Chapter -2

Experimental Techniques

2.1 Introduction

In this chapter, the techniques by which physical, thermal, structural, optical and electrical properties of the glasses samples have been determined experimentally are given. It also presents method of preparation of glass samples. Various techniques used in the present work include density, molar volume measurement, X-ray diffraction (XRD), Differential Scanning Calorimetry (DSC), Fourier Transform Infra-Red (FTIR) spectroscopy, Raman Spectroscopy, Ultra-Violet/Visible (UV/VIS) spectroscopy and these are discussed along with the measurements of the temperature and frequency dependent electrical conductivity of tellurite based oxide and halide glasses.

2.2 Glass Compositions

The details of the compositions of the glass systems investigated are:

1. 70 TeO₂-(30-x) BaO-x ZnCl₂; x = 5,10,15,20 and 25.
2. (70-x) TeO₂- 30 BaO- x ZnCl₂; x = 5,10,15,20 and 25.
3. 60 TeO₂ -x Bi₂O₃ - (30-x)B₂O₃-10 ZnO; x = 0, 5, 10, 15 and 20.

2.3 Glass Preparation Method

There are various methods of producing glass, from conventional methods to modern techniques and from small batch operations producing a few kilograms to large continuous processes producing tones per day. Before the development of the chemical vapour deposition and sol-gel processes, the melt-quenching technique was the only method by which the bulk glasses of acceptable size for practical applications could be obtained. Even today, glasses produced by the melt-quenching technique make up more than 99% of practical glasses in both volume and number of types. This process is based on the fusion of crystalline raw materials into a viscous liquid followed by quenching to a glass [1]. This process is distinguished from other methods of glass preparation in many aspects including the available systems, size and shape of the products, number of components, etc. The advantage of the melt-quenching technique over chemical vapour
deposition or the sol-gel process is the large flexibility of composition, since simple quenching of a melt does not require stoichiometry among constituents.

The glass samples in the system TeO$_2$-Bi$_2$O$_3$-B$_2$O$_3$-ZnO and TeO$_2$-BaO-ZnCl$_2$ were prepared by conventional melt quench technique using analar grade chemicals TeO$_2$, Bi$_2$O$_3$, H$_3$BO$_3$, ZnO, BaCO$_3$ and ZnCl$_2$ (more than 97-99% purity) in air under the normal air conditions. All the chemicals were in the form of fine powder. The starting materials were weighed in the appropriate amounts by using the electronic balance having accuracy of $10^{-4}$ g. The weighed quantities of the chemicals in appropriate proportions were thoroughly mixed in an agate pestle-mortar. The mixture was melted in silica crucible by putting it in an electrically heated muffle furnace (shown in Figure 2.1) and then raising the temperature. The furnace used was a programmable temperature controlled furnace (up to 1600°C) and the temperature was raised slowly to 700-800°C depending on composition. The temperature was maintained for 30 minutes and the melt was shaken frequently to ensure proper mixing and homogeneity. When the glass melt was thoroughly homogenized and attained desirable viscosity, it was poured quickly on to a stainless steel block and was immediately pressed by another stainless steel block at room temperature. The coin-shaped samples of thickness 1-2 mm were obtained. The quenched glass generally had thermal stresses due to the thermal shocks during the quenching process. Therefore, annealing is necessary to relieve the thermal stresses in the melt quenched glass. Annealing is carried out at in the vicinity of glass transition temperature (Generally 20-40°C below $T_g$). In the present work, glass samples were annealed by placing them in an oven at constant temperature below glass transition temperature for three hours. The annealed glass samples were then cooled to room temperature. After preparation, the samples were kept in a desiccator to protect them from atmospheric moisture.

Prepared glasses were processed to make samples for use in different characterization techniques. They were cut in desired shapes and polished to get appropriate surface finish. The polishing was done using different grades of polishing papers. For conductivity measurements, thin coating of silver paint was applied on either side of the glasses to serve as electrodes.
2.4 Physical Characterization

The physical characterization of the tellurite based oxide and halide glasses were performed by measuring and analysing the density ($\rho$), molar volume ($V_m$) and crystalline volume ($V_c$).

