (S_n) [7]. Especially, in glass materials, a point defects, defects clusters and ion tracks, can be formed along the ion projected range and at the end of the trajectory when passed through it. The stopping power and the range of the ions can be calculated by TRIM calculations. In most of the cases of ion irradiation, the contribution of electronic energy loss (S_e) is much more than that of nuclear energy loss (S_n) [8]. The energetic electrons lose energy to the silica medium through ionisation and excitation, which contributes mainly as a collisional energy loss. If the energy is sufficiently high, the displacement within the medium lattice by knocking out the atoms occurs and is termed as collisional energy loss. This processes induced the lattice damage in the form of Si-O bond breaking and Si-O-Si stretching events [9].

In the present study, Sodalime, Borosilicate and Fused silica glasses have been taken as they are prominent members of the glass family and show the various applications. Moreover, the sodalime glass and borosilicate glass are easy to prepare in the laboratory and they produced radiation induced vacancies and creates defects in the glass structure under different kinds of radiation [10]. Soda lime glass can trap electrons when silver is doped and the stability of induced color centers is greatly improved.

In addition to color centers and defects in the glass, radiation induced diffusion provide a potential in microelectronics, optoelectronics, sensors and detectors. It also provides high relevance to the future space missions. Radiation induced defects and diffusion in sodalime glass has a challenging applications [11]. Several studies suggest that silver and copper based materials containing oxidized silver develop an
antimicrobial action. It is therefore very important to study the antibacterial activity of silver and copper doped sodalime glasses and to study the control of the size of the nanoparticles using radiations, and the result is used to study antibacterial activity[12].

One more important application of borosilicate glass is Immobilisation of nuclear waste, which is carried out by vitrification technique. Vitrification involves melting of waste materials with glass-forming additives so that the final vitreous product incorporates the waste contaminants in its macro and micro-structure. Hazardous nuclear waste constituents are immobilised either by direct incorporation into the glass structure or by encapsulation[13].

Taking into account all the above features of the glasses, the thesis is divided into seven chapters.

1.2 History of the Glass Science

Glasses have been manufactured far back in human history. Egyptian glasses date from at least 700 B.C. It has been documented that the combination of sea salt (NaCl) and perhaps bones (CaO) present in the embers of a fire built on the sands (SiO₂) at the edge of a saltwater sea, sufficiently reduced the melting point of the sand to a temperature where crude, low quality glass could form. At some later time, some genius of ancient times realized that the glass found in the remains of such fires might be produced deliberately, and discovered the combination of materials which lead to the formation of the first commercial glass. The first crude man-made glasses were used to produce beads, or to shape into tools requiring sharp edges. According to Sir W.M.Flinders, the earliest pure glass was found in Egypt 700 B.C.and brought probably from Asia [14]. Eventually, methods for production of controlled shapes were developed. Bottles were produced by winding glass ribbons around a mould of compacted sand. Eventually, the concept of molding and pressing jars and bottles replaced the earlier methods and the quality of the glassware improved. In Roman times, it was used in windows. One also find glass sculptures in so many art museums and the stained glass windows of the cathedrals which are the examples of old glass technology and our heritage of glass applications.
It was a time then to produce glasses which were reasonably transparent, flawless and bobble less quality glass. This leads to the invention of glass blowing around the first century B.C. generated a greatly expanded range of applications for glasses. The quality of glass jars and bottles improved dramatically, glass drinking vessels became popular, and the first clear sheet glass became available; which eventually allowed the construction of buildings with enclosed windows. Colored glasses came into common use, with techniques for production of many colors regarded as family secrets, to be passed on from generation to generation of artisans. The method for producing red glasses by inclusion of gold in the melt was discovered. The combination of the discovery of many new colorants with the invention of glass blowing eventually lead to the magnificent stained glass windows of so many of the great cathedrals of Europe and the Near East.

In addition, there is a list of the few transparent natural solids includes diamonds, emeralds, rubies, and many other precious and semi-precious stones. It is difficult to think of a naturally transparent solid which is not highly valued for its transparency and brilliance. Our heritage as humans would seem to provide a bias toward placing a high value on such objects. We are still fascinated by naturally occurring “bright, shiny glassy objects.”

1.3 Synthesis of Glasses, Melting and Processing Techniques

Although, glasses can be made by a wide variety of methods, the vast majority are still produced by melting of batch components at an elevated temperature[15]. This procedure always involves the selection of raw materials, calculation of the relative proportions of each to use in the batch, weighing and mixing these materials to provide a homogeneous starting material. In this process, these raw materials undergo a series of chemical and physical changes. This melt require further processing, like the removal of impurities and bubbles as well as heat treatments to remove stresses and to produce glasses strengthened by thermal tempering. The common compounds and their compositions used to produce glasses are listed in Table 1. The gravimetric factors, of these compounds which allow calculation of the desired glass are also listed in this table.
Table 1. The common compounds and their compositions used to produce different glasses

<table>
<thead>
<tr>
<th>Name of the compound</th>
<th>Chemical Formula and composition</th>
<th>Gravimetric factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alumina</td>
<td>Al₂O₃</td>
<td>Al₂O₃=1.00</td>
</tr>
<tr>
<td>Lime Stone (Calcite)</td>
<td>CaCO₃</td>
<td>CaO =1.78</td>
</tr>
<tr>
<td>Lime</td>
<td>CaO</td>
<td>CaO = 1.00</td>
</tr>
<tr>
<td>Gypsum</td>
<td>CaSO₄·2H₂O</td>
<td>CaO = 3.07</td>
</tr>
<tr>
<td>Dolomite</td>
<td>CaCO₃·MgCO₃</td>
<td>CaO = 3.29, MgO =4.58</td>
</tr>
<tr>
<td>Caustic Potash</td>
<td>KOH</td>
<td>K₂O =1.14</td>
</tr>
<tr>
<td>Caustic Soda</td>
<td>NaOH</td>
<td>Na₂O =1.29</td>
</tr>
<tr>
<td>Boric acid</td>
<td>B₂O₅·3H₂O</td>
<td>B₂O₃ =1.78</td>
</tr>
<tr>
<td>Borax</td>
<td>Na₂O·2B₂O₃·10H₂O</td>
<td>Na₂O = 6.14, B₂O₃ = 2.74</td>
</tr>
<tr>
<td>Anhydrous borax</td>
<td>Na₂O·2B₂O₃</td>
<td>Na₂O = 6.14, B₂O₃ =1.45</td>
</tr>
</tbody>
</table>

The batch materials can be divided into five categories on the basis of their role in the process of glass formation that is, glassformer, flux, property modifier, colorant, and fining agent. The same compound may be classified into different categories when used for different purposes. Alumina, for example, serves as a glassformer in aluminate glasses, but is considered a property modifier in most silicate glasses. The most essential component of any glass batch is always the glassformer. Every glass contains one or more components which serve as the primary source of the structure. While these components are commonly designated as glassformers, 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 glassformer 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[16].
Silica itself forms an excellent glass with a wide range of applications, but it has high melting temperature (> 2000 °C) required to produce vitreous silica. Production of silicate glasses require the addition of a compound to reduce the processing temperature to within practical limits, e.g. < 1600 °C. Such materials are known as flux. The most common fluxes are the alkali oxides, especially Na₂O (soda) and PbO. The lead oxide PbO, which is an excellent flux and especially useful in dissolving any refractory or other impurity particles which might otherwise result in flaws in the final glass. Also, addition of fluxes to silica lead to decreased cost of glass formation [17].

The addition of large amounts of alkali oxides results in serious degradation in many properties. In particular, the chemical durability of silicate glasses containing large concentrations of alkali oxides is degraded to the point where they can no longer be used for containers, windows, or insulation fibres. The degradation in properties is usually countered by addition of compounds called property modifiers. Which include the alkaline earth and transition metal oxides, and, most importantly, aluminium oxide (alumina) is used as a property modifier. The property modifiers are usually added in lesser quantities than the fluxes, their use does not lead to excessively high processing temperatures. They also improve many of the properties of the resulting glasses. The properties are thus modified, or adjusted, by careful control of the amount and concentration of these oxides to obtain precisely the desired results.

Colorants are the oxides used to control the colour of the glass. Colorants are oxides of either the 3d transition metals or the 4f rare earths. Gold and silver are also used to produce colours by formation of colloids in glasses. Colorants are only used if control of the colour of the glass is desired, and are usually added in small quantities. Iron oxides, which are common impurities in the sands used to produce commercial silicate glasses, also act as colorants in many products[18].

Finally, fining agents are added to glass to remove of bubbles from the melt. Fining agents include the arsenic and antimony oxides, potassium and sodium nitrates, NaCl, fluorides such as CaF₂, NaF, and Na₃AlF₆ and a number of sulfates. These materials are usually present in very small quantities (< 1 wt%), and are usually added in such a way that they have only minor effects on the properties of the final glasses[19].
1.3.1. Compositional nomenclature

Conventionally, glass compositions were expressed in terms of weight percentages of the oxide components. A composition for a *soda-lime-silicate* glass might thus be given as 15% soda, 10% lime, and 75% silica. It is assumed that the percentages are based on weights of each component, and that soda is Na$_2$O and lime is CaO, while use of a weight fraction basis simplifies preparation of batches. On the other hand, use of a molar fraction or percentage basis, while very useful in understanding compositional effects. In either case, oxide formulations suggest that the components of the glass somehow exist as distinct, separate oxides in the melt or glass, which is certainly not the case. A glass containing 40 atom% arsenic and 60 atom% sulphur, for example, might be designated as either As$_2$S$_3$, As$_{40}$S$_{60}$, or As$_{0.4}$S$_{0.6}$.

Consider, for example, the general formula $x$Li$_2$O-(100-$x$)SiO$_2$ where glasses can be made with $x$ having any value between 0 and 40. If we use the atom% approach, this series of glasses would be described by the general formula Li$_{2x}$Si$_{(100-x)}$O$_{200-x}$ specific compositions, *e.g.*, $x = 33.33$, can be expressed as either 33.33Li$_2$O - 66.67SiO$_2$ or as Li$_{66.7}$Si$_{66.7}$O$_{166.7}$ or with reduction to simplified forms, as either Li$_2$O-2SiO$_2$ or as Li$_2$Si$_2$O$_3$ composition. The oxide formulation based on mol% of each oxide or carbonate compounds. Selecting of raw materials, calculation of each material, weighing and mixing of powders and occasionally liquids comes as the part of batching.

1.3.2 Batch calculations

Glass batch calculations can vary with the composition and the raw materials used to prepare the mixture. Batches containing only oxides in their exact state and expressed by the glass formula 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 calculations. All batch calculations follow the following procedure.

1. Determine the weight fraction of each component required to produce the desired molar composition and multiply the mole fraction of each component by the molecular weight of that component.

2. The total of these contributions determines the molecular weight of the glass.
3. Then divide each individual contribution by the molecular weight of the glass to determine the weight fraction of each component.

4. Finally, multiply the weight fraction of each component by the amount 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 [20].

