This chapter provides the basic understanding of the instruments and characterization techniques used to investigate the structural and optical properties of heavy metal oxide borosilicate glasses. It covers the details of designs of experiments, sample synthesis, and principles of operation of instruments used to study the behavior of the borosilicate glasses on interacting with the high energy radiations.

2.1 SAMPLE PREPARATION

Heavy metal oxide (HMO) borosilicate glasses were prepared by conventional melt-quenching method from chemically pure materials in an amount sufficient to produce 30 gm glass. Analytical pure reagents of boric oxide (B\textsubscript{2}O\textsubscript{3}), silicon oxide (SiO\textsubscript{2}), sodium carbonate (Na\textsubscript{2}CO\textsubscript{3}), cadmium oxide (CdO), barium carbonate (Ba\textsubscript{2}CO\textsubscript{3}), lead oxide (PbO) and bismuth oxide (Bi\textsubscript{2}O\textsubscript{3}) were taken as raw materials. All the chemicals used were of high purity (99.9% or above) so as to avoid the incorporation of impurities into the melt. The compositions of glass samples are shown in Table 2.1. Weight of the oxides was calculated using the following equation

\[ W_a = \frac{X_i Z_a}{\sum_{i=1}^{n} X_i Z_i} \]  

(2.1)

where \( W_a \), \( X_a \) and \( Z_a \) are weight fraction, the mole fraction and the molecular weight of the oxides incorporated in the glass composition. \( X_i \) and \( Z_i \) represents the mole fraction and the molecular weight of the individual glass components respectively. The amount required for carbonates which transform to oxides as the starting materials was calculated as follows:

\[ Z_i = W_i \frac{M_2}{M_1} \]  

(2.2)

where \( M_1 \) and \( M_2 \) are the molecular weights of the oxide and the corresponding carbonate. \( W_i \) represents the weight fraction of the oxide of the respective carbonate. Appropriate amount of the dried ingredients was weighed using a digital electronic balance and was mixed together using a pestle and mortar for half an hour. The dried
mixture was then transferred to alumina crucible of 50 ml capacity. The entire assembly was heated in an electric furnace capable of reaching a temperature of 1400 °C. The mixture was heated to a temperature range of 1050-1250 °C depending upon the composition. The homogenized melts were then poured in disc shaped preheated stainless steel moulds for the required dimensions. The prepared samples were immediately transferred to a muffle furnace regulated at 350 °C and after 1 h, the muffle was switched off to cool at a rate of 25 °C h⁻¹ to room temperature. All the glass samples were then finely powdered using a clean agate mortar pestle.

Homogeneity, thermal durability and pouring temperature are the three most important criteria used for the selection of glass composition. For this, ternary Na₂O–B₂O₃–SiO₂ glass system was used as the basis for the matrix composition selection. Glass made up from this system is referred here as base glass. Pure vitreous silica is thermally and chemically stable. The addition of SiO₂ increases the rigidity of the glass network by increasing the cross linking density. Sodium oxide (Na₂O) is used to expand the glass-forming region and provides low melting glass. Na₂O facilitates ion exchange and homogenization of the glass system, reducing defects and bubbles. B₂O₃ is a basic glass former, has high bond strength, lower cation size, and small heat of fusion. B₂O₃ increases the glass transparency. High SiO₂ and Na₂O compositions were avoided as SiO₂ increases pouring temperature and Na₂O decreases leach resistance. Thus glass compositions in the range of 15 mol % of SiO₂, 45–70 mol % B₂O₃, 15 mol % Na₂O and 0–25 mol % MO were selected, where MO= CdO, BaO, PbO and Bi₂O₃. The importance of adding these modifier oxides in the glass is discussed in chapter 1.

2.1.2 Preparation of glass thin films

To study the effect of swift heavy ions on the heavy metal oxide borosilicate glasses, thin glass films (for the glass samples of composition base, Ba4 and Bi4) were deposited on Quartz glass slide (1cm× 1cm) substrate by electron beam gun evaporation technique. The substrates were properly cleaned using trichloro ethylene (TCE), acetone and propanol so as to have good adhesion between the substrate and the glass thin film. Electron beam evaporation is a typical physical vapor deposition (PVD) process that is performed in a vacuum chamber and begins under the vacuum of 10⁻⁵ Torr or less. A schematic diagram of the electron beam evaporation technique is shown in Fig. 2.1.
Table 2.1: Chemical composition of the samples prepared in mol %.