2.4.1 Density ($\rho$)

Density, $\rho$ (g/cm$^3$), is a powerful tool, capable of exploring the changes in the structure of glasses and is affected by structural softening / compactness, changes in geometrical configurations and dimensions of interstitial spaces in the glass system. Density is generally measured by the fluid displacement method based on Archimedes’s principle.

According the Archimedes’s principle, the buoyancy equals the weight of the displaced fluid. The density of the glass samples is determined using xylene as the buoyant liquid. The density was obtained by employing the relation.

$$\rho = \left( \frac{w_a}{w_a - w_l} \right) \times \rho_l$$  \hspace{1cm} (2.1)

where $w_a$ is the weight of sample glass in air, $w_l$ is the weight of sample glass in buoyant liquid. ($w_a - w_l$) is the buoyancy. $\rho_l$ is density of buoyant liquid. All the measurements
were made at room temperature, with density measurement kit using physical balance of DEVNER Instrument model no, SI-234 shown in Figure 2.2.

![Density measurement setup](image)

**Figure 2.2 Density measurement setup**

### 2.4.2 Molar Volume and Crystalline Volume

The molar volume \( V_m \) of all the prepared glass samples was calculated by using the relation

\[
V_m = \sum x_i \frac{M_i}{\rho}
\]  

(2.2)

where \( x_i \), \( M_i \) and \( \rho \) represent the molar fraction, molecular weight of \( i^{th} \) component respectively and \( \rho \) is the density of the sample.

Crystalline volume \( V_c \) \( (\text{cm}^3 \text{ mol}^{-1}) \) of glass samples is determined using the formula

\[
V_c = \Sigma x_i V_i
\]  

(2.3)

where \( V_i \) is the molar volume of \( i^{th} \) component in crystalline phase

The oxygen packing density (OPD) is calculated from the density and composition of the system using the formula

\[
OPD = 1000C\left(\frac{\rho}{M}\right)
\]  

(2.4)

where \( C \) is number of oxygen atoms per formula unit.
2.4.3 Optical Basicity

Optical basicity is a numerical expression of the average electron donor power of the oxide species constituting the medium and thus it is used as a measure of the acid-base properties of the oxides and glasses [2]. The theoretical Optical basicity for the glass system under study has been calculated using the relation [3]:

$$\Lambda_{th} = X(\text{TeO}_2) \Lambda(\text{TeO}_2) + X(\text{Bi}_2\text{O}_3) \Lambda(\text{Bi}_2\text{O}_3) + X(\text{B}_2\text{O}_3) \Lambda(\text{B}_2\text{O}_3) + X(\text{ZnO}) \Lambda(\text{ZnO})$$

where $X(\text{TeO}_2)$, $X(\text{Bi}_2\text{O}_3)$, $X(\text{B}_2\text{O}_3)$ and $X(\text{ZnO})$ are the equivalent fractions of the different oxides i.e. the proportion of the oxide atoms they contribute to the glass system and $\Lambda(\text{TeO}_2)$, $\Lambda(\text{Bi}_2\text{O}_3)$, $\Lambda(\text{B}_2\text{O}_3)$ and $\Lambda(\text{ZnO})$ are the values of the optical basicity assigned to the constituent oxides taken from Ref.[4].

2.5 Thermal Characterization

Differential Scanning Calorimetry or DSC was developed by E.S. Watson and M.J. O'Neill in 1962 and was introduced commercially at the 1963 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy. DSC measures the temperatures and heat flows associated with transitions in materials as a function of time and temperature in a controlled atmosphere. These measurements provide quantitative and qualitative information about physical and chemical changes that involve endothermic or exothermic processes or changes in heat capacity. DSC is a thermo-analytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature. Both the sample and reference are maintained at nearly the same temperature throughout the experiment. Generally, the temperature program for DSC analysis is designed such that the sample holder temperature increases linearly as a function of time. The reference sample should have a well-defined heat capacity over the range of temperatures to be scanned.