Example 1
Glass composition: 65CaO-35Al₂O₃
Molecular weights of components (in g mol⁻¹):
CaO = 56.08 and Al₂O₃ = 101.96
Molecular wt of glass: (0.65 x 56.08) + (0.35 x 101.96) = 72.14 g mol⁻¹
Weight fraction of each component:
CaO = (0.65 x 56.08) / 72.14 = 0.505
Al₂O₃ = (0.35 x 101.96) / 72.14 = 0.495
For 100 grams of glass: CaO = 0.505 x 100 = 50.5 g
Al₂O₃ = 0.495 x 100 = 49.5 g

Example 2
Glass composition: 20Na₂O-80SiO₂
Molecular weights of components (in g mol⁻¹):
Na₂O = 61.98 and SiO₂ = 60.09
Molecular wt of glass: (0.20 x 61.98) + (0.80 x 60.09) = 60.47 g mol⁻¹
Weight fraction of each component:
Na₂O = (0.20 x 61.98) / 60.47 = 0.205
SiO₂ = (0.80 x 60.09) / 60.47 = 0.795
For 100 grams of glass:
Na₂O = 0.205 x 100 = 20.5 g
SiO₂ = 0.795 x 100 = 79.5 g
Sodium oxide is not stable in air, so we must use a batch component such as Na₂CO₃ which yields Na₂O after decomposition. It is necessary to multiply the desired quantity of Na₂O by the gravimetric factor for Na₂CO₃ (1.71), to obtain the weight of Na₂CO₃ (35.05 g) to be used to yield the desired 20.5 g of Na₂O.

Gravimetric factor (Gᵢ) = molar weight of raw material/molar weight of oxide.
Weight of raw material = weight of oxide \( \times G_f \)

**Example 3**

Glass composition: 20Na\(_2\)O - 5 Al\(_2\)O\(_3\) - 75 SiO\(_2\)

Molecular weights of components (in g mol\(^{-1}\)):

Na\(_2\)O = 61.98, Al\(_2\)O\(_3\) = 101.96, SiO\(_2\) = 60.09

Molecular wt of glass:

\[(0.20 \times 61.98) + (0.05 \times 101.96) + (0.75 \times 60.09) = 62.56 \text{ g mol}^{-1}\]

Weight fraction of each component:

Na\(_2\)O = \((0.20 \times 61.98) / 62.56 = 0.198\)

Al\(_2\)O\(_3\) = \((0.05 \times 101.96) / 62.56 = 0.0815\)

SiO\(_2\) = \((0.75 \times 60.09) / 62.56 = 0.720\)

For 100 grams of glass:

Na\(_2\)O = 0.198 x 100 = 19.8 g

Al\(_2\)O\(_3\) = 0.0815 x 100 = 8.15 g

SiO\(_2\) = 0.720 x 100 = 72.0 g

If we use albite feldspar as the source of alumina, we also obtain some of the soda and silica needed for the batch. Using the gravimetric factors for albite, we find that 41.89 g of albite will yield the required 8.15 g of alumina. This amount of albite also yields 4.95 g of soda and 28.89 g of silica (divide the weight of albite by the gravimetric factor to find the yield for a given amount of albite). After subtracting these quantities from the required amounts of soda and sand, we find that we must add 14.85 g of soda and 43.11 g of sand. If we use Na\(_2\)CO\(_3\) as the source of the additional soda, we will require 14.85 x 1.71 = 25.39 g of Na\(_2\)CO\(_3\)

Final Batch: Na\(_2\)CO\(_3\) = 25.39 g

Albite = 41.89 g

Sand = 43.11 g

**1.4: A brief account of glasses used in the experiments**

**1.4.1: Fused Silica**

Fused quartz is a non crystalline form of silicon dioxide (SiO\(_2\)), which is also called silica. The crystalline form of this material is called quartz and naturally occurring form of fused quartz is a rock known as quartzite. An increase in pressure and
temperature causes the quartz crystals within the rock to fuse together. An important distinction is that the quartz in quartzite is not an amorphous form [21].

Fused quartz is manufactured by melting naturally occurring quartz crystals of high purity at approximately 2000 °C using either an electrically heated furnace (electrically fused) or a gas/oxygen-fuelled furnace (flame fused). The other way to form the glass is by the traditional 'melt–quench' methods (heating the material to melting temperatures, then rapidly cooling to the solid glass phase), is called as 'vitreous' as in 'vitreous silica'. The term 'vitreous' is synonymous with 'glass', when used in the melt–quench context [22].

Vitrious silica is classified into two types (i) Fused quartz produced by melting natural quartz powder and (ii) Synthetic fused silica synthesized chemically from silicon tetrachloride or other appropriate silicon compounds. Fused quartz is further classified into four types by their OH content, when no OH content is present it is called Type-I silica. It is produced by melting natural quartz powder in an electric furnace. When OH content is 150-250 ppm it is called Type-II silica and it is produced by fusing the quartz powder in a hydrogen oxygen flame. Type-III fused silica is synthesized by flame hydrolysis of SiCl₄ in a hydrogen oxygen flame containing 1000 ppm of OH, and type IV silica is produced by chemical vapour deposition CVD and contains less than 5 ppm of OH [23].

Synthetic fused silica is made from a silicon-rich chemical precursor usually using a continuous flame hydrolysis process which involves chemical gasification of silicon, oxidation of this gas to silicon dioxide, and thermal fusion of the resulting fumes. This results in a transparent glass with an ultra-high purity and improved optical transmission in the ultraviolet region. One common method involves adding silicon tetrachloride to a hydrogen–oxygen flame, however use of this precursor results in environmentally unfriendly by-products including chlorine and hydrochloric acid. To eliminate these by-products, new processes have been developed, which has also resulted in a higher purity fused silica with further improved deep ultraviolet transmission [24].

Though quartz glass in theory contains only silicon and oxygen, industrially produced quartz glass / fused silica contains impurities. The typical impurities depend
on the starting material and the process used. The most dominant impurities are aluminium and titanium.

**Structure :-**

![Figure 1.1: The amorphous structure of glassy silica in two dimensions](image_url)

The amorphous structure of glassy silica (SiO$_2$) in two-dimensions is as shown in figure 1.1. It shows that there is no long-range order but there is local ordering with respect to the tetrahedral arrangement of oxygen (O) atoms around the silicon (Si) atoms. The fourth oxygen atom is bonded to each silicon atom, either behind the plane of the screen or in front of it, these atoms are shown in the adjacent figure [25].

The structure of quartz is readily suggested by Zachariasen using the network structural rules. Diffraction studies indicate that the shortest Si-O distance in this structure is 0.162 nm and that the shortest O-O distance is equal to 0.265 nm. These distances are consistent with those found within silicon-oxygen tetrahedra in crystalline forms of silica and in silicate minerals. These distances exhibit the basic tetrahedral building block. The next distance in the structure, is silicon atoms in the centers of linked tetrahedra, however, there is specific distribution in Si-O-Si angles. The maximum distribution occurs at 144° with a range in angles from 120° to 180° [26]. It has regions of highly stressed bonds and defects such as oxygen vacancies, represented by Si-Si bonds, and peroxy defects represented by Si-O-O-Si bonds. Additional defects occur at impurity sites, especially those associated with bound hydrogen species such as SiOH and SiH [27].
Quartz has a high melting point because of strong covalent bonds with oxygen and impurities. Because of its strengthened covalent bonds and high melting point (compared to ordinary glass), fused silica is used as an envelope for halogen lamps, which must operate at a high envelope temperature to achieve their combination of high brightness for long time. Specially prepared fused silica is the key starting material used to make optical fiber for telecommunications. The combination of strength, thermal stability, and UV transparency makes it an excellent substrate for projection masks for photolithography. The optical and thermal properties of fused quartz are advanced to those of other types of glass due to its purity. For these reasons, it is used in semiconductor technology and laboratory equipment. It has better ultraviolet transmission than all the other glasses, and so is used to make lenses and other optics for the ultraviolet spectrum. Its low coefficient of thermal expansion also makes it a useful material for precision mirror substrates [28].

1.4.2: Soda Lime Glass

Soda-lime glass is the most common form of glass produced. It is consist of about 70% silica (silicon dioxide), 15% soda (sodium oxide), and 9% lime (calcium oxide), with much smaller amounts of various other compounds. The soda serves as a flux to lower the temperature at which the silica melts, and the lime acts as a stabilizer for the silica [29]. Soda-lime glass is inexpensive, chemically stable, reasonably hard, and extremely workable, because it can be resoftened a number of times if necessary to finish an article. These qualities make it suitable for manufacturing a wide array of glass products, including light bulbs, windowpanes, bottles, and art objects.

![Two dimensional structure of Soda lime glass](image)

Figure 1.2: Two dimensional structure of Soda lime glass
Soda lime glass, contains large concentrations of sodium oxides, can be easily produced by melting silica with sodium carbonates. Glasses containing less than 10 mol% sodium oxide are considerably more difficult to melt. Literature shows that the addition of any sodium oxide to silica to form a binary glass results in major reductions in the viscosity of the melt (many orders of magnitude) and the glass transformation temperature goes low (= 500 K)[30]. The densities and refractive indices and the thermal expansion coefficients of the glasses increase with increasing sodium oxide concentration, and with the atomic number / mass of the particular sodium present. The Two dimensional structure of Soda lime glass is shown in figure 1.2 and the atomic arrangement of soda lime glass is shown in figure 1.3. The electrical conductivity of the sodium silicate glasses, which is due to diffusion of alkali ions, increases by orders of magnitude with increasing sodium oxide content [31].

These trends in properties are due to the formation of non-bridging oxygen, which increases the viscosity of the melt. The structure can be viewed as a network of silicon-oxygen tetrahedra with occasional breaks in connectivity due to the non-bridging oxygen. Each nonbridging oxygen must be associated with a nearby sodium ion to maintain local charge neutrality. These sodium ions occupy the interstices in the network, reducing the unoccupied free volume of the structure. The concentration of non-bridging oxygen increases, and the concentration of bridging oxygen decreases, directly in proportion to the sodium oxide content, until a network can no longer be maintained [32].

The glass used in the experiment has following composition

60 SiO$_2$ + 22 Na$_2$O + 12 K$_2$O + 2MgO + 2CaO + 2 TiO$_2$

In this case SiO$_2$ is used as a Glass Former, (Na$_2$O + K$_2$O) used as a Network Modifier (MgO + CaO) used as a Stabilizer and TiO$_2$ is used as a R.I. improver. The batch calculations for above glass is shown in Table 2.
Table 2: Batch calculations of the compounds used in soda lime glass

<table>
<thead>
<tr>
<th>Name of compound</th>
<th>Formula</th>
<th>% by weight</th>
<th>Batch calculations (gms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica</td>
<td>SiO$_2$</td>
<td>60%</td>
<td>12</td>
</tr>
<tr>
<td>Sodium carbonate</td>
<td>Na$_2$CO$_3$</td>
<td>22%</td>
<td>8.0511</td>
</tr>
<tr>
<td>Potassium carbonate</td>
<td>K$_2$CO$_3$</td>
<td>12%</td>
<td>2.2598</td>
</tr>
<tr>
<td>Magnesium carbonate</td>
<td>MgCO$_3$</td>
<td>2%</td>
<td>0.5136</td>
</tr>
<tr>
<td>Calcium carbonate</td>
<td>CaCO$_3$</td>
<td>2%</td>
<td>0.6145</td>
</tr>
<tr>
<td>Titanium dioxide</td>
<td>TiO$_2$</td>
<td>2%</td>
<td>0.4</td>
</tr>
</tbody>
</table>

The melting temperature of the glass is 1250°C annealed to the temperature 600°C.

1.4.3: Borosilicate glass

Borosilicate glass is widely used for laboratory glassware because it offers a high level of resistance to attack from water, acids, salt solutions, organic solvents and halogens. Its resistance to alkaline solutions is moderate and strong alkaline solutions cause rapid corrosion of the glass, like Hydrofluoric acid. Borosilicate glass has excellent thermal properties with its low coefficient of expansion and high softening point[33].

