Experimental Methods

This chapter gives the description of experimental methods employed in the preparation and characterization of Li$_2$O–PbO–B$_2$O$_3$–SiO$_2$–Bi$_2$O$_3$–M$_2$O$_3$:CuO/MnO/Fe$_3$O$_5$/V$_2$O$_5$ (M = viz., Al$_2$O$_3$, Ga$_2$O$_3$, In$_2$O$_3$ and Tl$_2$O$_3$) glasses. The details of the apparatus used and the techniques adopted for measuring XRD, electrical properties, IR, Raman, optical absorption, and ESR spectra are described in detail in this chapter.
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 III group ions doped glasses are presented. Various measurement techniques employed for characterization of the samples are also discussed. The description of the apparatus used and detailed procedure adopted for studying dielectric properties, Infrared spectra, Raman spectra, optical absorption, electron spin resonance of transition metal ions.

2.2 Glass preparation

2.2.1 Composition of the glass

The detailed compositions of the glasses used in the present study are as follows:

5. \(19.4\text{Li}_2\text{O}–20\text{PbO}–20\text{B}_2\text{O}_3–30\text{SiO}_2–(10-x)\text{Bi}_2\text{O}_3–0.6\text{CuO}: x\text{Al}_2\text{O}_3\) \((0 \leq x \leq 5)\)

6. \(19.5\text{Li}_2\text{O}–20\text{PbO}–20\text{B}_2\text{O}_3–30\text{SiO}_2–(10-x)\text{Bi}_2\text{O}_3–0.5\text{MnO}: x\text{Ga}_2\text{O}_3\) \((0 \leq x \leq 5)\)

7. \(19\text{Li}_2\text{O}–20\text{PbO}–20\text{B}_2\text{O}_3–30\text{SiO}_2–(10-x)\text{Bi}_2\text{O}_3–1.0\text{Fe}_2\text{O}_3: x\text{In}_2\text{O}_3\) \((0 \leq x \leq 5)\)

8. \(19\text{Li}_2\text{O}–20\text{PbO}–20\text{B}_2\text{O}_3–30\text{SiO}_2–(10-x)\text{Bi}_2\text{O}_3–1.0\text{V}_2\text{O}_5: x\text{Tl}_2\text{O}_3\) \((0 \leq x \leq 5)\)

(all in mol%)

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 \(\text{Li}_2\text{CO}_3\), \(\text{PbO}\), \(\text{H}_3\text{BO}_3\), \(\text{SiO}_2\), \(\text{Bi}_2\text{O}_3\), \(\text{CuO}\), \(\text{MnO}\), \(\text{Fe}_2\text{O}_3\), \(\text{V}_2\text{O}_5\), \(\text{Al}_2\text{O}_3\), \(\text{Ga}_2\text{O}_3\), \(\text{In}_2\text{O}_3\), and \(\text{Tl}_2\text{O}_3\).
(Sigma Aldrich). The compounds of required compositions were thoroughly mixed in an agate mortar and melted in a silica crucible. The furnace used was a PID temperature controlled furnace (Fig. 2.2). The glasses were melted at about 1300 - 1350 °C for an ½ 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 350 °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 1.0 cm x 1.0 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. The photographs of some of the glass samples (as quenched) are shown below.

![Photographs of the glass samples](image1)

**Fig. 2.1** Photographs of the glass samples
2.3 Characterization of the samples

2.3.1 X-Ray diffraction

The crystalline phases if any in the glasses samples were checked by X-ray diffraction spectra recorded on Rigaku D/Max ULTIMA III X-ray diffractometer (Fig. 2.3(a)) with CuKα radiation. (Fig. 2.3(b)) represents the schematic diagram of general X-ray diffractometer.
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. Fig. 2.4 represents the amorphous nature of the samples.

Fig. 2.3(a) Rigaku D/Max ULTIMA III X-ray diffractometer

Fig. 2.3(b) Schematic representation of X-ray diffraction

Fig. 2.4 X-ray Diffraction pattern of I₁ and G₅ samples.
2.3.2 Physical parameters

For weighing a VIBRA HT digital balance of direct reading (capacity 220 g with readability 0.0001g) was used. Programmed HT density measurement kit is used to determine the densities and molar volumes of bulk samples automatically. The density ($\rho$) of the glasses was determined by the standard principle of Archimedes’ using o-xylene (99.99 % pure) as the buoyant liquid. 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, 5]. The average errors in these physical parameters were calculated and given below.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density, $d$ (g/cm³)</td>
<td>±0.0001</td>
</tr>
<tr>
<td>Dopant ion concentration, $N_i$ (10²⁰/cm³)</td>
<td>±0.01</td>
</tr>
<tr>
<td>Inter-ionic distance of dopant ions, $R_i$ (Å)</td>
<td>±0.01</td>
</tr>
<tr>
<td>Polaron radius, $R_p$ (Å)</td>
<td>±0.01</td>
</tr>
</tbody>
</table>
2.4 Analytical techniques