The basic principle underlying this technique is that, when the sample undergoes a physical transformation such as phase transitions, more or less heat will need to flow to it than the reference to maintain both at the same temperature. Whether less or more heat flows to the sample depends on whether the process is exothermic or endothermic. For example, as the solid melts into liquid it will require more heat flowing to the sample to increase its temperature at the same rate as the reference. This is due to the absorption of heat by the sample as it undergoes the endothermic phase transition (melting) from solid to liquid. Likewise, as the sample undergoes exothermic process (such as crystallization) less
heat is required to raise the sample temperature. By observing the difference in heat flow between sample and reference, differential scanning calorimeters are able to measure the amount of heat absorbed or released during such transitions. DSC can be used to measure a number of characteristic properties of sample. Using this technique it is possible to observe fusion and crystallization events as well as glass transition temperatures ($T_g$). DSC can also be used to study oxidation, as well as other chemical reactions [5-7].

Glass transitions may occur as the temperature of an amorphous solid is increased. These transitions appear as a step in the baseline of the recorded DSC signal. This is due to the sample undergoing a change in heat capacity; no formal phase change occurs. As the temperature increases, an amorphous solid will become less viscous. At some point the molecules may obtain enough freedom of motion to spontaneously arrange themselves into a crystalline form. This is known as the crystallization temperature ($T_c$). This transition from amorphous solid to crystalline solid is an exothermic process, and results in a peak in the DSC signal. As the temperature increases the sample eventually reaches its melting temperature ($T_m$). The melting process results in an endothermic peak in the DSC curve (Figure 2.3). The ability to determine transition temperatures and enthalpies makes DSC a valuable tool in producing phase diagrams for various chemical systems.

![Figure 2.3 Typical DSC curve](image)

Differential Scanning Calorimetry (DSC) of the samples was carried out using a TA DSC (Q600 SDT) model (shown in Figure 2.3), at a heating rate of 10°C/min in nitrogen atmosphere over a wide temperature range, typically from 100°C to 800°C (Figure 2.4).
2.6 Structural Characterization

The structural characterization of the glass samples was carried out using X-ray Diffraction (XRD), Fourier Transform Infra-Red (FTIR) Spectroscopy and Raman Spectroscopy.

2.6.1 X-ray Diffraction

X-rays are electromagnetic radiations of wavelength about 1 Å (10^{-10} m), which is about the same size as an atom. The discovery of X-rays in 1895 enabled scientists to probe crystalline structure at the atomic level. X-ray diffraction has been in use in two main areas, for the fingerprint characterization of crystalline materials and the determination of their structure. Each crystalline solid has its unique characteristic X-ray powder diffraction pattern which may be used as a "fingerprint" for its identification. Once the material has been identified, X-ray crystallography may be used to determine its structure, i.e. how the atoms pack together in the crystalline state and what the interatomic distances and angles etc. are. X-ray diffraction is one of the most important characterization tools used in solid state chemistry and materials science. One can determine the size and the shape of the unit cell for any compound most easily using X-ray diffraction. About 95% of all solid materials can be described as crystalline. When x-rays interact with a crystalline substance (phase), one gets a diffraction pattern. In 1919, A. W. Hull published a paper titled, “A New Method of Chemical Analysis” in which he pointed out that “….every crystalline substance gives a pattern; the same substance always gives the same pattern; and in a
mixture of substances each produces its pattern independently of the others."[8]. The technique is normally useful to collect the data under ambient conditions, but in-situ diffraction as a function of external constraints, such as, temperature, pressure, stress, electric field, atmosphere, etc. is also important for the interpretation of solid-state transformations and material behaviour.

Bragg diffraction occurs when radiation, with wavelength comparable to atomic spacing, is scattered by the atoms of a crystalline system, and undergoes constructive interference. For a crystalline solid, the waves are scattered from lattice planes separated by the interplaner distance. When the scattered waves interfere constructively, they remain in phase since the path length of each wave is equal to an integer multiple of the wavelength. This leads to Bragg's law (Figure 2.5) which describes the condition for the constructive interference in certain directions and the production of diffracted scattered X-rays:

\[ 2d \sin \theta = n \lambda \]  

(2.5)

where \( n \) is a positive integer and gives the order of diffraction, \( \lambda \) is wavelength of incident X-rays, \( d \) is the interplaner spacing of the crystal and \( \theta \) is angle of incidence.

