CHAPTER 2

EXPERIMENTAL TECHNIQUES
2.1 Experimental Techniques

2.1.1 Method of preparation of glasses

Most of the traditional glasses are inorganic and non-metallic, but currently, a large number of organic glasses is in front line and they need different preparation techniques. Metallic glasses are also becoming very common with every passing year. Besides the conventional melt-quenched technique, glasses are also prepared by other methods such as physical vapour deposition, thermal evaporation, sputtering, glow discharge, chemical vapour deposition, sol-gel method, applying intense shock waves mechanical alloying etc.

Melt-quenching technique

Melt-quenching is the oldest but efficient process being used for the preparation of glass. Many materials need sufficiently rapid quenching in order that the melt solidifies into glass. Rates of cooling required for glassy phase formation are different for different materials. For example, certain glass formers such as $\text{B}_2\text{O}_3$, $\text{P}_2\text{O}_5$ etc. will form glassy phase even under conditions of slow cooling (like 1K/s). Most of the glasses with $\text{B}_2\text{O}_3$, $\text{SiO}_2$, and $\text{P}_2\text{O}_5$ etc. as network formers can be prepared by this method. However, for preparing metallic glasses, cooling rates of the order of $10^7$ K/s is required which require special techniques like melt spinning, melt extraction etc.

Glass samples preparation

Series of transition metal ions doped mixed alkali zinc borate glasses are prepared by using analar grade chemicals of $\text{ZnO}$, $\text{Li}_2\text{CO}_3$, $\text{Na}_2\text{CO}_3$, $\text{B}_2\text{O}_3$ and transition metal oxides ($\text{TMO} = \text{TiO}_2$, $\text{Cr}_2\text{O}_3$, $\text{Fe}_2\text{O}_3$, $\text{MoO}_3$) as starting materials with 99.9% of purity. These mixtures are sintered at 750 K and melted in an electric furnace in a silica crucible around 1250 K for nearly 1h. The melt is then quenched at room temperature in air to form a glass. The glasses so formed are
annealed at 700 K for 1h to relieve the structural stress. The images of the prepared samples are shown below.

**Undoped ZLN B Glasses**

![Undoped ZLN B Glasses](image)

**Titanium Doped ZLN B Glasses**

![Titanium Doped ZLN B Glasses](image)

**Chromium Doped ZLN B Glasses**

![Chromium Doped ZLN B Glasses](image)

**Iron Doped ZLN B Glasses**

![Iron Doped ZLN B Glasses](image)

**Molybdenum Doped ZLN B Glasses**

![Molybdenum Doped ZLN B Glasses](image)
2.1.2 Physical properties

Density measurements

Different materials usually have different densities and density may be relevant to buoyancy, purity and packaging. Density of solids is mostly the simplest physical property that can be measured. However, it would be a highly informative property if the structure of the material could be well defined. The density determination is performed by means of Archimedes principle (buoyancy method), which states that a body immersed in a fluid apparently loses weight by an amount equal to the weight of the fluid it displaces. This method allows determination of the density of solids, viscous and pasty substances, as well as liquids. Density data is used to calculate the volumes of structural units present in various types of glass. In contrast, in alkali borate glasses the volume of BO$_3$ unit and also that of BO$_4$ unit change markedly with the glass composition. Here the densities of all prepared glass samples are measured by Archimedes method with Xylene as an immersion fluid. In the present study Vibra HT/HTR density measurement kit was used to observe the density values as shown in Fig. 2.1.

![Fig. 2.1 Vibra HT/HTR density measurement kit](image)
Refractive Index

Every material has a fundamental property known as its refractive index, which indicates how a ray of light will refract (or bend) when it enters that material. A refractometer measures this property and is used to quickly and efficiently determine the concentration of a substance in solution, or even to identify different materials. The refractive index of a material medium is an important optical parameter since it exhibits the optical properties of the material. Its values are often required to interpret various types of spectroscopic data. The refractive index coefficients are important parameters in the design of a solid state laser. Quick measurements of refractive indices using simple techniques and refractometer can help controlling adulteration of liquids of common use to a greater extent. Sensitive determination of the refractive indices of certain materials is very important in many fields of research such as material analysis and environmental pollution monitoring.