Borosilicate glasses are produced in a wide range of compositions. The compositions of several common commercial borosilicate glasses are as follows:

SiO$_2$ = 50-82% , (Na$_2$O + K$_2$O) = 2-5% B$_2$O$_3$ = 10-25% TiO$_2$ = 1-10%

It consists of two vitreous phases. One of these phases is a very silica-rich glass, while the other phase contains almost all of the alkali and boric oxides. As a result, the properties of these glasses also vary over a wide range in accordance with the composition and proportion. They have better thermal shock resistance, chemical durability and higher electrical resistivity than soda-lime glass. The improvement in thermal shock resistance is due to the lower thermal expansion coefficient. The improved chemical durability and higher electrical resistivity of these glasses is due to the absence of mobile monovalent ions. Addition of B$_2$O$_3$ lowers the immiscibility temperature and TiO$_2$ allows glass to avoid visible light scattering[34]. The composition used for the experiment is

$$60 \text{SiO}_2 + 15 \text{B}_2\text{O}_3 + 7 \text{Na}_2\text{O}^+ + 12 \text{K}_2\text{O} + 2\text{MgO} + 2\text{CaO} + 2\text{TiO}_2$$
The batch calculations of the compounds used in this glass are tabulated in Table 3.

**Table 3: Batch calculations of the compounds used in borosilicate glass**

<table>
<thead>
<tr>
<th>Name of compound</th>
<th>Formula</th>
<th>% by weight</th>
<th>Batch calculations (gms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica</td>
<td>SiO₂</td>
<td>60%</td>
<td>12</td>
</tr>
<tr>
<td>Borax</td>
<td>B₂O₃</td>
<td>15%</td>
<td>3</td>
</tr>
<tr>
<td>Sodium carbonate</td>
<td>Na₂CO₃</td>
<td>7%</td>
<td>5.501</td>
</tr>
<tr>
<td>Potassium carbonate</td>
<td>K₂CO₃</td>
<td>12%</td>
<td>2.145</td>
</tr>
<tr>
<td>Magnesium carbonate</td>
<td>MgCO₃</td>
<td>2%</td>
<td>0.5136</td>
</tr>
<tr>
<td>Calcium carbonate</td>
<td>CaCO₃</td>
<td>2%</td>
<td>0.604</td>
</tr>
<tr>
<td>Titanium dioxide</td>
<td>TiO₂</td>
<td>2%</td>
<td>0.4</td>
</tr>
</tbody>
</table>

Melting Temperature of this glass is 1100 °C and Annealed to the temperature of 600°C

**1.5: Interaction of Radiation with Glasses**

Fused silica is considered to be a regular tetrahedron with each Si atom at the center of a tetrahedron and four oxygen atoms at the vertexes forming O-Si-O angles of 109.5° (fig.1.4). Each oxygen atom binds two silicon atoms and bridges two tetrahedra.
and a point defect can be visualized as a local distortion of the atomic structure caused by a bond rupture, an over or undercoordinated atom, the presence of an impurity atom (homo or heterovalent substitution, interstitial,...), etc. [35]. These defects are usually indicated as intrinsic when they are due to irregular arrangements of the crystal atoms (Si and O for SiO$_2$), and extrinsic when they are related. When Na$_2$O is added into SiO$_2$, the oxygen atom from Na$_2$O attaches itself to Si atom and breaks one link of Si-O-Si bond. This makes two oxygen atoms bounded to only one Si with two Na atoms in the nearby interstices to provide charge neutrality. These are called nonbridging oxygen atoms or oxygen half ions.

The study of the point defects are made on the basis of their electronic configuration: those having unpaired electrons constitute paramagnetic defects, and the others are the diamagnetic defects. Both typologies could in principle be characterized by optical activities as absorption and emission bands. The paramagnetic defects have a further feature since they are responsible for a non-zero magnetic moment, having unpaired electrons, and are responsible for the magnetic resonance absorption. Many extrinsic defects in amorphous silica are associated to metallic, halogen and substitutional elements trapped in the starting materials or involved in the manufacturing procedure[36]

1.5.1: Mechanism of Interaction of Different Radiations with Glasses in Brief

When the radiation such as X-rays, electrons, gamma rays, heavy ions etc are incident on the glass, the non bridging oxygen atoms are strongly affected by the radiations and yields radiation damage in the glass. The nature of radiation damage in glass depends on the type of the radiation (i.e. ionizing versus particle) and energy of radiation impinging on the material. The Irradiation usually results in the occurrence of following processes.
(1) Atomic displacement by momentum and energy transfer.
(2) Ionization and charge trapping.

The relative contributions to the net damage depend on the type and energy of radiation.

1.5.1.1: Atomic displacement by momentum and energy transfer:

Figure 1.5: Sodalime glass before irradiation

Figure 1.6: Sodalime glass before, during and after irradiation

When high energy electrons enter the glass, they transfer most of their momentum and dissipate their energy in the structure and carry out ionisation and excitation of atoms in the glass structure. They come to rest at some depth and produce net negative charge. The metallic ions present in the glass structure are then neutralized by these electrons and produce color centers. This process is called an electron browning and the surrounding region is called brown region.
1.5.1.2: Ionization and charge trapping

When glasses are subjected only to ionizing radiation, the principal effects will result from electronic processes. Electrons are excited to leave their normal position and move through the glass network. For each ionizing electron one electron deficient region or hole is formed. Absorption bands observed are due to centers formed by electron trapping or hole trapping. The most general description of a material capable of supporting a color center is given by Nassau [37]. Two kinds of precursors are needed: a hole precursor A+, which can lose an electron. After absorbing irradiation, to form a hole center A+ (HC); and an electron precursor B which can gain the electron lost from A to form the electron center B (EC). Precursors can be pre-existing defects and/or they can be created by atomic displacements or radiolytic processes derived from high energy radiation. Either A+ or B+ can be the color center itself that absorbs light, or even both can do so. On heating, the electron is released from B and returns to A+, thus restoring the colorless state of A plus B.

Most ordinary glasses yield a yellow to dark brown color on irradiation. The color is the result of the redistribution of electrons due to hole centers (HC) with broad absorption bands in the visible range. The absorption bands in the UV range are due to electron centers (EC).

It is possible to create many different types of electron and hole centers by trapping or removing an electron from impurities and defects. The induced absorption spectra are the superposition of a large number of individual absorption bands. Examples of the point defects are: the vacancy (an atom is removed from its “reticular” position), the interstitial (an atom is in a non-reticular position) and the valence defect (a bond Si-O is broken) [38]. In particular, among the intrinsic defects in silica we found the neutral oxygen vacancy [39] O≡Si-Si≡O, the peroxy bridge ≡O-Si-O-O-Si≡O, the non-bridging oxygen O≡Si-O¹ (NBOHC), the tricoordinated silicon O≡Si¹ (usually named E¹ center), the twofold coordinated silicon O=Si². Some of these defects are pictorially reported in figure 1.7. It is worth to note that these defects may present several charge states due to electron or hole trapping. Many extrinsic defects in amorphous silica are associated to metallic, halogen and substitutional elements trapped in the starting materials or involved in the manufacturing procedure.
Gamma irradiation leads to a compacting of the glass network. A decrease in the band gap and a red shift of the cutoff wavelength can be linked to the increased electron density after irradiation. The vibrational spectra indicate major change in the structural units before and after irradiation and supports the compacting and cross linking of the network by formation of metaborate, pyroborate and orthoborate groups. Gamma irradiation leads to changes in the structure and to irradiation effects, depending on the composition and structure of the glass. Vibrational spectra indicate the formation of new broad bands. These results is useful for the preparation of radiation-hard glass materials.

High energy swift heavy ion (SHI) makes elastic collisions with atoms of the solid and loses its energy through electronic processes called electronic energy loss (S_e), and nuclear processes called nuclear energy loss (S_n) [40,41]. Especially in glass materials, a point defects, defects clusters and ion tracks, can be formed along the ion projected range and at the end of the trajectory when passed through it. It has been suggested that the defects formation in silica glass under high energy heavy ions, irradiation is highly related to the electronic energy losses [42]. However, small effect of nuclear energy loss has also been observed. Moreover, an absorption
band can be induced in the silica glass mainly by X-ray, gamma ray and electron irradiation. The energies and the full widths at half-maximum (FWHM) of most of these bands are known.

1.6 : The Radiation Sources Used
1.6.1: Electron Source (Race-Track Microtron)

There are several types of electron accelerators used for various basic and applied research works. The ‘Race-Track Microtron’ is an electron accelerator. The schematic diagram of the Race-Track Microtron of Pune University is shown in Figure 1.8. In this Race-Track Microtron instead of one circular magnet four sector magnets are used. The Pune University Race-Track Microtron has a single cavity, which is powered by 1 MW pulsed Magnetron.

![Figure 1.8 (a): Schematic diagram showing the principle acceleration in “Race-Track Microtron”. 1-Electron gun, 2-Microwave cavity, 3-Sector magnets, 4-magnetic gap and 5-Extraction port. (b) : Photograph of Microtron (c) : Control Panel](image)

Figure 1.8 (a): Schematic diagram showing the principle acceleration in “Race-Track Microtron”. 1-Electron gun, 2-Microwave cavity, 3-Sector magnets, 4-magnetic gap and 5-Extraction port. (b) : Photograph of Microtron (c) : Control Panel
The magnetron is operated at 2.8 MHz frequency. A vacuum of 1 X 10^-6 Torr is maintained in the system. The electrons emitted by the electron gun are having 25 KeV energy, these electrons are then injected into the cavity. For electron, passing through the cavity the maximum energy gain per pass through the cavity is 1 MeV. All the operational parameters of the Microtron such as injection energy, radio frequency, drift space length and magnetic field in the sector electromagnet are adjusted in such a way that the beam can come out from the extraction port. The above parameters are controlled and monitored from the control panel. The beam is extracted from 8th orbit and thereby gives 8 MeV electrons beam. The pulsed duration is about 1.6 to 2 μs with repetition frequency of 50 PPS. Using radio frequency these electrons are then accelerated. Adequate shielding is provided with the help of lead blocks and concrete blocks. A view of the Race-Track Microtron and the control panel are shown in the Figure 1.8. This machine can be operated in the energy range from 0.5 to 1 MeV and 6 to 8 MeV.

1.6.2 : Co-60 Gamma Source
Cobalt-60 (Co-60) is a radioactive isotope of cobalt, with a half life of 5.27 years. Co-60 decays by negative beta decay to the stable isotope Nickel-60 (60Ni). In the process of decay, Co-60 emits one electron with energy of up to 315 keV and then two gamma rays with energies of 1.17 and 1.33 MeV, respectively. The decay scheme Co-60 is shown below in figure 1.9

![Figure 1.9: Decay Scheme of Co-60; Emission of Gamma Rays](image)
1.6.2.1 Gamma Radiation: Gamma rays are the radiations having shortest wavelength ((below about 10 picometer) and highest energy (around 100 keV) in the electromagnetic spectrum. These are the most energetic amongst all the electromagnetic radiations. Due to shortest wavelength gamma rays have the greatest ability to penetrate through any gap, even a subatomic one.