Figure 2.5 Incident and scattered X-rays from a pair of atoms in different lattice planes.

The crystalline materials are characterized by sharp peaks in their diffraction patterns. Unlike this, diffraction pattern of glasses is characterized by one or two broad humps/halos. This is because glasses have short range order rather than long range periodicity and there is considerable distribution of bond lengths and bond angles among the constituent atoms.
The diffractograms of all the samples were recorded using Rigaku Miniflux-II Table-Top X-ray diffractometer (shown in Figure 2.6). Cu K$_\alpha$ X-ray source having fixed wavelength, $\lambda = 1.5418$ Å, was used to record the patterns. All the patterns were recorded between 10°-80° range at a scanning speed of 2°/min for glass samples.

**Figure 2.6 Rigaku Miniflux-II desktop X-Ray Diffractometer.**

2.6.2 Fourier Transform Infra-red (FTIR) Spectroscopy

Infrared spectroscopy has been a workhorse technique for material analysis in the laboratory for over seventy years. Infrared spectroscopy is the study of interactions between matter and electromagnetic (EM) fields in the IR region. In this spectral region, the EM waves mainly couple with the molecular vibrations. In other words, a molecule can be excited to a higher vibrational state by absorbing IR radiation. The probability of a particular IR frequency being absorbed depends on the actual interaction between this frequency and the molecule. In general, radiations of a particular frequency will be strongly absorbed if its photon energy coincides with the vibrational energy levels of the molecule. IR spectroscopy is, therefore, a very powerful technique which provides fingerprint information on the chemical composition of the samples.

In infrared spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a
molecular fingerprint of the sample. Like a fingerprint, no two unique molecular structures produce the same infrared spectrum. Therefore, infrared spectroscopy can result in a positive identification (qualitative analysis) of every different kind of material. In addition, the size of the peaks in the spectrum is a direct indication of the amount of material present. With modern software algorithms, infrared is an excellent tool for quantitative analysis.

The FTIR spectroscopy is based on an instrument called Michelson interferometer, which is used to produce an interferogram [9]. The interferogram is related to IR spectrum by the mathematical operation, the Fourier transformation (FT). The fundamental part of the instrument is the so-called Michelson interferometer as shown in Figure 2.7. It is an optical device consisting of a fixed mirror, movable mirror and a beam splitter. The interferometer shifts the phase of one of the beams with respect to the other by moving one of the mirrors and keeping the other mirror at a fixed position. When the two beams overlap, depending on whether they are in phase or out of phase, constructive and destructive interferences take place.

![Michelson interferometer](image)

*Figure 2.7 Michelson interferometer*

The powdered samples were thoroughly mixed with dry KBr in the ratio 1: 20 by weight and then pellets were formed under a pressure of 8-10 tons. The infrared transmission spectra were recorded at room temperature using Shimadzu FTIR-8001PC and Perkin Elmer Spectrometer over the range 400 to 2000 cm$^{-1}$ for the oxide glasses. These pellets were introduced into the sample chamber for recording the IR spectra while
the referencing was done by recording a blank KBr pellet. The instrument used in the present work is shown in Figure 2.8.

**Figure 2.8. Shimadzu FTIR-8001 spectrometer**

### 2.6.3 Raman Spectroscopy

The phenomenon of inelastic scattering of light was first postulated by Smekal in 1923 [10] and first observed experimentally in 1928 by Raman and Krishnan [11]. Since then, the phenomenon has been referred to as Raman spectroscopy. In the original experiment, sunlight was focussed by a telescope onto a sample which was either a purified liquid or a dust-free vapour. A second lens was placed behind the sample to collect the scattered radiations. A system of optical filters was used to show the existence of scattered radiations with an altered frequency from the incident light – the basic characteristic of Raman spectroscopy.