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>CdO</th>
<th>Na₂O</th>
<th>B₂O₃</th>
<th>SiO₂</th>
<th>Sample Code</th>
<th>BaO</th>
<th>Na₂O</th>
<th>B₂O₃</th>
<th>SiO₂</th>
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<tr>
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<td>70</td>
<td>15</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td>15</td>
<td>65</td>
<td>15</td>
<td>Ba1</td>
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<td>15</td>
<td>65</td>
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<td>60</td>
<td>15</td>
<td>Ba2</td>
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<td>15</td>
<td>60</td>
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</tr>
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<td>55</td>
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<td>Ba3</td>
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<td>15</td>
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<td>15</td>
<td>50</td>
<td>15</td>
</tr>
<tr>
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<td>15</td>
<td>45</td>
<td>15</td>
<td>Ba5</td>
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<td>15</td>
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<table>
<thead>
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<th>Na₂O</th>
<th>B₂O₃</th>
<th>SiO₂</th>
<th>Sample Code</th>
<th>Bi₂O₃</th>
<th>Na₂O</th>
<th>B₂O₃</th>
<th>SiO₂</th>
</tr>
</thead>
<tbody>
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<td>15</td>
<td>Bi1</td>
<td>5</td>
<td>15</td>
<td>65</td>
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</tr>
<tr>
<td>Pb2</td>
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<td>60</td>
<td>15</td>
<td>Bi2</td>
<td>10</td>
<td>15</td>
<td>60</td>
<td>15</td>
</tr>
<tr>
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<td>15</td>
<td>15</td>
<td>55</td>
<td>15</td>
<td>Bi3</td>
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<td>15</td>
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</tr>
<tr>
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<td>Bi5</td>
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<td>15</td>
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<td>15</td>
</tr>
</tbody>
</table>
A high dc voltage is applied to heat the tungsten filament. The filament becomes hot enough to emit electrons. The emitted electrons form a beam which is deflected and accelerated towards the target. The beam is focused on the target material to be evaporated by means of magnetic or electric fields. The stream of electrons emitted excites the targeted solid and turns it into vapor, which travels to the substrate. As they reach the surface, they condense and form a thin film coating. The entire gun assembly is located outside the evaporation zone to avoid any contamination by the evaporant. Also, since the intensity of heat generated by the electron beam is very high the evaporant holder is cooled by water to prevent it from melting. In an electron beam evaporation method, large amount of heat is concentrated on a very small area so high rates of deposition are possible. A 200 nm thin film of heavy metal oxide borosilicate glass was deposited at a pressure of $10^{-6}$ Torr. The photograph of the cryo-pump operating at high vacuum (HV) used for electron beam evaporation is shown in the Fig. 2.2. During the deposition, the distance from the source to substrate was 135 mm and the thickness of the thin film was monitored using quartz crystal thickness monitor.

*Figure 2.1*: A schematic diagram of the electron beam evaporation technique.

(*Picture Courtesy: Polyteknik AS © 2012, Denmark*)
2.2 SOURCES OF IRRADIATION

To study the interaction of radiation with the target material, two different sources of irradiation were used viz. gamma source and heavy ion source which are described below.

2.2.1 Gamma irradiation source

The gamma irradiation of the glass samples was carried out using $^{60}$Co source at Inter University Accelerator Center (IUAC), New Delhi. The Gamma chamber (model GC 1200) was manufactured by Board of Radiation and Isotope Technology (BRIT), Mumbai as shown in Fig. 2.3. Gamma Chamber 1200 is a compact self shielded cobalt-60 gamma irradiator providing an irradiation volume of approximately 1200 cc. The unit mainly consists of the source and cylindrical source cage, lead flask as biological shield, central drawer with sample chamber, mechanical driver system and external cabinet. The material for irradiation is placed inside an irradiation chamber located in the vertical drawer in a lead flask. This drawer can be moved up and down with the help of a system of motorized drive thereby enabling the precise positioning of the irradiation chamber at the centre of the radiation field. Samples were subjected to five radiation doses of 0.1 kGy, 1 kGy, 5 kGy, 15 kGy and 60 kGy. The glass samples were irradiated for required time interval to achieve the desired overall dose. The dose rate was 7.27 kGy/hr. All the powdered glass samples were wrapped in butter paper and then packed in polythene sachets before irradiation.