Instrumentation

A refractometer measures the extent to which light is bent (i.e. refracted) when it moves from air into a sample and is typically used to determine the index of refraction (refractive index or n) of a sample. The refractive index is a unit less number, between 1.3000-1.7000 for most compounds. In the present case the refractive indices of all prepared glass materials are measured by using Atago NAR-4T Abbe’s Refractometer (Fig. 2.2). Abbe’s refractometer working principle is based on critical angle. In the Abbe’s refractometer, sample is put between two prisms-measuring and illuminating. Light enters sample from the illuminating prism, gets refracted at critical angle at the bottom surface of measuring prism and then the telescope is used to measure position of the border between bright and light areas. Telescope reverts the image, so the dark area is at the bottom. The construction of Abbe’s refractometer is shown in Fig. 2.3.
Fig. 2.2 Abbe’s refractometer

Fig. 2.3 Construction of Abbe’s refractometer
The physical properties of transition metal ions doped glasses can be investigated by measuring their basic physical parameters like density and refractive index. The density and refractive index are the most important parameters in the industrial glass production and are required for calculating the other parameters such as optical dielectric constant, elastic property, thermal conductivity, molar refractivity, ionic concentration, electronic polarizability, inter-ionic distance and polaron radius etc. The physical transport properties of semi conducting glasses are very interesting and provide useful information regarding the structure and conduction mechanism. The nature and the diffusivities of alkali ions of the glass systems may change the properties of physical parameters which lead to non-linear behaviour.

2.1.3 Powder X-ray diffraction

Powder XRD is perhaps the most widely used X-ray diffraction technique for characterizing materials. X-rays are electromagnetic radiation with typical photon energies in the range of 100 eV - 100 keV. For diffraction applications, only short wavelength X-rays (hard X-rays) in the range of a few angstroms to 0.1 angstrom (1 keV - 120 keV) are used. Because the wavelength of X-rays is comparable to the size of atoms, they are ideally suited for probing the structural arrangement of atoms and molecules in a wide range of materials. The energetic X-rays can penetrate deep into the materials and provide information about the bulk structure.

X-ray diffraction patterns of powdered glass samples are recorded on PANalytical Xpert Pro diffractometer. This technique indicates the nature of the material whether it is crystalline or amorphous. Glassy or amorphous materials do not have a long range atomic order i.e., atoms are randomly arranged or lack of periodicity. Therefore a diffraction pattern containing sharp peaks is not expected.
as observed in crystalline materials. No sharp peaks are observed in all the investigated diffraction patterns of glass samples which indicate the amorphous nature of materials. PANalytical Xpert Pro diffractometer is used to record the diffraction patterns of the prepared samples and is shown in Fig. 2.4. It consists of three basic elements: an X-ray tube, a sample holder and an X-ray detector. X-rays are generated in a cathode ray tube by heating a filament to produce electrons, accelerating the electrons towards a target by applying a voltage and bombarding the target material with electrons. When electrons have sufficient energy to dislodge inner shell electrons of the target material, characteristic X-ray spectra are produced. The pattern was recorded by Cu Kα radiation with λ of 1.5406 Å and nickel monochromator filtering the wave at tube voltage of 40 kV and tube current of 30 mA.

Fig. 2.4 PANalytical X-Pert Pro diffractometer
2.1.4 FT-IR spectrophotometer

Theory

A molecular vibration occurs when atoms in a molecule are in periodic motion while the molecule as a whole has constant translational and rotational motion. In general, a molecule with N atoms has \((3N-6)\) normal modes of vibration, but a linear molecule has \((3N-5)\) such modes, as rotation about its molecular axis cannot be observed. The vibrational states of a molecule can be probed in a variety of ways. The most direct way is through infrared spectroscopy, as vibrational transitions typically require an amount of energy that corresponds to the infrared region of the spectrum. IR radiation does not have enough energy to induce electronic transitions as seen with UV. Absorption of IR is restricted to compounds with small energy differences in the possible vibrational and rotational states.

For a molecule to absorb IR, the vibrations or rotations within a molecule must cause a net change in the dipole moment of the molecule. The alternating electrical field of the radiation interacts with fluctuations in the dipole moment of the molecule. If the frequency of radiation matches the vibrational frequency of the molecule then radiation will be absorbed, causing a change in the amplitude of molecular vibration.

Molecular rotations

Rotational levels are quantized and absorption of IR by gases yields line spectra. However, in liquids or solids, these lines broaden into a continuum due to molecular collisions and other interactions.
Molecular vibrations

The positions of atoms in a molecule are not fixed; they are subject to a number of different vibrations. Vibrations fall into the two main categories of stretching (Fig. 2.5) and bending (Fig. 2.6).