Raman spectroscopy provides information about molecular vibrations that can be used for sample identification and for both qualitative and quantitative applications. Raman scattering is a spectroscopic technique that is complementary to infrared absorption spectroscopy. The technique involves shining a monochromatic light source (i.e. laser) on a sample and detecting the scattered light. The majority of the scattered light is of the same frequency as the excitation source; this is known as Rayleigh or elastic scattering. A very small amount of the scattered light (i.e. $10^{-5} \%$ of the incident light
intensity) is shifted in energy from the incident (laser) frequency due to interactions between the incident electromagnetic waves and the vibrational energy levels of the molecules in the sample. This shift provides information about vibrational, rotational and other low frequency transitions in molecules. Plotting the intensity of this "shifted" light versus frequency results in a Raman spectrum of the sample. On this scale, the band positions will lie at frequencies that correspond to the energy levels of different functional group vibrations. Raman spectroscopy can be used to study solid, liquid and gaseous samples. Raman spectroscopy uses a radiation of single frequency to irradiate the sample and it is the radiation scattered from the molecule, one vibrational unit of energy different from the incident beam, which is detected. Thus, unlike infrared absorption, Raman scattering does not require matching of the incident radiation to the energy difference between the ground and excited states. In Raman scattering, the light interacts with the molecule and distorts (polarizes) the cloud of electrons round the nuclei to form a short-lived state called a virtual state, this state is not stable and the photon is quickly re-radiated.

The energy changes one detects in vibrational spectroscopy are those required to cause nuclear motion. If only electron cloud distortion is involved in scattering, the photons will be scattered with very small frequency changes, as the electrons are comparatively light. This scattering process is regarded as elastic scattering and is the dominant process. For molecules it is called Rayleigh scattering. However, if nuclear motion is induced during the scattering process, energy will be transferred either from the incident photon to the molecule or from the molecule to the scattered photon. In these cases the process is inelastic and the energy of the scattered photon is different from that of the incident photon by one vibrational unit. This is Raman scattering. It is inherently a weak process in that only one in every $10^6$–$10^8$ photons which scatter is Raman scattered.

Figure 2.9 shows the basic processes which occur for one vibration. At room temperature, most molecules, but not all, are present in the lowest energy vibrational level. Since the virtual states are not real states of the molecule but are created when the laser/ incident radiation interacts with the electrons and causes polarization, the energy of these states is determined by the frequency of the light source used. The Rayleigh process will be the most intense process since most photons scatter this way. It does not involve any energy change and consequently the light returns to the same energy state. The Raman scattering
process from the ground vibrational state (m) leads to absorption of energy by the molecule and its promotion to a higher energy excited vibrational state (n). This is called Stokes scattering. However, due to thermal energy, some molecules may be present in an excited state such as (n). Scattering from these states to the ground state (m) is called anti-Stokes scattering and involves transfer of energy to the scattered photon. The relative intensities of the two processes depend on the population of the various states of the molecule. At room temperature, the number of molecules expected to be in an excited vibrational state other than any really low-energy ones will be small. Thus, compared to Stokes scattering, anti-Stokes scattering will be weak and will become weaker as the frequency of the vibration increases, due to decreased population of the excited vibrational states. Further, anti-Stokes scattering will increase relative to Stokes scattering as the temperature rises. The difference in intensities of Raman bands in Stokes and anti-Stokes scattering can also be used to measure temperature.

![Diagram of the Rayleigh and Raman scattering processes.](image)

**Figure 2.9** Diagram of the Rayleigh and Raman scattering processes. The lowest energy vibrational state (m) is shown at the foot with states of increasing energy above it. Both the low energy (upward arrows) and the scattered energy (downward arrows) have much larger energies than the energy of a vibration.

The Raman spectra of the polished samples were recorded using Renishaw Invia Reflex Micro Raman Spectrometer with Ar ion laser (514 nm) under back scattering configuration over the spectra range 100-2000 cm⁻¹ at room temperature. The Raman spectrometer is shown in Figure 2.10.
2.7 Optical Characterization

2.7.1 UV-VIS Spectroscopy

Ultraviolet (UV) and visible radiations comprise only a small part of the electromagnetic spectrum, which includes such other forms of radiation as radio, infrared (IR), cosmic, and X rays (Figure 2.11).

