CHAPTER 2

EXPERIMENTAL METHODS

This chapter gives the description of experimental methods employed in the preparation and characterization of Li$_2$O-MoO$_3$-B$_2$O$_3$ glasses. The details of the apparatus used and the techniques adopted for measuring electrical properties, optical absorption, IR, ESR spectral and photo luminescence spectra are also described in detail in this chapter.
Experimental Methods

2.1 Introduction

In this chapter the detailed description of the methods used in the preparation of pure as well as transition metal ions and rare earth ions doped glasses are presented. Various measurement techniques employed for characterization of the glasses are also discussed. The description of the apparatus used and detailed procedure for studying dielectric properties are presented. The details of measurements of IR, optical absorption and electron spin resonance spectra of transition metal ions doped Li2O-MoO3-B2O3 glasses are also included.

2.2 Glass preparation

2.2.1 Composition of the glass

The compositions of the glasses used for the present study are:

1. 40 Li2O-4 MoO3-(56-x) B2O3: x V2O5 (0 ≤ x ≤ 1.5)

2. 40 Li2O-(4-x) MoO3-56 B2O3: x CuO (0 ≤ x ≤ 1.2)

3. 40 Li2O-4 MO-55 B2O3: 1 Ln2O3 (Ln3+ = Pr3+, Nd3+, Sm3+ and Er3+)
   where MO = Nb2O5, MoO3 and WO3.

2.2.2 Methods of preparation of glasses

The glasses used for the present study are prepared by the melting and quenching techniques [1-3]. The starting materials used for the preparation of the present glasses were analytical grade reagents (99.9 % pure) of Li2CO3, H3BO3, MoO3, Nb2O5, WO3, V2O5, CuO and Pr2O3, Nd2O3,
Sm$_2$O$_3$, Er$_2$O$_3$. The compounds of required compositions were thoroughly mixed in an agate mortar and melted in a platinum crucible. The furnace used was a PID temperature controlled furnace (Fig. 2.1). The glasses were melted at about 900 - 950 °C for an hour till a bubble free liquid was formed. The resultant melt was poured on a rectangular brass mould (containing smooth polished inner surface) held at room temperature. The samples were subsequently annealed at 250 °C in another furnace. The glasses were then ground and optically polished. The approximate final dimensions of the glasses used for studying the electrical and optical properties are 1 cm x 1 cm x 0.2 cm. For dielectric measurements thin coating of silver paint was applied on either side of the glasses, to serve as electrodes.

Fig. 2.1 Schematic sketch of atmosphere controlled furnace.
2.3 Characterization of the samples

2.3.1 X-Ray diffraction

The crystalline phases in the glass ceramic samples were checked by X-ray diffraction spectra recorded on SEIFERT diffractometer model SO-DEBYE FLUX 202 fitted with copper target and nickel filter operated at 40 kV, 30 mA. Fig. 2.2 represents the schematic diagram of general X-ray diffractometer.

SO-DEBYE FLUX 202 X-ray Diffracto meter
Glassy or amorphous materials do not have a long-range atomic order, i.e., atoms are arranged randomly. Therefore, a diffraction pattern containing sharp peaks is not expected as observed in crystalline materials. All glasses investigated were subjected to the X-ray diffraction measurements to ascertain the samples amorphous nature. The absence of peaks indicates the amorphous nature of these materials i.e., long-range atomic order is absent.

2.3.2 Scanning electron microscopy

Scanning electron microscopy studies were also carried out on these glasses to check the crystallinity in the samples using JEOL JSM-5600 Scanning Electron Microscope.
2.3.3 Physical parameters

The density (d) of the glasses was determined by the standard principle of Archimedes' using o-xylene (99.99 % pure) as the buoyant liquid. A direct reading balance (capacity 100 gm, readability 0.1 mg) was used for weighing. The bulk glass was suspended on a very thin copper strand that was set in the immersion liquid container; the density of the samples was determined by weighing them in the liquid and in air. From the measured values of density d and calculated average molecular weight $\bar{M}$, various physical parameters such as metal ion concentration $N_i$, mean ion
separation $R_i$, which are useful for understanding the physical properties of these glasses were evaluated using standard formulae [4].

The average errors in these physical parameters were calculated and given below.