1.6.2.2: Co-60 Gamma Facility in Department of Chemistry, University of Pune: In this work, the gamma ray facility was used from the Department of Chemistry, University of Pune. The geometry of pencils in the source is arranged in such a fashion that it provides uniform dose throughout the irradiation cavity. The design of the source and photograph is shown in figure 1.10

1.6.3: 15 UD Pelletron: Heavy Ions

The ‘Pelletron’ facility of Nuclear Science Center, New Delhi was used for irradiating the glass samples with swift heavy ions. A sketch of Pelletron is shown in the Figure 1.11. The availability of various ion beams with good energy resolution makes this accelerator extensively versatile. This accelerator is capable of accelerating almost any ion beam from hydrogen to uranium with energies from few tens of MeV to hundreds of MeV. This accelerator is a vertical tandem accelerator of
~ 26.5 m in height and of ~ 5.5 m in diameter. As shown in Figure 1.11, the main part ‘terminal’ of the accelerator is situated in an insulating tank filled with sulphur hexafluoride gas. Inside this tank, at the center a high voltage terminal, of 1.52 m in diameter and of 3.61 m of height, is fixed. This terminal can be charged to high voltage, which can be varied from 4 MV to 16 MV. The 15 UD Pelletron accelerator consists of ions source, focusing lenses, mass analyzer, accelerating column, irradiation chamber, arrangement for ion dose measurement, high vacuum systems and sample displacement facility. The vacuum in the Pelletron beam line is maintained around $10^{-8}$ Torr. Initially negative ions are produced and pre-accelerated to few hundreds of keV and mass analyzed before injecting into the high accelerating column. The negative ions get accelerated while traveling through the accelerating tube from the column top up to the top of the terminal. While passing through the terminal these negative ions also passes through the stripper, which removes some electrons from the negative ions, thus transforming them into positive ions.

![Figure- 1.11: Schematic diagram showing the principal of acceleration of ions in “Pelletron” and photograph](image)

These positive ions are then repelled away from the highly positive terminal and are get accelerated towards the ground potential, at the bottom of the tank. In this manner the same terminal voltage is used twice for accelerating the ion. After leaving from the accelerating column, the ions of particular energy is selected and sent to a horizontal plane magnet known as switching magnet. This magnet diverts the ion beam into various beam lines for experiments in the beam hall. This entire accelerator is computer controlled and operated from the control room. The energy of the
accelerated ion available depends on the charge state \((q)\) of the ion and the terminal potential \(V_t\).

\[
E = E_{\text{inj}} + (q + 1) V_t \quad \text{MeV} \\
\text{............(1.1)}
\]

Where

- \(V\) = the terminal voltage in MV
- \(q\) = charge state of the positive ion
- \(E_{\text{inj}}\) = energy of the injected ion

**1.7: Characterization Techniques**

The radiation induced damages and modifications in the glasses have been investigated using several techniques such as, UV-Visible spectroscopy, FTIR, Energy Dispersive Spectroscopy (EDS), X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Photoluminescence Spectroscopy (PL), Raman Spectroscopy, etc. The following are the details about the techniques.

**1.7.1: UV-Visible Spectroscopy:**

(a) **Basic Principles:** The absorption in UV-Visible and IR regions are governed by Beer- Lambert’s law which is given by

\[
A = \log \frac{I_o}{I} = \epsilon c l \\
\text{..................(1.2)}
\]

Where

- \(A\) = Absorbance = \(\log(I_o/I)\)
- \(I_o\) = intensity if incident light
- \(I\) = intensity of transmitted light
- \(\epsilon\) = molar extinction coefficient = molar absorptivity
- \(c\) = molar concentration of the solute
- \(l\) = length of the sample cell

The molar extinction coefficient is directly proportional to probability of transition. It may be noted that infrared vibrations cause only excitation of various vibrations in molecules, however, the interaction of UV-Visible radiation involves excitation or deexcitation of electrons in outer orbits. Most of the organic species are transparent to
electromagnetic radiation in UV-Visible region. However, the UV-Visible spectroscopy along with IR spectroscopy can furnish useful information about glass. The UV-Visible transitions occur in the energy range 125 to 650 KJ/mole. The interaction of UV-visible part of radiation with organic species such as glass involves promotion of electrons in outer orbits from lower energy levels to higher ones. When a glass is exposed to continuous range of radiation in UV-Visible region, a part of this radiation may be absorbed, as result of which the molecule is raised from ground state to excited state [43].

This is a quantum process. In general the absorption in UV-Visible regime corresponds to transitions from occupied levels (such as $\sigma$, $\pi$, n orbitals) to unoccupied levels (such as $\sigma^*$, $\pi^*$). The excited states corresponding to $\sigma$, $\pi$ and n are usually vacant and are represented by $\sigma^*$, $\pi^*$ orbitals. The electrons in n orbitals are non bonding electrons and hence there is no excited state for them. $\sigma^*$, $\pi^*$ are called are anti-bonding orbitals. The most probable transition is from highest occupied molecular orbital to lowest unoccupied molecular orbital. The electrons in $\sigma$ bond are tightly bound and hence excitation from $\sigma$ bond requires large energy, hence these transitions occur at very short wavelengths. The other transitions in the UV-Visible regime are excitation of charge transfer electrons and electrons in d and f orbitals. The transitions in UV-Visible region are schematically shown in figure 1.12. A few transitions are forbidden due to selection rules. The transitions in UV-Visible region are electronic, while those in IR region are vibrational [44].

![Figure 1.12: Transitions in UV-Visible region](image)

(b) The UV-Visible Spectrophotometer: The UV-Visible spectrophotometer consists of sources of UV (deuterium) and visible (tungsten) radiations, monochromator (diffraction grating), sample cell (quartz), detector (photodiode) and a computer. A schematic diagram and the photograph of the UV-Visible spectrophotometer used in the present work are
shown in figure 1.13. The UV-Visible spectrometer used in the present work was Perkin Elmer Lambda-950 UV-Visible spectrometer. The spectra were recorded in the range 200-700nm.

**Figure 1.13 : The schematic and photograph of UV-Visible spectrometer**

Usually, UV-Visible spectrometers consist of two beams, one for sample and another for reference. The instrument plots the graph of absorbance Vs wavelength, which is called as UV-Visible spectrum. UV-Visible spectra are generally plotted in the region 200-700 nm. A group of atoms or a chemical species that absorbs in a specific region of UV-Visible spectrum is called as a chromophore. The substitution of the atoms in the chromophore by other chemical species results in the modification in the UV-Visible spectrum. This modification may be a shift in \( \lambda_{\text{max}} \) or change in the absorbance. The \( \lambda_{\text{max}} \) shows a red shift after conjugation. The role of chromophore and conjugated systems is very important in UV-Visible spectroscopy. Usually presence of chromophores and conjugated systems imparts colors to the organic species. Generally, two parameters namely wavelength corresponding to maximum absorption (absorption edge, \( \lambda_g \)) and the optical band gap (\( E_g = h \nu / \lambda_g \)) are considered important while analyzing the UV-Visible spectra [45]. The band gap is usually calculated using Tauc’s expression which is given by

\[
W^2c_2 = (h \nu - E_g)^2 \quad \text{.........(1.3)}
\]

UV-Visible spectroscopy is also be used to calculate an optical band gap, Urbach energy and the defect concentration of the irradiated silica glass. The plot of \( (\alpha h \nu)^{1/2} \) against \( h \nu \) is used to calculate optical band gap (\( \alpha \) is called absorption coefficient, \( h \nu \))
is the energy of the incident photon) and is determined by the extrapolation of the linear portion of this graph to \((\alpha \hbar \nu)^{1/2} = 0\). Urbach law \(\alpha \hbar \nu = \alpha_0 \exp (\hbar \nu / E_0)\) is used to calculate Urbach energy \(E_0\) (\(\alpha_0\) is constant). The graph of \(\alpha\) against \(\hbar \nu\) is fitted to \(y = a \exp (b x)\) and the Urbach energy \(E_0 = 1/b\) is calculated. The changes in the parameter of the optical band gap and the Urbach energy are an indicative of the change in the structure of the glass matrix

1.7.2 : FTIR analysis

1.7.2.1: Role of Various Electromagnetic Radiations in Spectroscopy: As discussed earlier, the radiation induces several structural changes in glasses, which include ionization, excitation, breaking of bonds etc. These changes cause significant modifications in the mechanical, electrical, thermal and optical properties of glass. Spectroscopic techniques are a few of important and powerful procedures that can be used to investigate radiation induced structural changes in glass. Mainly UV (400 to 200 nm), Visible (700 to 400 nm), Infrared (2.5 to 200 nm i.e. 4000 cm\(^{-1}\) to 50 cm\(^{-1}\)) and X-rays (1 nm to 1 pm) in the electromagnetic spectrum are frequently used for spectroscopic analysis.

1.7.2.2 Basic Principles of FTIR Spectroscopy: The IR transitions occur in the energy range 8 to 40 KJ/mole. Almost any compound having covalent bonds, whether organic or inorganic, absorbs various frequencies of electromagnetic radiation in infrared region of the electromagnetic spectrum. The absorption of infrared radiation in the molecule is a quantized process. The molecules having covalent bonds can absorb those frequencies in the radiation which coincide with the natural frequency of the bond. Another condition necessary for the absorption is that the dipole moment of the bond must change with time.

The covalently bonded atoms in the molecules are in the continuous state of vibrations that occur at quantized frequencies, which are given by

\[
y = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}
\]

………………(1.4)

Where \(c\) = speed of light, \(k\) = force constant and \(\mu\) = reduced mass [46]

Each bond (such as C-H or O-H or N-H etc.) in the molecule has its own characteristic quantum frequency of vibration. If an Infrared radiation of same
frequency is incident, then it is absorbed and as a result, the corresponding vibration is increased in amplitude. The above formulae indicate that

The frequency of vibration increases with the force constant i.e. strength of the bond. Thus, the triple bonds are observed at higher frequencies than single ones.
The bonds involving heavier atoms are observed at lower frequencies than lighter ones. Thus, C-H bonds are observed at higher frequencies than C-I bonds.
The position of a bond in the IR spectrum is also affected by hybridization, resonance etc. Different molecules functional groups having different bond structures absorb different frequencies. The absorption also slightly depends upon the environment of the bond. The infrared spectrum can be considered as a fingerprint of the molecule.
The same type of absorption range applies to same type of bond. Each bond such as Si-OH, Si-O-Si, N-H, O-H, C-H, C-X, CO, C=O, C-C, C=C, C≡C, C≡N etc. has its own characteristic narrow absorption range.