Ultraviolet-visible (UV-Vis) absorption spectroscopy is based on the measurement of the attenuation of a beam of light after it passes through a sample or after reflection from a sample surface. Oxide glasses generally absorb strongly both in the far IR and UV spectral regions. The former is associated with the interaction of light with the molecular vibrations and the latter with the electronic transitions between the valence band and the conduction band or between the excitation levels.
Most of the oxide glasses are highly transparent in the visible region with a broad absorption edge in the UV region. The position and shape of the absorption edges depend on the composition as well as the nature of the network former and modifier cations in glass samples. Most materials absorb some light, and the degree to which they absorb light is a function of the wavelength of the light. Because optical absorption in the visible and near-UV portions of the spectrum is generally the result of absorption of light by electrons in atoms, ions or molecules, the absorption characteristics can yield a considerable amount of information regarding their electronic structure. This technique can also provide information about the optically induced transitions (direct and indirect), band structure and band gap of materials. The UV/VIS absorption in insulating materials particularly in disordered materials such as oxide glasses is generally believed to involve the excitation of electrons associated with anions, i.e., of electronic nature. Basically two types of electronic transitions may be responsible [12], viz. the promotion of an electron from a localized orbital, on one ion (or molecule) either to a higher energy but still localized orbital, or to a collective energy level for the system-the conduction band. If, in the first case, the excited electron is localized on the same ion or molecule, the new state is described as an “exciton” and the associated absorption band is called an exciton band. However, if the excitation transfers the electron to an orbital lying wholly or partly on another atomic species, then the observed absorption is generally called a “charge transfer” process.

The crystalline and glassy non-metallic materials share some similarities between their energy band structures but whereas the crystalline solids show well defined energy bands having sharp conduction and valance band edges, the glassy materials exhibit band tailing into the normally forbidden energy gap [13]. These tails are proposed to be due to the presence of impurities, structural defects or other kinds of inhomogeneties. Presence of impurities or defects in a material makes it possible for electrons to acquire those energy levels, which are otherwise forbidden. Amorphous or glassy materials contain high densities of these localized trapping levels usually distributed over a relatively large part of the energy gap [14]. The study of these energy levels is helpful in understanding the electrical and optical properties of these materials.

The instrument used in ultraviolet-visible spectroscopy is called a UV/Vis spectrophotometer. The schematic diagram of a typical optical spectrophotometer is shown in Figure 2.12. It uses two light sources, a deuterium (D$_2$) and tungsten (W) lamps
for ultraviolet and visible light, respectively. After bouncing off a mirror (mirror 1), the light beam passes through a slit and hits a diffraction grating. The rotation of grating permits selection of a specific single wavelength which, in turn, passes through a slit. A filter is used to remove unwanted higher orders of diffraction. The monochromatic beam then hits a second mirror before it gets split by a half mirror such that half of the light is reflected while the other half transmitted. These two beams are subsequently allowed to pass through reference (or substrate) and the sample, respectively. The intensities of the resulting transmitted light beams are measured and compared. If the intensity of the transmitted beam associated with the reference and the sample beam are $I_0$ and $I$ respectively, absorbance of the sample film of thickness ($t$) is given by

$$I = I_0 \exp (-\alpha t) \quad \text{and} \quad A = (\ln I_0/I) = \alpha t$$

(2.6)

where $A$ is absorbance, $\alpha = (4\pi k/\lambda)$ is the absorption coefficient, $\lambda$ is the wavelength of the light and $k$ is the extinction coefficient.