- Density, $d (\text{g/cm}^3)$ ±0.001
- Dopant ion concentration, $N_i (10^{20}/\text{cm}^3)$ ±0.01
- Inter-ionic distance of dopant ions, $R_i (\text{Å})$ ±0.01
- Polaron radius, $R_p (\text{Å})$ ±0.01
- Field strength, $F_i (10^{15} \text{ cm}^{-2})$ ±0.001

2.3.4 Differential scanning calorimetry studies

Differential scanning calorimetry studies was carried out using Universal V2.6D TA instrument with a programmed heating rate of 10 °C / min, in the temperature range 30-600 °C, to determine the glass transition temperature and other glass forming ability parameters to an accuracy of ± 1°C.

Universal V2.6D TA Differential Scanning Calorimeter
2.4 Analytical techniques

2.4.1 Dielectric measurements

The dielectric measurements of the samples used in the present investigation were taken on HP 4263B LCR Meter in the frequency range $10^2 - 10^5$ Hz [5] in the temperature range 30 – 350 °C. For some of the samples the measurements were taken in the high frequency range using a Radart Q-Meter.

2.4.1 (a) HP 4263B LCR Meter

Capacitance measurements were made with HP 4263B LCR Meter. The HP 4263B LCR Meter is a fully automatic high performance test instrument used to measure a wide range of parameters. The measurement speed of the instrument is 29 ms; it has a very fast quick recovery and has got built in comparator. It can measure the capacitance to a high accuracy and wide measurement range. The two measurement display sections, capacitance (C) and dissipation factor (D) provide the direct read out of the parameters. The instrument has got two modes of measurement viz., normal mode and average mode; in normal mode operation, the instrument
performs measurements at very high speed whereas in the average mode it has short, medium or long range rate of average of the measurement results.

The second mode has been adopted in the present measurements; show a high reliable and repeatable value than in the normal mode of the measurement. The accuracy in the measurement of dielectric constant is ~ 0.001 and that in loss is ~10^{-4}.

2.4.1 (b) Sample holders

Two different types of sample holders have been used for room and high temperature dielectric measurements:

i) For measurements at room temperature a laboratory made sample holder with teflon base and micrometer arrangement (Fig. 2.3(a)) was used for dielectric loss measurements.

ii) For the temperature variation of the dielectric properties at a fixed frequency the sample holder shown in Fig. 2.3(b) has been used. The sample was held in between two silver electrodes and the holder was heated by a 200 W nichrome heater. The heating was controlled by adjusting the current with a variac. For good thermal stability, cold water was circulated round the jacket. The readings were recorded after the sample had attained the steady temperature. A chromel – alumel thermo couple was attached to the sample holder very close to the sample. The thermo emf developed across the junction was measured using digital PID temperature controller.
2.4.2 Spectroscopic properties

Under the spectroscopic properties (a) the optical absorption, (b) electron spin resonance spectra (c) the infrared transmission spectra and (d) luminescence spectra of Li$_2$O-MoO$_3$-B$_2$O$_3$ glasses doped with V$_2$O$_5$, CuO and Ln$_2$O$_3$ were studied.

2.4.2 (a) Optical absorption spectra

The optical absorption spectra of the glasses were recorded using a CARY 100 (varian) Spectrophotometer in the wavelength range 300-1200 nm.
A schematic diagram of the optical spectrophotometer arrangement in the equipment is shown in Fig. 2.4. The light beam emitted from the light source is reflected by the mirror $M_1$ and directed into the monochromator. Deuterium lamp $D_2$ is used as a light source from 200 nm to light source switching wavelength (whose initial value is 350.5 nm) and halogen lamp $W_1$ from light source switching wavelength 1100 nm, which are interchanged automatically according to the wavelength range.

![Schematic diagram of the optical system of the spectrophotometer.](image)

The light source position is automatically controlled for maximum sensitivity and the light source condenser mirror is located outside the light source housing so as not to be exposed to heat rays and ozone. All the optical elements excluding the light source are sealed from the external
atmosphere by the window plate W so as to be dust free. The slit width of the monochromator is fixed at 2 nm.