2.2.2 Swift heavy ion beam irradiation

The heavy ion irradiation was performed with 120 MeV $^{7+}$Ag ions at different fluence ranging from $10^{12}$ ions cm$^{-2}$ to $10^{13}$ ions cm$^{-2}$ at the 15 UD Pelletron tandem accelerator at Inter University Accelerator Centre, New Delhi. To ensure uniform irradiation, the beam was made incident upon the samples in the scanning mode. The selected zone of the beam area was 1 cm by 1 cm. The expected ranges of the films allowed the ions to cross the whole thickness of the films giving rise to homogeneous damage in the bulk.
Figure 2.2: The high vacuum (HV) pump used during thin film deposition.

Figure 2.3: Gamma chamber GC 1200.
The 15 UD Pelletron accelerator at Inter-University Accelerator Center (IUAC), New Delhi is a tandem electrostatic accelerator (Kanjilal et al., 1993) capable of accelerating almost any ion from proton to uranium, except inert gases, in the energies ranging from 50 to 250 MeV depending upon the type of ion. A schematic diagram of the Pelletron accelerator is shown in Fig. 2.4. The Pelletron having vertical geometry is installed in an insulating tank which is 26.5 m long and 5.5 m in diameter. The tank is filled with sulfur hexa-fluoride ($\text{SF}_6$) insulating gas at a pressure of about 6-7 bars. The ion source in the top is capable of producing negative ions. There are three different types of ions sources available, which are, (i) Alphatros (ii) MCSNICS and (iii) Duoplasmatron. Among all of these, MCSNICS (Multi Cathode Source of Negative Ions by Cesium Sputtering) is most commonly used for ion production. The negative ions are pre-accelerated to about 250 keV by the deck potential. The negative ions of different masses are then focused and analyzed by a $90^\circ$ dipole magnet called injector magnet before injecting them in the low energy accelerating tubes. Injector magnet bends the negative ions by $90^\circ$ in vertically downward direction in the accelerating column. Inside the vertical accelerating tank, in the middle; there is a high voltage terminal of about 1.52 m in diameter and 3.81 m in height. This terminal can be charged to very high potential varying from 4 MV to 15 MV. A potential gradient is maintained through the tube from the top of the tank to the bottom with ceramic titanium diffusion bonded accelerating tubes.

The portion above the terminal is called low energy section and portion below the terminal is called high energy section. The injected ions get accelerated down towards the high voltage terminal at the middle. On reaching the terminal, the negative ions pass through a stripper that can be a very thin carbon foil or a small volume of gas (e.g. $\text{N}_2$ gas). During this passage through this stripper, the negatively charged ions lose electrons and are thus converted into positive ions. These newly created positively charged ions get repelled down towards the ground potential through the high energy accelerating tube. A second stripper assembly is located in the high energy dead section. This helps in further stripping and yields higher charge state and hence higher energy of an ion.
The entire unit is computer controlled and is operated from the control room. These high energy ions are analyzed in energy with the help of a $90^\circ$ bending magnet known as analyzer magnet. The positive ions are then directed to the desired experimental beam line with the help of a multiport switching magnet which can deflect the beam in any of the seven beam lines present in the beam hall. The whole beam line of the 15 U/D Pelletron accelerator operates in an ultra-high vacuum (UHV). Fig. 2.5 shows the photograph of the high vacuum chamber in materials science beam line. The flux of the ion beam can be calculated using the pre calibrated Faraday cups.

2.3 CHARACTERIZATION TECHNIQUES

2.3.1 X-ray diffraction analysis

X-ray diffraction technique was used to check for possible crystallinity of the samples after quenching and annealing. The X-ray diffraction data for all glasses was obtained using Bruker AXS diffractometer (Model D8 Advanced) at IUAC, New Delhi and Shimadzu (XRD-7000) diffractometer at GNDU, with Cu Kα line of width $\lambda = 1.54 \text{ Å}$. The pattern was recorded at a scanning rate of 2 degree min$^{-1}$ and at angular rate $(2\theta)$ of 10-60$^\circ$.