Thus, presence or absence of a bond can be identified by infrared spectrum. If a particular peak is absent in the IR spectrum, then it can be certainly concluded that the corresponding functional group is absent in the sample. The molecular vibrations have different modes. The simplest modes which are infrared active are stretching (change in bond length along the bond axis) and bending (change in bond angle). However, the other relatively complicated modes of vibrations which are also infrared active are scissoring, wagging, twisting, and rocking. Further, a given mode of vibration may be symmetric or asymmetric; and it may also have overtones or combinational modes. Though rotational modes are not infrared active, their combination with above mentioned modes may give absorption in infrared region.
The frequency of absorbed IR radiation depends upon strength of bond. As stretching vibrations are stronger than rotational ones, the absorbance corresponding to stretching vibrations occur at higher energies i.e. higher wave numbers, while the peaks corresponding to rotational vibrations occur at lower energies i.e. lower wave numbers [47]. In general, stronger the bond higher is the position of corresponding peak in the FTIR spectrum. The typical positions of some important chemical bonds in the FTIR spectra are shown in Table 4.
Table -4: Assignments of infrared bonds in glasses

Positions and assignment of observed infrared absorption bands

<table>
<thead>
<tr>
<th>Peak Position ( cm⁻¹)</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Silicate chain</strong></td>
<td></td>
</tr>
<tr>
<td>1065-1095</td>
<td>Si-O-Si antisymmetric stretching of bridging oxygen within tetrahedron</td>
</tr>
<tr>
<td>940-970</td>
<td>Si-O stretching with one non bridging oxygen</td>
</tr>
<tr>
<td>860-940</td>
<td>Si-O stretching with two non bridging oxygen</td>
</tr>
<tr>
<td>460-510,600</td>
<td>Si-O-Si and O-Si-O bending mode</td>
</tr>
<tr>
<td><strong>Borate chain</strong></td>
<td></td>
</tr>
<tr>
<td>(a) BO₃ stretching</td>
<td></td>
</tr>
<tr>
<td>1420-1550</td>
<td>B-O bonda vibrations</td>
</tr>
<tr>
<td>1550-1400</td>
<td>B-O vibrations of various borate groups</td>
</tr>
<tr>
<td>1250</td>
<td></td>
</tr>
<tr>
<td>1220-1250</td>
<td>Boroxol rings, tri, tera, and pentaborate groups, pyro and other borates</td>
</tr>
<tr>
<td>(b) BO₄ stretching</td>
<td></td>
</tr>
<tr>
<td>1050</td>
<td>Tri, tera, and pentaborate</td>
</tr>
<tr>
<td>900-1000</td>
<td>Diborate</td>
</tr>
<tr>
<td>880</td>
<td>Tri, tera, and pentaborate, oxygen ridges between tera and triborate</td>
</tr>
<tr>
<td>760-770</td>
<td></td>
</tr>
<tr>
<td>(c) Other groups</td>
<td></td>
</tr>
<tr>
<td>1640</td>
<td>Molecular water</td>
</tr>
<tr>
<td>1460</td>
<td>Carbonate groups</td>
</tr>
<tr>
<td>3000-3750</td>
<td>Hydrogen, Molecular water, Sinol group (Si-OH)</td>
</tr>
</tbody>
</table>

1.7.2.3: The FTIR Spectrophotometer

The spectrometer consists of an infrared source, collimator, beam chopper, mirrors for splitting the beam into reference and sample beam, a diffraction grating, sample (gas, liquid or solid), infrared detector and a computer. A schematic diagram and the photograph of the FTIR spectrophotometer used in this work are shown in figure 1.14.
In the present work the FTIR spectrometer used was SHIMADZU FTIR 8400. The spectra were recorded in the 4000 to 400 cm\(^{-1}\) range.

In FTIR spectrometer, the IR radiation of continually varying wave number is incident on the sample and the transmitted radiation is dispersed through grating and then detected. The facility of double beam can provide a graph of relative intensity of a sample beam w.r.t. reference beam. The modern spectrometers consist of a technique called as Fourier transform, in which there is a provision to take several interferograms of the sample. A Fourier transform of these interferograms gives the spectrum with better signal to noise ratio in lesser time. FTIR spectrometers are thus more sensitive and faster than IR spectrometers. These spectrometers provide the FTIR spectrum of the sample in the typical range of 4000-350 cm\(^{-1}\). Almost all important functional groups and chemical bonds in the organic compounds can be investigated in this region. The infrared spectrometer determines the positions and relative sizes of all the absorptions, or peaks in the infrared region and plots them against the wavenumber (1/\(\lambda\), cm\(^{-1}\)) . This is called as infrared spectrum. While interpreting the infrared spectrum of a given compound the position, relative intensity, and size and shape of the peak is considered to be important. A molecule consisting of \(n\) atoms has 3\(n\)-6 modes of vibrations and it can absorb these many frequencies in the IR regime. Therefore, the FTIR spectrum of organic species consists of large number of absorption peaks. The FTIR spectra of glass are so characteristic that sometimes they are considered as their ‘fingerprints’.
1.7.3: Electron Spin Resonance (ESR) Spectroscopy

The phenomenon of electron spin resonance spectroscopy can be explained by considering the behavior of a free electron. According to quantum theory, the electron has a spin which can be understood as an angular momentum leading to a magnetic moment. Consequently, the negative charge that the electron carries is also spinning and constitutes a circulating electric current. The circulating current induces a magnetic moment \( S \) which, if the electron is subjected to a steady magnetic field \( B_0 \parallel z \), causes the electron to experience a torque tending to align the magnetic moment with the field. The relation between the magnetic moment and the spin vector is

\[
\mu_s = \frac{g\mu_B}{\hbar} S
\]

……………..(1.5)

where \( \mu_B \) is the Bohr magneton and \( g \) is the Lande g factor. The energy of the system depends upon the projection of the spin vector along \( B_0 \). Quantum theory stipulates that only two values are permitted for an electron \( S_z = \hbar /2 \), which means that the electron magnetic moment can only assume two projections onto the applied field Consequently,

\[
\mu_z = \pm \frac{1}{2} g\mu_B
\]

………(1.6)

and the ensemble of energy levels therefore reduce to the two values as shown above

\[
E_\pm = \pm \frac{1}{2} g\mu_B B_0
\]

………(1.7)
If electromagnetic radiation is applied at a frequency that corresponds to the separation between the permitted energies equal to

\[ \Delta E = E_+ - E_- = g \mu_B B = h\nu. \]  

…………(1.8)

energy is absorbed from the electromagnetic field. This is the phenomenon of ESR.

The equation \( \Delta E = g_e B \) i.e \( h\nu = g_e B \) is called the fundamental equation of EPR. For electrons bound into an atom or a molecule, the phenomenon of ESR may not be observed at all, because electron spins pair off in atomic or molecular orbitals so that virtually no net spin magnetism is exhibited and the material is said to be diamagnetic. When an atom or a molecule has an odd number of electrons, however, complete pairing is clearly not possible and the material is said to be paramagnetic. In that case, ESR can be observed. So far we have considered a single electron interacting with an external magnetic field. In the present experiment, however, we deal with a macroscopic sample which means a statistical ensemble of magnetic moments. Therefore, we need to consider the relative populations of the energy levels \( N^+ \) and \( N^- \) which are given by the Boltzmann distribution:

\[ \frac{N^+}{N^-} = \exp\left(-\frac{\Delta E}{k_B T}\right) \]  

…………(1.9)

where \( E = E_+ - E_- \), \( k_B \) Boltzmann’s constant, and \( T \) the absolute temperature. Since it is the absorption, due to the slightly greater population of the lower level, that is observed, this difference between the two populations should therefore be made as large as possible. At room temperature \( N^+ \) and \( N^- \) for a Zeeman splitting corresponding to a frequency of 10 GHz

Experimentally, \( \Delta E = g_e B \) i.e \( h\nu = g_e B \) permits a large combination of frequency and magnetic field values, but the great majority of EPR measurements are made with microwaves in the 9000–10000 MHz (9–10 GHz) region, with fields corresponding to about 3500 G (0.35 T).

1.7.3.1: Origin of an EPR signal

In principle, EPR spectra can be generated by either varying the photon frequency incident on a sample while holding the magnetic field constant or doing the reverse.
In practice, it is usually the frequency that is kept fixed. A collection of paramagnetic centers, such as free radicals, is exposed to microwaves at a fixed frequency. By increasing an external magnetic field, the gap between the $m_s = +1/2$ and $m_s = -1/2$ energy states is widened until it matches the energy of the microwaves. At this point, the unpaired electrons can move between their two spin states. Since there typically are more electrons in the lower state, according to the Maxwell-Boltzmann distribution, there is a net absorption of energy, and it is this absorption that is monitored and converted into a spectrum.

Figure 1.15: Absorbance and the first derivative of EPR signal

As an example of how $\hbar \nu = g_e \mu_B B_0$ can be used, consider the case of a free electron, which has $g_e = 2.0023$. For the microwave frequency of 9388.2 MHz, the predicted resonance position is a magnetic field of about $B_0 = h\nu / g_e \mu_B = 0.3350$ tesla = 3350 gauss. The EPR spectra are recorded and viewed only as first derivatives shown in figure 1.15.
1.7.3.2: ESR Spectrometer

Figure -1.16 : Schematic and photograph of ESR spectrometer

The schematic and photograph is shown in figure 1.16 and its details are given below. It consists of following blocks:

1. A monochromatic microwave source
2. A waveguide for guiding the microwave power to the sample
3. A cavity designed to ensure a proper coupling between the sample and the incoming wave.
4. A detector for microwave power to detect the response of the sample to microwave irradiation.

The different parts used in this experiment are listed below:

1. A gun oscillator is a monochromatic source of microwave. The fundamental frequency is here \( v = 10 \text{GHz} \). Tuning of the frequency is achieved by slowly turning the screw on the top of the metallic case of the oscillator. The frequency can be read out with the frequency counter located next to the source.
2. A calibrated attenuator is use to control the level of microwave power from the source. The scale is logarithmic
3. "T-hybrid" is the 4-ports device used to control the phase
4. The detector is a crystal rectifier (diode) which consists of a semi-conducting material. The incident microwave power causes the current to flow. This current \( I \) increases with the microwave power \( P \) and the sensitivity of the detection strongly depends on the slope \( dI/dP \)
5. The waveguide is a rectangular opened-ended metallic tube delimit a dielectric media in which electromagnetic waves propagate according to Maxwell equations. Boundary conditions have to be fulfilled by the electrical and magnetic components of the wave on the metallic walls. Consequently the propagation is restricted to a set of modes occurring at well defined frequencies which are the characteristic values of the wave equation. There is a cut-off wavelength above which no propagation is allowed.

6. The cavity is a closed metallic box with an iris to allow the microwave to couple in and out. Any cavity possesses resonant frequencies at which the energy stored reaches large values. These frequencies are related to the dimensions of the cavity. The quality factor Q of a cavity measures the frequency width of the resonance or equivalently.

Electronic equipments used to get output of ESR signal comprising of following electronic circuitry:

1. An oscilloscope with its X and Y channels.
2. A plotter also with its X and Y channels.
3. The pre-amplifier amplifies in two successive steps: first dc amplification and an ac amplification through a 115 Hz-bandpass filter.
4. The GUN power supply delivers 15V.
5. A Hall-probe measures the static magnetic field.
6. The gaussmeter converts the voltage measured from the Hall-probe into a value of magnetic field (the maximum deviation corresponds to 1V).
7. The two sets of coils I and II generate the static magnetic field \( B_0 \) and the small modulating field \( B_m \) respectively.
8. The magnet power supply supplies the current to the pair of coils I which produces the static field. It is controlled by the ramp-generator.
9. The current is extremely stable in order to avoid spurious noise that could interfere with the measurement.
10. The low frequency oscillator creates a sinusoidal current at the frequency of 115 Hz in the second pair of coil (II). This produces the field \( B_m \) and provides the external reference signal for the lock-in amplifier.
11. The ramp-generator produces a ramp of magnetic field by varying continuously the current in the pair of coils I. The voltage output of the ramp can be connected to the X-channel of the plotter.
12. The lock-in amplifier amplifies signals at frequencies close to the frequency of a reference signal.

1.7.4 : Raman Spectroscopy

Raman scattering is a very sensitive technique for the characterization of material properties such as composition, phase, crystallinity, point defects, stresses, etc. In this study we have used Raman to investigate the degree crystallinity and stresses in few virgin and ion irradiated crystalline silicon samples. When an electromagnetic wave is incident on a medium, some of it is reflected but most of the radiation is either transmitted or absorbed. A very tiny fraction of the light gets scattered almost at the same wavelength as the incident light either elastically or inelastically. Scattering of monochromatic light in which there is an inelastic collision between the incident photon and the molecules where the quantum of their rotational, vibrational or electronic energy are either absorbed or emitted as a result of collision is known as Raman scattering. In this work, all the crystalline silicon samples were characterized by the Raman scattering technique. For this study each sample was excited with the 514.5 nm line of Ar+ laser at 45° incident angle. The laser power at the sample surface was ~ 40 mW. The scattered light was collected in the backscattering geometry and analyzed using a diffraction grating monochromator in the photon counting mode using a Photo-multiplier tube.