**Stretching:** Change in inter-atomic distance along bond axis

**Bending:** Change in angle between two bonds. There are four types of bend:

- Rocking
- Scissoring
- Wagging
- Twisting

FT-IR (Fourier Transform Infrared) is a technique which is used to obtain an IR spectrum of absorption, emission, photoconductivity or Raman scattering of a solid, liquid or gas. In IR spectroscopy, IR radiation is passed through a sample. Some of the IR radiation is absorbed by the sample and some of it is passed through (transmitted). The resulting spectrum represents a fingerprint of a sample
with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms making up the material. Because each different material is a unique combination of atoms, no two compounds produce the exact same IR spectrum. Therefore, IR spectroscopy can result in a positive identification (qualitative analysis) of every different kind of material. IR stretching frequencies are controlled by the functional groups and to determine which functional groups are present/absent in a molecule by IR spectrometer [1].

Instrumentation

FT-IR spectrometry was developed in order to overcome the limitations encountered with dispersive instruments. The main difficulty was the slow scanning process. A method for measuring all of the IR frequencies simultaneously, rather than individually, was needed. A solution was developed which employed a very simple optical device called an interferometer. The interferometer produces a unique type of signal which has all of the IR frequencies “encoded” into it. Most interferometers employ a beam splitter which takes the incoming IR beam and divides it into two optical beams. One beam reflects off of a flat mirror which is fixed in place. The other beam reflects off of a flat mirror which is on a mechanism which allows this mirror to move a very short distance (typically a few millimeters) away from the beam splitter. The two beams reflect off of their respective mirrors and are recombined when they meet back at the beam splitter. Because the path that one beam travels is a fixed length and the other is constantly changing as its mirror moves, the signal which exits the interferometer is the result of these two beams “interfering” with each other. The resulting signal is called an interferogram. Because a frequency spectrum is required, a well-known mathematical technique called the Fourier transformation is performed by the computer which then presents the user with the desired spectral information for analysis. The layout of a spectrometer is shown in
Fig. 2.7. In the present investigations, FT-IR spectra are recorded on a Bruker FT-IR spectrophotometer in the region 500-2000 cm$^{-1}$ and it is shown in the Fig. 2.8.
2.1.5 Electron paramagnetic resonance spectrophotometer

Electron Paramagnetic Resonance (EPR) is a valuable technique for obtaining detailed information on the geometric and electronic structure of materials, in particular, transition metal containing materials. On the other hand, paramagnetic defects in crystalline or amorphous solid materials, such as semiconductors, optical glasses and ceramics, can be stable for very long times. Such defect or impurity centres may significantly influence the electrical and optical properties of these materials even at very low concentration.

Like a proton, the electron has “spin”, which gives it a magnetic property known as a magnetic moment. The magnetic moment makes the electron behave like a tiny bar magnet. When we supply an external magnetic field, the paramagnetic electrons can either orient in a direction parallel or antiparallel to the direction of the magnetic field. This creates two distinct energy levels for the unpaired electrons and allows us to measure them as they are driven between the two levels. In order for the transition to occur we must also have the external magnetic field at a specific strength, such that the energy level separation between the lower and upper states is exactly matched by the microwave frequency. The condition where the magnetic field and the microwave frequency are just right to produce an EPR resonance (or absorption) is known as the resonance condition and is described by the equation as shown in the Fig. 2.9.

The magnetic field $B_0$ produces two energy levels for the magnetic moment $\mu$ of the electron. The unpaired electron will have a state of lowest energy when the moment of the electron is aligned with the magnetic field and a stage of highest energy when $\mu$ is aligned against the magnetic field. The two states are labelled by the projection of the electron spin, $m_s$ on the direction of the magnetic field. Because the electron is a spin $\frac{1}{2}$ particle, the parallel state is designated as $m_s= -1/2$ and the antiparallel state is $m_s= +1/2$. The energy of each orientation is
the product of $\mu$ and $B_0$. For an electron $\mu = m_e g_e \beta$, where $\beta$ is a conversion constant called the Bohr magneton and $g_e$ is the spectroscopic $g$ factor of the free electron and equals 2.0023 ($\approx 2.00$). Therefore, the energies for an electron with $m_s = +1/2$ and $m_s = -1/2$ are:

$$E_{+1/2} = +1/2 \ g_e \beta B_0$$
$$E_{-1/2} = -1/2 \ g_e \beta B_0$$

As a result there are two energy levels for the electron in a magnetic field (Fig. 2.10). Here $B_0$ is the magnetic field strength, $\beta$ is Bohr magneton.