![Figure 2.12 Ray diagram of an optical spectrophotometer](image)

Optical absorption spectra of glassy materials are characterized by a broad absorption edge. The onset of optical absorption can be obtained from the extrapolation method and can be correlated with the band gap energy ($E_g$) values of the glasses. The optical absorption spectra in glasses generally contain three regions, namely:
(a) High absorption region with absorption coefficient, $\alpha(\nu) \geq 10^4$ cm$^{-1}$, and is interpreted in terms of indirect interband optical transitions between conduction and valance bands, $\alpha(\nu)$ in this region is given by

$$\alpha(\nu) = \frac{A(h\nu - E_g) r}{h\nu}$$  \hspace{1cm} (2.7)

where $A$ is a constant called band tailing parameter, $E_g$ is band gap energy, $r$ is the index which can have different values, viz. 2, 3, 1/2 and 1/3 corresponding to indirect allowed, indirect forbidden, direct allowed and direct forbidden transitions, respectively. After rearranging Eq. (2.7), a plot of $(ah\nu)^r$ vs. $h\nu$ (Tauc’s plot [15]) gives a straight line, whose intercept on the energy axis gives $E_g$ and slope gives the value of constant $A$.

(b) The spectral region with $\alpha(\nu)$ lying between $10^2 - 10^4$ cm$^{-1}$ is defined as Urbach’s exponential tail region and the absorption coefficient in this region follows the Urbach’s rule [16] expressed as

$$\alpha(\nu) = \alpha_0 \exp\left(\frac{h\nu}{\Delta E}\right)$$  \hspace{1cm} (2.8)

where $\alpha_0$ is a constant and $\Delta E$ is the Urbach’s energy interpreted as the optical transition energy between localized tail states adjacent to the valance band and the extended states in the conduction band above the mobility edges.

(c) The region $\alpha(\nu) \leq 10^2$ cm$^{-1}$ involving low energy absorption is due to the optical transitions between localized states.

Optical spectra of the present polished glass sample were recorded using a dual beam Varian Carry 5000 UV/VIS/NIR spectrophotometer shown is Figure 2.13 at room temperature in the range 200-3000 nm.

Figure 2.13 Varian Carry 5000 UV/VIS/NIR Spectrophotometer
2.8 Electrical Characterization

Impedance spectroscopy (IS) is a relatively new and powerful method of characterizing many of the electrical properties of materials and their interfaces with electronically conducting electrodes. The study of dielectric properties of glasses helps in understanding their structure. The intrinsic disordered environment of charge carriers in glasses is believed to give rise to distinct transport mechanism such as the usually observed frequency dependent conductivity. Therefore, it is interesting to study the dynamics of the mobile ions in disordered ionic conductors, by interpreting their frequency dependent dielectric response. It may be used to investigate the dynamics of bound or mobile charges in the bulk or interfacial regions of any kind of solid or liquid material: ionic, semiconducting, mixed electronic-ionic and even insulators (dielectric). Every material has a unique set of electrical characteristics that are dependent on its dielectric properties. Accurate measurements of these properties can provide scientists and engineers with valuable information to properly incorporate the material into its intended applications for more solid designs. A dielectric material measurement can provide critical design parameter information for many electronics applications.

An alternating current (AC) circuit is a circuit driven by a voltage source (emf) that oscillates harmonically in time

\[ \hat{V} = V_0 e^{i\omega t} \]  

where, \( \hat{V} \) is the instantaneous voltage, \( V_0 \) represents the peak voltage, \( \omega \) is angular frequency, and \( t \) representing time. In the physical regime where non-linear effects can be neglected, the response is linear. Thus, aside from transients, the current also oscillates harmonically, and takes the form

\[ \hat{I} = I_0 e^{i(\omega t + \phi)} \]  

where, \( \hat{I} \) is instantaneous current, \( I_0 \) is the peak value of the current, and \( \phi \) is the phase difference between the external field and the induced current. By definition, the impedance of a sample can be expressed as

\[ \hat{Z} = \frac{\hat{V}}{\hat{I}} \]
Using the values of \( \hat{V} \) and \( \hat{I} \) from Eqs. (2.9) and (2.10), respectively, Eq. (2.11) can be rewritten as

\[
\hat{Z} = \frac{V_o}{I_o} e^{-i\omega t} = \left| \hat{Z} \right| (\cos \varphi - i \sin \varphi) = R - iX
\]

(2.12)

where, \( \left| \hat{Z} \right| = \frac{V_o}{I_o} \) is modulus of impedance, \( R \) is the resistance and \( X \) is reactance of sample. The admittance (\( \hat{Y} \)) and impedance are related by a simple relation

\[
\hat{Y} = \frac{1}{\hat{Z}} = \frac{R}{R^2 + X^2} + i\frac{X}{R^2 + X^2} = G + iB
\]

(2.13)

where, \( G \) is conductance and \( B \) is susceptance.