1.7.5 : Scanning Electron Microscopy (SEM) :

SEM provides the surface/topographical analysis with incredible details. The characteristic feature of SEM is its ability to focus the high energy electron beam within an extremely small area of fraction of a nanometer as well as its ability to perform a raster scan over a considerably large area of sample. The magnification in SEM ranges over a wide range from ×25 to ×250000, while the resolution ranges from 1 to 20 nm. Figure 1.17 shows the schematic diagram and the photograph of a Scanning Electron Microscope used in this work. The SEM used in the present work was JEOL JSM-6360A.
The electron beam obtained from electron gun is focused on the surface of a sample coated with conductive coating (such as gold or platinum). The high energy beam is focused using magnetic lenses, while the raster scan is made using X-Y coils. The incident beam of energetic electrons interacts with the sample within its interaction volume. This interaction results in the emission of secondary electrons (due to inelastic scattering), backscattered electrons (due to elastic scattering) as well as X-rays. These are then detected using specialized detectors, after which the signals are converted to images with the aid of computer.

**1.7.6: Energy Dispersive Spectroscopy (EDS):**

Energy Dispersive Spectroscopy (EDS or EDAX) is basically a technique where Scanning Electron Microscope can be used for elemental analysis. The atom of each element has characteristic energy level diagram.

When a high energy electron is incident on the inner shells of atom, a vacancy (hole) is created is shown in figure 1.18. This vacancy is filled by an electron from the higher orbit, resulting in the emission of X-ray, whose energy/wavelength is characteristic to the element from which it is emitted. A detector can measure the
energy/wavelength and the number of X-rays. This allows the detection of elements and measurement their percentage. The EDS equipment, which comes along with SEM, has an electron source, magnetic lenses, X-ray detector and analyzer. The surface of the sample, which is coated with conductive coating is scanned using high energy focused electron beam. The characteristic X-rays are then detected and analyzed.

Figure 1.18 : Effect of high energy electrons on atom and production of characteristic X-rays

1.7.7: X-ray Diffraction:
1.7.7.1: X-Ray Diffraction Technique and X-Ray Diffraction Spectrophotometer:

X rays are the electromagnetic radiations of wavelengths ranging from 0.1 Å to 1000 Å. The typical X-ray spectrometers, which are used for X-ray diffraction analysis, consist source of collimated X-rays. A schematic diagram and the photograph of the X-ray spectrometer used in the present work are shown in figure 1.19.

Figure 1.19: A schematic diagram and the photograph of X ray spectrometer
The X-rays are then made to fall on the sample to be analyzed. The diffracted beams of X-rays are enhanced/intensified along angles which satisfy the Bragg equation. Such Bragg diffracted X-Rays are enhanced/intensified along angles which satisfy the Bragg equation. Such Bragg diffracted X-ray beams are recorded by X-ray detectors connected to computers. The X-ray diffraction pattern is considered as a fingerprint of the crystalline structure of the specimen under analysis. The intensified reflections in particular directions are due to the family of Bragg planes, which are enriched in atoms or molecules. The arrangement of family of atom-enriched Bragg planes depends upon the type of crystal and various Miller indices. In order to access all Bragg planes in all orientations, the specimen is either rotated in all directions or used in powder form. Thus, the X-ray diffraction pattern of a specimen is a complete fingerprint of its crystal structure. In this work the XRD analysis was made using BRUKER D8 ADVANCE X ray spectrometer. X-ray diffraction analysis (position of diffraction maxima, their intensity and width) can be used to understand many aspects of the crystalline structure of the glass, disorder in the crystal structure and orientation. The positions of the atoms in the unit cell can be determined from the relative intensities of the diffracted beams. These relative intensities also signify the relative crystallinity of the glass. The packing of chains is described most completely in terms of the unit cell and its contents. The volume of the unit cell, and hence the volume occupied in the crystal by a single repeat unit, can be obtained by the repeat distance and the positions of the diffracted X-ray beams. The Bragg angles of diffraction maxima thus indicate the type of unit cell. The width of these diffraction maxima signifies the size of crystalline zones i.e. crystallites. The large intensity and small width of diffraction maxima indicates higher degree of crystallinity, while diffraction maxima of less intensity and greater width signify lesser degree of crystallinity. Another use of X-ray diffraction technique is to identify defects (such as vacant lattice sites, foreign elements)[48]. These defects, if present, will broaden the diffraction maxima Molecular weight also affects the crystallinity.

1.7.8 : Contact Angle

Contact angle is the angle with which the liquid interface meets the solid surface. Geometrically, it is defined as the angle formed by a liquid at the three phase boundary where the liquid, gas and the solid intercept. It can be measured by the
angle between the tangent to the liquid-air interface and the tangent to the solid-air interface, as shown in figure 1.20

![Contact angle of a liquid drop](image.png)

Figure 1.20 : Contact angle of a liquid drop

Contact angle is a direct and quantitative measure of wetting of a solid by liquid and thus it signifies wettability of surfaces. Hydrophilic surfaces have good wettability while the wettability of the hydrophobic surfaces is poor. The solid surfaces are classified into hydrophilic, hydrophobic and superhydrophobic according to the contact angles. For hydrophilic surfaces the contact angle is between 0-90° and for hydrophobic and superhydrophobic surfaces it ranges from 90-150° and 150-180° respectively[49]. The contact angle is specific for a given system and is determined by interactions across the three interfaces. The theoretical description of the contact arises from the thermodynamic equilibrium between three phases; the liquid phase of the droplet (L), the solid phase of the substrate (S) and gas/vapor phase of the ambient (G). At equilibrium the chemical potential of the three phases must be equal. It is convenient to frame the discussion in terms of interfacial energies. Let the solid-vapor interfacial energy be $\gamma_{SG}$, solid-liquid interfacial energy be $\gamma_{SL}$ and liquid vapor interfacial energy i.e. surface tension be $\gamma_{LG}$ (refer figure 1.21 )
Neglecting the effects of gravity, the equation that must be satisfied in the equilibrium is called as Young equation and is given by

$$0 = \gamma_{SG} \cdot \gamma_{SL} - \gamma_{LG} \cos \theta$$  \hspace{1cm} \ldots \ldots \hspace{1cm} \text{(1.20)}

$$\cos \theta_r = \frac{\gamma_{SG} - \gamma_{SL}}{\gamma_{LG}}$$  \hspace{1cm} \ldots \ldots \hspace{1cm} \text{(1.21)}

Where $\theta_Y$ is the contact angle on the smooth surface and is called as Young angle. In addition to the interfacial surface energies, surface roughness plays an equally important role in the wettability of a surface. When a water droplet completely wets a rough surface on which it sits, the impact of the surface roughness on the contact angle is given by Wenzel equation

$$\cos \theta_w = r \cos \theta_Y$$  \hspace{1cm} \ldots \ldots \hspace{1cm} \text{(1.22)}

This relates the observed contact angle on the rough surface $\theta_w$ (Wenzel angle), with the roughness ratio “$r$” of the surface and its contact angle on the smooth surface $\theta_Y$ (Young angle). Since the roughness ratio compares the true surface area of rough surface (effective area) with the surface area of a comparatively sized smooth surface (geometric area), this ratio will always be larger than one (increased roughness avails greater area for contact between solid and liquid). Wenzel’s relation also shows that increase in surface roughness will decrease the contact angle of a droplet on a smooth i.e. hydrophilic surface ($\theta_Y < 90^\circ$) or will increase the contact angle for a droplet on a hydrophobic surface ($\theta_Y > 90^\circ$). If the water droplet does not entirely wet the surface and leaves pockets of air shown in figure 1.22 between the droplet and the substrate, then the observed contact angle is
influenced by the fraction $f$ of the droplet that is actually in contact with the surface. This heterogeneous contact angle is given by Cassie-Baxter equation [50]

$$
\cos \theta_{CB} = f \cos \theta_{CB} + f - 1
$$

Therefore, it is possible to have hydrophobic range contact angles from intrinsically hydrophilic surfaces when heterogeneous wetting occurs

![Figure - 1.22: A Schematic Illustration of the Difference Between the (a) Homogeneous (Wenzel) and (b) Heterogeneous (Cassie-Baxter) Wetting Regimes.](image)

The contact angle is also related with the interfacial energy i.e. work of adhesion. This is given by Young – Dubre equation [51]

$$
W_a = \gamma_{LG} \left( 1 + \cos \theta \right)
$$

The work of adhesion is defined as work required for separating liquid and solid phases or negative free energy associated with the adhesion of the liquid and solid phases. It is used to express the strength of interaction between liquid and solid phases. Thus in addition to the roughness, contact angles are also governed by the chemistry of liquid-solid-vapor interfaces.

The Young Dubre equation, Wenzel equation and Cassie-Baxter equation indicate that the data of contact angle can be used to measure some useful parameters associated with liquid solid interactions such as work of adhesion (wettability), roughness and area fraction of liquid solid interaction respectively.

1.7.9 : Photoluminescence

Photoluminescence spectroscopy is a contactless, nondestructive method of probing the electronic structure of materials. Light is directed onto a sample, where it is absorbed and imparts excess energy into the material in a process called photo-excitation. One way this excess energy can be dissipated by the sample is through the emission of light. Photo-excitation causes electrons within a material to move into permissible excited states. When these electrons return to their equilibrium states, the
excess energy is released and may include the emission of light (a radiative process) or may not (a nonradiative process). The energy of the emitted light (photoluminescence) relates to the difference in energy levels between the two electron states involved in the transition between the excited state and the equilibrium state. The quantity of the emitted light is related to the relative contribution of the radiative process. The photoluminescence spectra of the irradiated samples were carried out using Perkin Elmer LS-55 luminescence spectrometer with different excited wavelength. The spectrum was taken in the wide range of the wavelength from 200 nm to 800nm. The spectrometer is used in emission as well as excitation mode. It is used to investigate the changes in luminescent properties and defects of glasses and E’ centres. The peaks recorded in emission spectra were further confirmed in excitation spectra. It has following applications

**Bandgap Determination.** The spectral distribution of PL from a glass samples can be analyzed to determine the electronic bandgap. This provides a means to quantify the elemental composition of material.

**Impurity Levels and Defect Detection.** The PL spectrum at low sample temperatures often reveals spectral peaks associated with impurities contained within the host material. The high sensitivity of this technique provides the potential to identify extremely low concentrations of impurities that can strongly affect glasses.

**Recombination Mechanisms:** The quantity of PL emitted from a nanomaterials is directly related to the relative amount of radiative and nonradiative recombination rates. Nonradiative rates are typically associated with impurities and thus, this technique can qualitatively monitor changes in material quality as a function of processing conditions[52].

### 1.7 : A Brief Outline of the Thesis

In the present work, Sodalime, borosilicate and silica glasses have been taken as they are prominent members of the glass family and shows the various applications. Moreover, the sodalime glass and borosilicate glass are easy to prepare in the laboratory and they produced radiation induced vacancies and creates defects in the glass structure under different kinds of radiation. Soda lime glass can trap electrons when silver is doped and the stability of induced color centers is greatly improved.
In addition to color centers and defects in the glass, radiation induced diffusion provide a potential in microelectronics, optoelectronics, sensors and detectors. It also provides high relevance to the future space missions. Radiation induced defects and diffusion in sodalime glass has a challenging applications. Several studies suggest that silver and copper based materials containing oxidized silver develop an antimicrobial action. It is therefore very important to study the antibacterial activity of silver and copper doped sodalime glasses and to study the control of the size of the nanoparticles using radiations, and the result is used to study antibacterial activity.