2.4.1 Dielectric measurements

The dielectric measurements of the samples used in the present investigation were taken on LF-impedance analyzer (Hewlett-Packard model 4192A in the frequency range $10^3 – 10^6$ Hz [6] in the temperature range 30 –300 °C. The accuracy in the measurement of dielectric constant is $\sim 0.01$ and that of loss is $\sim 0.001$. 
2.4.1 (a) L F Impedance Analyzer

Capacitance measurements were made with L F Impedance Analyzer. The HP 4192 A 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⁻¹; it has a very fast quick recovery and got built in comparator. It can measure the capacitance to a high accuracy and wide measurement range, which allows making precise measurements of some continuity frequencies. The two measurement display sections, capacitance and dissipation factor 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 where as in the average mode it has short, medium or long range rate to average the measurement results. The second mode that has been adopted in the present measurements to have a high reliable and repeatable value than in the normal mode of the measurement.
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 teflan base and micrometer arrangement (Fig. 2.6(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. 2.6(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.

Fig. 2.6(a) Laboratory made dielectric sample holder used at room temperature.  Fig. 2.6(b) High temperature sample holder.
2.4.1c. Dielectric breakdown strength

Dielectric breakdown strength for all the glasses at room temperature in air medium was determined using a high a.c. voltage insulation breakdown tester ITL (Instruments Techniques Pvt. Ltd., Hyderabad) Model BDV–7 operated with an input voltage of 230 V± 10% V and a frequency of 50 Hz.

The sample holder for breakdown tester is just similar to the one used for room temperature dielectric measurements. A schematic illustration of breakdown testing is given in Fig 2.7.

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) Raman spectra of glasses prepared have been studied.
2.4.2 (a) Optical absorption spectra

The optical absorption spectra of the glasses and glass ceramics were recorded at room temperature in the spectral wavelength range covering 300–2100 nm with a spectral resolution of 0.1 nm using JASCO Model V-670 UV–vis–NIR spectrophotometer (Fig. 2.8(a)).

![Fig. 2.8(a) Jasco Model V-670 UV-vis-NIR spectrophotometer](image)

![Fig. 2.8(b) Schematic diagram of the optical system of the spectrophotometer.](image)
A schematic diagram of the optical spectrophotometer arrangement in the equipment is shown in Fig. 2.8(b). 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.

The light beam coming from the monochromator is passed through the stray-light cut off filter $F$, reflected by mirror $M_2$ and then split by the half mirror $M_3$ into the sample and reference beams. Each beam passes through the respective cell to photo diode detector. Fig. 2.9 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.

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.

![Diagram](image)

**Fig. 2.9** Schematic diagram of electrical system of the spectrophotometer.

### 2.4.2 (b) Electron spin resonance spectra

The electron spin resonance spectra of Li$_2$O-PbO-SiO$_2$-B$_2$O$_3$-Bi$_2$O$_3$ glass doped with some transition metals ions were recorded at liquid nitrogen temperature using E11Z Varian X-band ($\nu = 9.5$ GHz) JEOL JES-TE5100 X-band ESR spectrometer (**Fig. 2.10**) of 100 kHz field modulation that works.
The principle of microwave spectrometer used for Electron Spin Resonance and the schematic diagram of the JOEL ESR spectrometer are shown in Figs. 2.11 & 2.12. The arrangement consists of a microwave unit (a preamplifier, 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. 2.10** JEOL ESR spectrometer

**Fig. 2.11** Principle of a microwave spectrometer used for recording ESR
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 preamplifier 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 of the sample 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

**Fig. 2.12** Schematic diagram of the JEOL ESR spectrometer.
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. 2.13.
2.4.2 (c) Infrared transmission spectra

Infrared transmission spectra were recorded on a (Fig. 2.14) with a resolution of 0.1 cm$^{-1}$ in the spectral 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 ~680MPa. The spectra were recorded on Jasco-FT/IR-5300 spectrophotometer.

**Fig 2.14** JASCO-FT/IR–5300 spectrophotometer
2.4.2 (d) Raman spectra

Micro Raman spectra are recorded using a Horiba Jobin-Yvon-UV800 Lab Ram HR spectrometer with a 17 mW internal He-Ne (Helium-Neon) laser source of excitation wavelength 632.8 nm with a spectral resolution of about \(~0.33 \text{ cm}^{-1}\).

![Horiba Jobin-Yvon-UV800 Lab Ram HR spectrometer](image)

**Fig. 2.15** Horiba Jobin-Yvon-UV800 Lab Ram HR spectrometer
References