![Fig. 2.9 EPR resonance condition](image)

![Fig. 2.10 Induction of the spin state energies as a function of the magnetic field $B_0$](image)
The expression for the resonance of the ion is \( h\nu = g\beta B \), where \( h \) is Planck's constant, \( \beta = \frac{eh}{2mc} \) and \( g \) is Lande g-factor. This condition can be satisfied by varying any one of the variables \( \nu \) or \( B \). The value of g-factor which represents the rate of divergence of magnetic energy levels with field is calculated from the equation \( h\nu = g\beta B \) after achieving the resonance condition. The value of \( g \) for a free electron is 2.0023. The energy levels of an ion are further split due to the interaction of electron spin with the spin of its own nucleus and also due to the spins of surrounding nuclei. Spin-orbit coupling and crystal field effects also modify the energies of the levels resulting from the ground state. For perfectly octahedral site symmetry, the g-values do not change with orientation of the crystal. But g-values vary with the orientation in a low symmetry fields. In general, there exists three g-values corresponding to x, y, z axes of the crystal: \( g_x, g_y \) and \( g_z \). In the case of a tetragonal site, \( g_x = g_y \) and this g-value is often referred to as \( g_L \). This value can be obtained when the external magnetic field is applied perpendicular to the principal axis (z-axis). When the magnetic field is parallel to z-axis, the g-value \( g_z \) is referred to as \( g_\parallel \). Based on the g-values, the site symmetry of the central metal ion can be known [2].

**Instrumentation**

The basic components of an EPR spectrometer are shown in Fig. 2.11. EPR spectroscopy can be carried out by either (a) varying the magnetic field or holding the frequency constant or (b) varying the frequency and holding the magnetic field constant (as is the case for NMR spectroscopy). Commercial EPR spectrometers typically vary the magnetic field and holding the frequency constant. There are a variety of EPR techniques; each having its own advantages. In continuous wave EPR (CW-EPR), the sample is subjected to a continuous beam of microwave irradiation of fixed frequency and the magnetic field is swept. Different microwave frequencies may be used and they are denoted as S-band (3.5 GHz), X-band (9.25 GHz), K-band (20 GHz), Q-band (35 GHz) and W-band (95 GHz).
In the present investigations, EPR spectra of all glass samples are recorded on JEOL JES TE100 EPR spectrometer and are shown Fig. 2.12.

![Block diagram of a typical EPR spectrometer](image1)

**Fig. 2.11** Block diagram of a typical EPR spectrometer

![JEOL JES TE100 EPR spectrometer](image2)

**Fig. 2.12** JEOL JES TE100 EPR spectrometer
2.1.6 Optical absorption spectrophotometer

Spectroscopy is the measurement and interpretation of electromagnetic radiation absorbed or emitted when the molecules or atoms or ions of a sample move from one energy state to another energy state. This change may be ground state to exited state or vice-versa. When energy is applied to matter it can be absorbed, emitted, cause a chemical change (reaction), or be transmitted. Electromagnetic spectrum consists of various wavelengths of different regions and is shown in the following Fig. 2.13.

A spectrophotometer is a photometer (a device for measuring light intensity) that can measure intensity as a function of color or more specifically, the wavelength of light. To obtain absorption information, a sample is placed in the spectrophotometer and UV-VIS-NIR light at a certain wavelength or range of wavelengths is transmitted through the sample. The spectrophotometer measures how much of the light is absorbed by the sample. Instruments for measuring the absorption of radiation are made up of the following components:

1. Sources
2. Wavelength selector (monochromator)
3. Sample containers
4. Detector
5. Signal processor and readout

In a double beam spectrometer, the radiation coming from the monochromator is split into two beams with the help of a beam splitter. These are passed simultaneously through the reference and the sample cell. The transmitted radiations are detected by the detectors and the difference in the signal at all the wavelengths is suitably amplified and sent for the output. The general arrangement of a double beam spectrometer is shown in Fig. 2.14. There could be variations
depending on the manufacturer, the wavelength regions for which the instrument is designed, the resolutions required etc.

In the present investigation JASCO V-670 UV-VIS-NIR Spectrophotometer (Fig. 2.15) is used to record optical absorption spectra for the prepared samples. The sources of radiation in UV-VIS and NIR regions are deuterium lamp and iodine tungsten lamp respectively. The difference in the intensities of the light transmitted through the sample is measured using suitable detectors. Photomultiplier tube R928 in UV-VIS region and PbS in NIR region act as detectors. The optical absorbance is the difference in the intensities in the transmitted light through the sample and the reference is plotted against wavelength of light on the screen. The total data is stored in the computer and the data can be magnified and displayed on the monitor [3].

![Various wavelength regions of electromagnetic spectrum](image)

**Fig. 2.13 Various wavelength regions of electromagnetic spectrum**
Fig. 2.14 Schematic diagram of a double-beam spectrophotometer

Fig. 2.15 JASCO V-670 UV-VIS-NIR spectrophotometer
2.2 References