One more important application of borosilicate glass is Immobilisation of nuclear waste, which is carried out by vitrification technique. Vitrification involves melting of waste materials with glass-forming additives so that the final vitreous product incorporates the waste contaminants in its macro and micro-structure. Hazardous nuclear waste constituents are immobilised either by direct incorporation into the glass structure or by encapsulation. Taking into account all the above features of the glasses, the thesis is devided into seven chapters.

The first chapter comprising of, the history of glass is summarised to consolidate the concepts of the glass. Although, glasses can be made by a wide variety of methods, the vast majority are 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. Therefore, synthesis, melting and processing techniques are also incorporated in this chapter. In order to know fundamental commercial glass types, three different types of glasses have been studied, viz. Fused silica, Soda lime, and borosilicate glass. These glasses are produced for specialized applications.

Amorphous silicon dioxide is used in low loss optical fibre waveguides, the gate oxide in MOS transistors, and more widely as a thin cover in solar cells. Mostly, the electronic components used in the satellite are enclosed with such type of silica glass to insulate electrically and held transparent for the solar radiation. When the solar cells and MOS structures transistors comes under space radiation
environment, the structural defects exerts profound influence on the device performance. Therefore, the generation of point defects in amorphous silica by irradiation with high energy particle is very much useful to understand their origin and the mechanism of defect formation for the future development of SiO$_2$ systems. Therefore, the next section of this chapter explores the interaction of different energetic radiations with matter. Furthermore, the radiation sources such as, electrons, heavy ion, Co-60 gamma rays are explained in brief. The radiation damages caused by these radiations in the glass leads to formation of free radicals and modifies a number of properties of the glass. The interaction mechanism of these radiation with glasses are explained in this section. In addition, several characterization techniques, such as UV-VIS spectroscopy, FTIR, ESR, Raman Spectroscopy, SEM, EDS, contact angle measurement, Photoluminesence (PL) etc, are employed to investigate the effect of radiation damages in glasses. The principle of these techniques are briefly discussed in this chapter.

Second chapter deals with irradiation of glasses with Co-60 gamma rays, hence the interactions of Gamma rays with glasses is already discussed in the previous chapter. The modifications in the mechanical, optical, electrical and structural properties of fused silica, soda lime and borosilicate glass under the effect of gamma rays have been studied with the help of various characterisation techniques. UV Visible spectroscopy shows peaks to confirm the nature of the defects such as NBOHC, E$^f$ centre, oxygen deficiency centres etc. The absorption spectra is fitted by multi-Gaussian functions. Using fitting parameters and Smakula’s equation the concentration of defects are calculated. UV-Visible spectroscopy can also be used to calculate an optical band gap and Urbach energy of the irradiated glass. The changes in the parameter of the optical band gap and the Urbach energy are an indicative of the change in the structure of the glasses. Actually, Urbach energy indicates the structural disorder of the glass under irradiation.

In case of fused silica glass, the optical band gap found to be decreased from 5.75 eV to 3.21 eV and the Urbach energy found to be increased from 0.63 eV to 3.21 eV respectively and the corresponding defect concentration found to be increased from $7.11 \times 10^{17}$ cm$^{-3}$ to $8.45 \times 10^{19}$ cm$^{-3}$ with increase in the gamma dose from 14.2 KGy to 57 KGy. However, in case of borosilicate glass, the optical band gap found to be decreased from 3.957 eV to 3.14 eV and the Urbach energy found to be increased from 0.75 eV to 3.17 eV respectively and the corresponding
defect concentration found to be increased from $6.14 \times 10^{19}$ cm$^{-3}$ to $9.15 \times 10^{21}$ cm$^{-3}$ with increase in the gamma dose from 14.2 KGy to 57 KGy. Whereas, in case of sodalime glass, the optical band gap found to be decreased from 3.90 eV to 3.18 eV and the Urbach energy found to be increased from 0.132 eV to 0.60 eV respectively and the corresponding defect concentration found to be increased from $3.24 \times 10^{20}$ cm$^{-3}$ to $5.75 \times 10^{23}$ cm$^{-3}$ with increase in the gamma dose from 14.2 KGy to 57 KGy.

Radiation induced defects also play an important role in the formation of color centers (RCC and PCC, respectively) in glasses. These centers can be analysed by Photoluminescence spectra (PL). The defects created by Co-60 gamma radiation in the glasses give rise to photoluminescence (PL) bands centred at definite energy and can be clearly visible when excited by proper wavelength determined by the band gap of the glass. The band centered at 1.9 eV is attributed to nonbridging oxygen hole centers (NBOHC), while the band centred at 2.7 eV and 4.3 eV are attributed to oxygen-deficiency Centre (ODC). The emission spectra at 396 nm (3.13 eV) is proposed as one of the important centre i.e. oxygen deficiency centre (ODC) . Therefore, in case of fused silica, the existence of oxygen deficiency centre (ODC) is observed in PL band at 287 nm (4.3 eV) and 460 nm (2.7 eV) at $\lambda_{\text{exc}}=250$ nm (4.9 eV). The FWHM of the emission spectra is also found to be a function of the gamma dose. The broad nature of these bands are typical for deep centres in wide-band-gap amorphous solids, which give rise to strong electron-phonon coupling. The intensity ratio of the emission and excitation of PL band are also varied for different gamma dose. But in case of sodalime glass, a well defined peak is observed at 472 nm (FWHM = 99 nm). The intensity of this peak increases with increase in gamma dose. This peak is assigned to L-centers, described by a sodium cation bound to a silanolate center, while in borosilicate glass, a well defined peak is observed at 472 nm. This peak is same as L-centers.

FTIR spectra of virgin and gamma irradiated glasses have been studied to know changes in the Si-O-Si vibrational frequency of the oxygen atom in Si-O-Si structure and Si-O-Si bond angle. In case of silica glass, there is a shift observed in the spectrum from 1271 cm$^{-1}$ to 1265 cm$^{-1}$, when the sample is irradiated at maximum dose at 57 KGy. While in case of soda lime glass, there is a slight shift of the Si–O–Si stretching mode at 1042 cm$^{-1}$ towards the lower wavenumber. It is an
indicator of a change of the average bond angle. However, in case of borosilicate glass, no prominent shift is observed. In addition, the broadening of the band is a manifestation of a statistical distribution of different bonding arrangements at each silicon atom site. The shift towards smaller wavenumber corresponds to the smaller bond angle. Therefore, under gamma irradiation, there is a change of phase in which structure has the minimum free energy and is a highly localized phase. It is distinguished from unirradiated phase by reducing the most probable Si-O-Si angle about 10°. This process is therefore called as radiation induced compaction. It is distinctively observed in fused silica and soda lime glass.

The FTIR spectra in the range 2000 cm\(^{-1}\) to 2500 cm\(^{-1}\) show peak at 2254 cm\(^{-1}\) in fused silica which correspond to harmonics of the fundamental mode of bridge bonds or the stretching mode of Si–H bonds. It seems likely that gamma irradiation breaks Si–O–Si bonds to form =Si+ and Si–O– defects and give rise to atomic displacements in the glass network, followed by the attachment of H+ and OH- ions. The gamma irradiation increases the Si–OH and Si–H bond concentration which is clearly observed at 2254 cm\(^{-1}\) in silica glass and attests to a rise in structural damage and inhomogeneity in the silicon–oxygen network. Also, there is remarkable increase in the intensity with gamma dose for the band centred at 3434 cm\(^{-1}\), in case of borosilicate and soda lime glass, which is assigned to the silanol group (SiOH) or water molecule vibrations.

ESR technique is used to investigate and confirm mainly of \(E_i\) centre and its splitting factor \(g\) calculated by the standard relation. The number of the defects (spins) participating in the structure can be calculated by comparing the area under the absorption curve with that of a standard (CuSO\(_4\) . 5H\(_2\)O in the present case) of a known concentration by numerical double integrating the first derivative of the ESR spectrum of the known concentration. It is observed that the virgin glass does not exhibit any ESR peak, but gamma irradiated glass shows an ESR spectrum with increasing in intensity of the magnetic field. The number of spins (defects) are calculated for different gamma doses. \(E_i\) centre is clearly observed in all the glasses with splitting factor \(g = 2.0023\) and NBOHC is observed only in soda lime glass. It is also observed that, there is increase in the concentration of \(E_i\) centre with increase in the gamma dose for all the glasses and the concentration of \(E_i\) centre in soda lime glass is found to be more as compared with fused silica and borosilicate glass.
The electrical properties of silica glasses are usually attributed to the presence of impurities, especially of sodium, hydrogen and aluminium contents appear to influence the electrical resistivity. At the same time, it is assumed that the diffusion of sodium ions are bound more tightly by the silica groups than by the aluminosilicate centres. However, gamma irradiation breaks the Si-O-Si and O-Na-O bonds which in turn change the dielectric constant and the dielectric loss of the glasses. The change in the dielectric constant is due to the relaxation processes and place changing mechanisms in the glass network. This in turn leads to change in the resistivity of the glasses. The variation in the electrical resistivity for fused silica is from $0.2 \times 10^{13}$ $\Omega \cdot m$ to $1.2 \times 10^{13}$ $\Omega \cdot m$, for borosilicate glass from $2 \times 10^{12}$ $\Omega \cdot m$ to $1.6 \times 10^{13}$ $\Omega \cdot m$ while in sodalime glass from $7.3 \times 10^{11}$ $\Omega \cdot m$ to $1.9 \times 10^{12}$ $\Omega \cdot m$ respectively with increase in gamma dose. The variation in the dielectric constant at 100KHz for fused silica is from 4.8 to 5.0, for borosilicate glass from 3.4 to 3.7, while for sodalime glass from 3.3 to 3.6 with increasing gamma dose.

Third chapter deals with irradiation of glasses with 6 MeV electrons and their corresponding defects. When electron of a definite energy pass through material, it deposits energy through electronic energy loss. This energy loss is due to the inelastic (Electron excitation loss) and elastic (Coulomb encounter loss) collisions of the electrons with the atomic electrons and nucleus, by which, the atoms are excited or ionized or displaced, which breaks the chemical bonds in the glass network. This leads to the formation of point defects and color centers in the glass network. This interaction mechanism of high energy electrons with glass is explained in this section.

Using UV Visible spectroscopy, the various defects in the glass such as NBOHC, $E^1$ centre, oxygen deficiency centres etc are identified. The UV-VIS absorption spectra of a fused silica show a peak at 235 nm (5.28eV) at $8 \times 10^{14}$ ele/cm$^2$ and the shift is observed from 235nm(5.28eV) to 229 nm(5.42eV) when the electron fluence was increased upto $64 \times 10^{14}$ ele/cm$^2$. This is a nanophase formation of SiO$_2$ silica glass. The intensity of the peak found to be increased as increase in electron fluence. The plot of $(\alpha h\nu)^2$ against $h\nu$ for different electron fluences show the variation of the band gap with the electron fluence. They show increase in the band gap of the silica glass with the increase in the electron fluence. This increase in the band gap is due to blue shift of the absorption curve and size of the nanoparticles. While, in case of sodalime glass a broad absorption peak centered at 430nm is
observed. It is assigned to the absorption of NBOHC\textsubscript{1}. However, borosilicate glass shows absorption peaks centred at 620nm, it is attributed to the absorption of NBOHC\textsubscript{2} centre.