The light beam coming from the monochromator is passed through the stray-light cut off filter F, reflected by mirror M₂ and then split by the half mirror M₃ into the sample and reference beams. Each beam passes through the respective cell to photo diode detector. Fig. 2.5 shows the electrical system. In the electrical system of the spectrophotometer, the main control element is a microcomputer CPU which controls the light source lighting, light source switching, filter switching, wavelength scan, CRT display, keyboard and printer.

Fig. 2.5 Schematic diagram of electrical system of the spectrophotometer.
The sample and the reference beams are detected by photodiode detectors. These beams are then logarithmically converted and their difference is obtained by a differential amplifier. Some amount of the signal is then added so that the signal zero and level zero may correspond to ABS zero. The signal passes through the amplifiers 1 and 2. Amplifier 1 serves to finely adjust the signal level and amplifier 2 serves to apply a GAIN up to 10-fold to the signal. Then, after A/D-converter the signal is read by the CPU. The resolving power of the instrument is 0.1nm.

2.4.2 (b) Electron spin resonance spectra

The electron spin resonance spectra of Li$_2$O-MoO$_3$-B$_2$O$_3$ doped with transitional metal ions were recorded at room temperature using E11Z Varian X-band ($\nu = 9.5$ GHz) ESR spectrometer of 100 kHz field modulation that works.

JEOL ESR spectrometer
The principle of microwave spectrometer used for Electron Spin Resonance and the schematic diagram of the JOEL ESR spectrometer are shown in Figs. 2.6 & 2.7 The arrangement consists of a microwave unit (a pre amplifier, a Gunn oscillator and an automatic frequency control circuit), a cavity resonator, a detector to measure the variations of the microwave power, a modulating system for the amplification of the signal, a recording unit, an electromagnet to produce uniform magnetic field and an electronic system to measure the variations in magnetic field.

Fig. 2.6 Principle of a microwave spectrometer used for electrons spin resonance.
The Gunn diode oscillator generates microwaves over a frequency range of 8.8 to 9.6 GHz (microwave X-band). The automatic frequency control circuit is used to match the frequency of the Gunn oscillator with the resonant frequency of the cavity resonator. When ESR is excited, microwaves from the resonator are reflected and enter the balance mixer that is made up of magic T and a crystal mount. The waves are then detected and amplified by the pre amplifier of the microwave unit. The magnetic field produced by the electromagnet operated at 200 V, 2 kVA can be varied with a field sweep of ± 2500 gauss. DC magnetic field modulation is used to reduce the noise contribution. The fine powder (the sample) of the glass is placed at the middle of the cavity resonator such that it is at the middle of the poles of the electromagnet. The sample is subjected the microwave magnetic field of a constant frequency which is perpendicular to the external
dc magnetic field. When the resonance condition is satisfied, the Q value of the cavity resonator changes and this variation is detected, amplified and recorded as a function of the field. A typical ESR absorption and first derivative signals are shown in Fig. 2.8.

![ESR Absorption and Differential Curve](image)

**Fig. 2.8 (a) ESR absorption curve**  
**Fig. 2.8 (b) ESR differential curve**

### 2.4.2 (c) *Infrared spectra*

Infrared transmission spectra were recorded on a Bruker IFS 66 V – IR spectrophotometer with a resolution of 0.1 cm⁻¹ in the range 400-2000 cm⁻¹ using potassium bromide pellets (300 mg) containing pulverized sample (1.5 mg). These pellets were pressed in a vacuum die at ~680 MPa.
2.4.2 (d) *Excitation and photoluminescence spectra*

The photoluminescence spectra of rare earth doped glasses were recorded on Fluoromax-3 (Jobin-Yvon, Horiba) fluorescence spectrophotometer with a monochrometer and photomultiplier tube for detecting the luminescence response in the appropriate wavelength regions.

The brief sketch of the methods employed in recording the absorption, excitation and photoluminescence spectra are shown in Fig 2.9.
Fig. 2.9 Brief sketch of the methods adopted in recording (a) absorption, (b) excitation and (c) photoluminescence spectra.

In general it is to be pointed out the data have been taken with the several Li$_2$O-MoO$_3$-B$_2$O$_3$ glasses doped with different transition metal oxides and rare earth oxides are found to be reproducible with in the accuracies mentioned.
References