The application of harmonically varying electric field to a dielectric sample produces a time-dependent polarization, \( P(t) \). In the frequency domain, the spectral dependence of the polarization is related to the electric field \( E(\omega) \) variation by

\[
P(\omega) = \varepsilon_\infty \chi(\omega) E(\omega)
\]

(2.14)

where \( \varepsilon_\infty \) is the permittivity of free space, and \( \chi(\omega) \) is the dielectric susceptibility, in general, a complex quantity, i.e.,

\[
\chi^*(\omega) = \chi'(\omega) - i\chi''(\omega)
\]

(2.15)

The imaginary part \( \chi''(\omega) \) is termed as the ‘dielectric loss’ (and the resulting current due to this is in phase with the driving field). The dielectric loss in disordered solids usually exhibits a peak, much like that characterizing dielectric relaxation in dipolar liquids. The components of the dielectric susceptibility are related to those of the complex relative permittivity

\[
\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)
\]

(2.16)

As

\[
\varepsilon'(\omega) = 1 + \chi'(\omega)
\]

(2.17)

\[
\varepsilon''(\omega) = \chi''(\omega)
\]

(2.18)

Furthermore, the frequency-dependent relative permittivity or dielectric constant, \( \varepsilon^*(\omega) \) can be expressed in terms of conductivity by the following relation
\[
\sigma^*(\omega) = \sigma'(\omega) + i \sigma''(\omega)
\]
\[
= i\omega\varepsilon_o\varepsilon^*(\omega)
\]
\[
= i\omega\varepsilon_o [\varepsilon'(\omega) - i\varepsilon''(\omega)]
\]
(2.19)

The real part of \(\sigma^*(\omega)\) is usually denoted by \(\sigma'(\omega)\) and is given by

\[
\sigma'(\omega) = \varepsilon_o\omega\varepsilon''(\omega)
\]
(2.20)
to which any dc conductivity component should be added, and, equivalently, the imaginary part of the ac conductivity is given by

\[
\sigma''(\omega) = \varepsilon_o\omega\varepsilon'(\omega)
\]
(2.21)

Clearly, \(\sigma''(\omega) \neq 0\) reflects a phase difference between field and free charge carrier. Below phonon frequencies, whenever the conductivity is frequency dependent the charge carrier displacement always lags behind the electric field. The total measured conductivity at a given frequency \(\omega\) is separable into dc and ac components, namely

\[
\sigma_{tot} = \sigma_{dc} + \sigma(\omega)
\]
(2.22)

where \(\sigma(\omega)\) is ac conductivity.

Transport, which occurs under the application of a unidirectional unit field, is known as direct current (dc) conductivity, \(\sigma_{dc}\). For most oxide glasses, over a wide range of temperatures, the dc electrical conductivity, \(\sigma_{dc}\) is described by the well known Arrhenius law:

\[
\log \sigma_{dc} = A - (B/T)
\]
(2.23)

where \(A\) and \(B\) are constants. This equation is often written in the more familiar Arrhenius form as

\[
\sigma_{dc} (T) = \sigma_o \exp \left[-\frac{E_a}{kT}\right]
\]
(2.24)

where \(\sigma_o\) is the pre-exponential parameter which depends on the semiconductor nature, \(E_a\) denotes the thermal activation energy of electrical conduction and \(k\) is Boltzmann constant and \(T\) is temperature in Kelvin.

*The conductivity measurements of the glass samples were carried out using Alpha – A High Resolution Dielectric, Conductivity, Impedance, and Gain Phase Modular Measurement System by Novocontrol Technologies GmbH & Co. KG in the frequency*
range $10^{1}$ Hz to $10^{5}$ Hz and temperature ranging from 453 K- 593 K. The instrument used in the present work is shown in Figure 2.14.

![Figure 2.14 Photograph of Alpha-A impedance analyzer (Novocontrol)](image)

**References**