2.3.2 Fourier transform infrared (FTIR) spectroscopy

FTIR is a beneficial tool for the identification of chemical bonds in a molecule or the molecular structure of materials by producing an infrared absorption spectrum. The absorption of infrared light occurs only at those frequencies where it affects the dipolar moment of the molecule.

Fourier transform infrared (FT-IR) spectra of all the powdered samples before and after gamma irradiation were recorded at room temperature in the range 4000-400 cm$^{-1}$ using Thermo Nicolet 380 spectrometer. The glass samples were mixed in the form of fine powder with KBr in the ratio 1:100 (1 mg glass powder: 100 mg KBr). The weighed mixtures were then subjected to a pressure of $1.47 \times 10^7$ Pa to produce homogeneous pellets. The infrared absorbance measurements were carried out immediately after preparing the pellets. FTIR spectroscopic analysis of the thin film samples was done using Shimadzu IR Affinity-1 spectrometer at Kurukshetra University, Kurukshetra.
**Figure 2.4:** A schematic representation of 15 UD Pelletron.

**Figure 2.5:** High vacuum chamber in materials science beam line at IUAC, New Delhi.
2.3.3 UV-visible spectroscopy

UV–visible absorption spectra were recorded at room temperature in the wavelength range of 200-900 nm using a double beam Shimadzu 1800 UV–visible absorption spectrophotometer, Japan. UV–visible measurements of gamma irradiated glass samples were carried out by dispersing the powder of glasses in methanol. The spectrum was normalized with respect to methanol.

A spectrum is a graphical representation of the amount of light absorbed or transmitted by matter as a function of the wavelength. A UV-visible spectrophotometer measures absorbance or transmittance from the UV range to which the human eye is not sensitive to the visible wavelength range to which the human eye is sensitive. The UV-vis region of energy for the electromagnetic spectrum covers 1.5 - 6.2 eV which relates to a wavelength range of 800 - 200 nm. A UV-Vis double beam spectrophotometer (Fig. 2.6) consists of a:

i. Single light source (usually a deuterium or tungsten lamp)
ii. Sample holder
iii. Monochromator
iv. Detector
v. Splitter
vi. Series of mirrors to get the beam to a reference sample and the sample to be analyzed.

This allows for more accurate readings.

2.3.3.1 Optical band gap and Urbach energy

The primary electronic effect of the cations in a glass network is to form an optical mobility gap similar to the energy-band gap of crystals. This results in the leakage of charge carriers across the mobility gap thereby, forming a tail of energy-density states. On absorbing the ultraviolet and visible light, the outer electrons of the glass sample are excited to higher energy levels. The amount of energy required for this excitation is equal to the difference in energy between the two electron energy bands. These energy values are unique and quantized for all species in the sample. This theory does not take into account the energy tail above the mobility gap and is not appropriate for glasses with a small gap. Therefore, a more accurate model was proposed by Mott.
and Davis (1979) which takes into account even the material with small band gap. According to this model, the linear absorption coefficient alpha (α) varies with photon energy, E, as follows:

$$\alpha (E) = B \frac{(E - E_g)^2}{E}$$  \hspace{1cm} (2.4)

where B is a constant. The optical mobility gap, $E_g$, can be calculated by plotting $(\alpha E)^{1/2}$ as a function of photon energy, E. The value of $E_g$ was then calculated from a linear extrapolation to zero ordinate.

To calculate the width of the energy tail, also designated as Urbach energy $\Delta E$, the model proposed by Urbach (1953) and Tauc (1987) is followed. According to this model, the following relation is valid:

$$\alpha = C \exp \left(\frac{E}{\Delta E}\right)$$  \hspace{1cm} (2.5)

where C is a constant. $\Delta E$ can be then obtained from the reciprocal of the slope of the plot of the natural logarithm of $\alpha$ versus the photon energy. Both of these parameters i.e. band gap energy, $E_g$ and Urbach energy, $\Delta E$ is very useful for describing the structural disorder (Sharma et al., 2006).

**Figure 2.6**: Schematic diagram of UV-Vis double beam spectrophotometer.

(*Picture Courtesy: http://www2.chemistry.msu.edu)