The comprehensive analysis of Si nanoparticles in fused silica formed by 6MeV electrons can be explained by PL measurements at room temperature with 280 nm excitation wavelength. The emission spectra consist of one broad band located at 564 nm, which arises due to the formation of Si nanoparticles in the SiO\textsubscript{2} matrix and it is assigned to the Si naoclusters in the fused silica glass structure. Sodalime glass shows PL peak at 472nm when excited to 240nm. This PL peak is assigned to L-centers and the peak described by a sodium cation bound to a silanolate center, \textasciitilde{Si–O–Na}. Borosilicate glass also shows PL peak at 472nm when exited to 240nm, which is assign to L-centers. The intensity for all the peak of the glasses found to be increased with increase in electron fluence and the intensity of these peaks also increases with increase in electron fluence.

The structural modifications caused in the electron irradiated glasses and the formation of nc-Si is carried out by Raman spectroscopy. Virgin glasses show a broad spectrum in the range of 500-600 cm\textsuperscript{-1}, which represents a peak of amorphous silica. However, for the fused silica glass irradiated at 40 \times 10^{14} ele /cm\textsuperscript{2}, distinct peaks are observed at 493 cm\textsuperscript{-1} and 603 cm\textsuperscript{-1} respectively, which mainly represents D\textsubscript{1} and D\textsubscript{2} bands corresponds to symmetric oxygen vibrational mode of SiO\textsubscript{4} embedded as a defect in the glass structure. However, sodalime and borosilicate glass show a broad Raman peak centred at 561 cm\textsuperscript{-1}, but no distinct peaks of nc-Si are observed. SEM images for the silica glass irradiated at the fluence of 40 \times 10^{14} ele/cm\textsuperscript{2} show a large number of spherical shape crystalline agglomerates. The average size of the Si nanoparticles is in the range of \sim 50 nm. However sodalime and borosilicate glass did not show any formation of nanophase under electron irradiation.

Forth chapter comprises interaction of 100 MeV Ag\textsuperscript{7+} ions with the glass. A few glass samples having 1 cm\textsuperscript{2} area and 0.1 cm thickness were irradiated with 100 MeV energy Ag\textsuperscript{7+} ions for the fluences ranging from 1 \times 10^{12} ions/cm\textsuperscript{2} to 5 \times 10^{13} ions/cm\textsuperscript{2}. The UV-Visible spectra for 100MeV Ag\textsuperscript{7+} ion irradiated fused silica glass show two peaks in the absorption band, one appeared at 248 nm (5eV) and the additional weak peak at 214 nm (5.8 eV). The intensity of the absorption band
is found to be increased with increase in the ion fluence. The absorption band 214 nm (5.8 eV) is assigned to E\textsuperscript{l} centre, whereas the peak at 248 nm (5 eV) corresponds to B\textsubscript{2} band or ODC-II. The origin of these defect centres is due to the strain in the normal SiO\textsubscript{2} structure ion irradiation and the production of electronically-induced displacements. Whereas, the optical band gap found to be decreased from 4.65 eV to 4.39 eV and the Urbach energy found to be increased from 0.060 eV to 0.162 eV. The defect concentration of ODC (II) and E\textsuperscript{l} centres found to be increased from 1.5 X 10\textsuperscript{13} to 1.69 X 10\textsuperscript{13} cm\textsuperscript{-3} and 2.05 X 10\textsuperscript{13} to 3.134 X 10\textsuperscript{14} cm\textsuperscript{-3} respectively. In PL spectra, the peak appeared at 1.92 eV and 2.7 eV envisage the defects of non-bridging oxygen hole centres and B\textsubscript{2} oxygen deficient centres respectively. ESR spectra also confirms the existence of E\textsuperscript{l} and NBOHC centres. FTIR spectra shows scissioning of Si-O-Si bonds and the formation of Si-H and Si-OH bonds, which supports to the co-existence of the defects induced by Ag\textsuperscript{7+} ion irradiation.

In case of Sodalime glass, two characteristic visible absorption bands with maxima at about 620 and 430 nm are observed. The absorption bands of 620 and 430 nm in soda-lime silicate glass have been identified as absorption of NBOHC, but borosilicate glass shows existence of B\textsubscript{2} band at 530 nm in UV Visible spectra. In PL spectra, Sodalime glass confirms the existence of NBOHC at 1.9eV, while borosilicate glass shows absorption band with maxima at 444 nm. The absorption bands at 444 nm is attributed to H\textsubscript{2}\textsuperscript{+} centre. FTIR spectra shows radiation induced compaction of Si-O-Si around 1270 cm\textsuperscript{-1} in all three glasses, but 3nm shift is observed in borosilicate glass. Therefore, we can conclude that borosilicate glass does not show much change in the structure when irradiated with 100MeV Ag\textsuperscript{+7} ion. ESR spectrum of fused silica shows the existence of E\textsuperscript{l} centre with splitting factor g = 2.0023. The confirmation of NBOHC in soda lime glass shows g = 1.99 and borosilicate glass shows a distinct peak of E\textsuperscript{l} centre with g = 1.995 and a trapped electrons with g = 1.95.

Fifth chapter deals with the diffusion of silver in soda lime glass by 6 MeV electron irradiation and Ion exchanged method. In this work, silver (Ag) is diffused by irradiating solutions, prepared by AgNO\textsubscript{3} solid dissolved in the distilled water and 1N solution. The solutions are then poured into the plastic cylinder of appropriate size. The sample holder was placed at the bottom of the cylinder and then the sample
was mounted vertically in each cylinder. The samples were then irradiated with 6MeV energy electrons with the fluences ranging from $8 \times 10^{14}$ to $34 \times 10^{14}$ electron/cm$^2$. These irradiated sample were characterized by UV Visible spectrometer, X-ray diffraction and scanning electron microscopy.

UV –Visible spectroscopy show a peak at 425 nm. This peak attributes to the diffusion of Silver. The vacancies produced by the concentration of NBOHC helps to enhance the diffusion of silver in the sodalime glass. XRD peaks appearing at $2\theta$ values $38.19^0$ and $64.41^0$ are matching very well with (111) and (220) crystalline planes of the face centered cubic (FCC) of silver crystal structure.

There is another method of diffusion of silver into sodalime glass called ion exchanged method. In this process the samples were dipped into the molten solution of sodium nitrate and silver nitrate taken in the molar ratio of 1:2 at the temperature 350$^0$C for 30 minutes. These samples were then irradiated with 6 MeV energy electrons in the fluences ranging from $10 \times 10^{14}$ to $40 \times 10^{14}$ electrons/cm$^2$ and annealed for the temperature 400$^0$C. The optical properties and the corresponding induced effects are characterised by the techniques such as UV-Visible, Fourier transform infrared spectroscopy (FTIR), SEM( Scanning electron microscopy ), and XRD (X ray diffraction). The UV-Vis absorption spectra show a peak at 432 nm which corresponds to the absorption band of metal silver nanocluster. The intensity and the FWHM of the optical absorption peak also increases with increase in the electron fluence. The XRD peaks show $2\theta$ position at $38.08^0$, $44.28^0$, $64.57^0$, and $77.26^0$ respectively which corresponds to (111), (200), (220), (311) planes of nanocrystalline silver. SEM image of diffused silver nanoparticles observed about an average size of 40 nm and the rate of agglomeration of the silver nanoparticles increases with increase in the electron fluence.

Similarly, an attempt was also made to diffuse copper in sodalime glass by ion exchange and 6 MeV electron irradiation. Soda lime samples were dipped into a molten salt bath of copper sulphate and sodium sulphate in the molar ratio of 54:46 at the temperature 545$^0$C for 10 minutes. These samples were then irradiated with 6 MeV energy electrons in the fluences ranging from $10 \times 10^{14}$ to $40 \times 10^{14}$ electrons/cm$^2$ and annealed for the temperature of 400$^0$C. The optical properties and the corresponding induced effects were characterised by the techniques such as, UV-Visible, Fourier transform infrared spectroscopy (FTIR), and SEM( Scanning electron microscopy ), and XRD (X ray diffraction). The UV-Vis absorption
spectra show two peaks, one at 754 nm and other at around 533 nm. The intensity of the peaks and the FWHM of the optical absorption peaks found to be increased with increase in the electron fluence. The XRD peak at 2θ position at 43.19° which corresponds to (111) plane of nanocrystalline copper having FFC structure. SEM image of diffused copper nanoparticles show average size around 15 nm for the electron fluence of 40 X 10^{14} ele/cm^2 and the EDS confirms the diffusion and existence of copper into the soda lime glass.

The chapter six describes the application of silver doped soda lime glass for the antibacterial activity. The pathogenic strains of *Candida albicans* (BX and BH) and *Candida lipolytica* (NCIM 3589) were used to determine the antifungal activity of the silver nanoparticles. The stock fungal cultures were maintained on MGYP slants containing malt extract, 3.0; peptone, 10.0; dextrose, 10.0 g per liter of distilled water. The bacterial test cultures included *Citrobacter koseri* (MTCC 1657), *Enterobacter aerogenes* (MTCC 111), *Escherichia coli* (MTCC 728), *Klebsiella* sp., *Proteus vulgaris* (MTCC 426) and *Pseudomonas aeruginosa* (MTCC 728). The bacterial cultures were maintained on Nutrient Agar slants that contained peptone, 5.0; meat extract, 1.0; yeast extract, 2.0; sodium chloride, 5.0; agar 15.0 g per liter of distilled water. The test fungal or bacterial suspensions (100 µl) containing 10^4 cells ml^{-1} were spread on freshly prepared silver nanoparticles. Control samples lacking the silver nitrate were used to assess the antimicrobial activity of the BPE. The samples were initially incubated for 15 min at 4°C (to allow diffusion) and later on at 37°C for 24 or 48 h for the bacterial and fungal cultures. The SEM image of these samples were taken and the growth of bacteria are observed for the different sized nanoparticles both in silver and copper doped glasses. It has been observed that small sized nanoparticles kills bacteria more effectively than larger sized nanoparticles and mainly silver nanoparticles observed to be strong to destroy and kill the outermost layer of the bacteria as compared to the copper nanoparticles.

Chapter seven consists of various types of nuclear wastes are discussed and the importance of the nuclear waste is summarised. The immobilisation is the conversion of a waste into a another waste form by solidification, embedding or encapsulation. It facilitates handling, transportation, storage and disposal of radioactive wastes. Immobilisation reduces the potential for migration or dispersion of contaminants including radionuclides. Immobilisation of nuclear waste in glass matrix and it is done mainly by vitrification technique. Vitrification involves
melting of waste materials with glass-forming additives so that the final vitreous product incorporates the waste contaminants in its macro and micro-structure. The glass composition is selected and varied according to the application of the glass. A borosilicate glass have been used in the present experiment because of its properties which are useful in the immobilisation process. Four glasses were prepared with the same batch calculation. One was virgin glass without any nuclear waste doping, the other three were made by doping of 1gm, 1.5gm and 1.7gm of nuclear waste i.e. uranyl nitrate. For the characterisation of immobilised glass with nuclear waste, a gamma ray spectromemeter was used. The radiation from a given nuclear radioactive waste material before and after doping in the glass matrix was studied along with the background. The data was collected before and after the immobilisation of nuclear waste in the glass matrix. It is seen from the linear absorption coefficient that before doping the uranium nitrate in glass matrix were more in number than the after doping, and the activity of the uranium fission fragments found to be reduced by 54% after the immobilization. Hence one can conclude that an immobilization has taken place efficiently and successfully in the glass matrix.

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