This chapter gives the description of experimental methods employed in the preparation and characterization of Li$_2$O–PbO–P$_2$O$_5$ glasses doped with tin and rare-earth ions. The details of the apparatus used for synthesizing the samples and the techniques adopted for measuring dielectric, optical absorption, IR, ESR and photoluminescence spectra are also described 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 tin and rare earth 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, optical absorption, electron spin resonance and luminescence spectra of tin ions and rare earth ions doped Li$_2$O–PbO–P$_2$O$_5$ glasses are also included.

2.2 Glass preparation

2.2.1 Composition of the glass

Within the glass forming region of Li$_2$O–PbO–P$_2$O$_5$ system the following compositions are chosen for the present study. The details of the compositions are:

1. 20 Li$_2$O–20PbO–(60-x)P$_2$O$_5$: x SnO$_2$,

2. 20 Li$_2$O–20PbO–(59-x)P$_2$O$_5$–1.0Er$_2$O$_3$: x SnO$_2$,

3. 20 Li$_2$O–20PbO–(59-x)P$_2$O$_5$–1.0Gd$_2$O$_3$: x SnO$_2$

with x = 0, 1.0, 3.0, 5.0, 7.0
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 glasses were analytical grade reagents (99.9 % pure) of Li₂O, PbO, P₂O₅, Gd₂O₃, Er₂O₃ and SnO₂. 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 800 - 850 °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 300 °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 Photograph of Li₂O–PbO–P₂O₅ glasses doped with tin oxide.
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) with CuKα radiation. (Fig. 2.4) represents the schematic diagram of general X-ray diffractometer.

Fig. 2.2 (a) PID controller and the photographs of (b) Melting furnace (c) Annealing furnace.
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.

The X-ray diffraction pattern for some of the glass samples investigated are presented in Fig. 2.5. The pattern clearly confirms the samples investigated are amorphous in nature.
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 HITACHI S-3400N Scanning Electron Microscope. The pictures have indicated virtually no crystallinity in the samples.

Fig. 2.5 XRD pattern of some of the glasses.

Fig. 2.6 SEM photograph of the glass $S_3$. 

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 g, 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.

Fig. 2.7 Vibra HT density kit used for measuring density

From the measured values of density d and calculated average molecular weight \( \overline{M} \), 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 refractive index \( (n_d) \) of the glass and glass ceramic samples was measured (at \( \lambda = 589.3 \) nm) at room temperature using Abbe refractometer with monobromo naphthalene as the contact layer between the glass and the refractometer prism.

![Abbe refractometer (Model NAR-4T)](image)

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

- Density, \( d \) (g/cm\(^3\)) \( \pm 0.0001 \)
- Dopant ion concentration, \( N_i \) (\( 10^{20} \)/cm\(^3\)) \( \pm 0.01 \)
- Inter-ionic distance of dopant ions, \( R_i \) (Å) \( \pm 0.01 \)
- Polaron radius, \( R_p \) (Å) \( \pm 0.01 \)
- Field strength, \( F_i \) (\( 10^{15} \) cm\(^{-2}\)) \( \pm 0.01 \)
2.4 Analytical techniques

2.4.1 Dielectric measurements (4294A precision impedance analyzer)

The dielectric measurements of the samples used in the present investigation by using Agilent 4294A precision impedance analyzer in the frequency range 100 Hz to 1 MHz in the temperature range 200 K – 370 K.

The auto balancing bridge method is commonly used in modern LF impedance measurement instruments. Its operational frequency range has been extended up to 110 MHz. A detailed discussion of the operating theory of a practical instrument using Agilent 4294A precision impedance analyzer as an example will now be discussed. Table 2.1 lists the 4294A’s key specifications, and Figure 2.9 shows the 4294A arrangement.
Table 2.1. Agilent 4294A precision impedance analyzer key specifications

| Test signal                          | Frequency: 40 Hz to 110 MHz, 1 MHz resolution  
|                                    |      | Signal level: 5 mV to 1 V rms               |
| Impedance measurement parameters    | [Z], [Y], θ, R, X, G, B, L, C, D, Q         |
| Impedance measurement range         | 3 mΩ to 500 MΩ                             |
| Basic measurement Accuracy          | 0.08% of reading                           |
| Display                              | Color graphic display, 6 digits            |
| DC bias                              | 0 V to ±40 V, 0 mA to ±100 mA              |
2.4.2 Spectroscopic properties

Under the spectroscopic properties (a) optical absorption, (b) electron spin resonance spectra (c) infrared transmission spectra (d) luminescence spectra were studied.

2.4.2 (a) Optical absorption spectra

The optical absorption spectra of the glasses 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. 2.10(a)).

Fig. 2.10(a) Jasco Model V-670 UV-vis-NIR spectrophotometer
A schematic diagram of the optical spectrophotometer arrangement in the equipment is shown in Fig. 2.10(b). The light beam emitted from the light source is reflected by the mirror M₁ and directed into the monochromator. Deuterium lamp D₂ is used as a light source from 200 nm to light source switching wavelength (whose initial value is 350.5 nm) and halogen lamp W₁ from light source switching wavelength 1100 nm, which are interchanged automatically according to the wavelength range.

Fig. 2.10 (b) Schematic diagram of the optical system of the spectrophotometer.
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 onto the mirrors M₃ and M₄ generating the sample and reference beams respectively. Each beam passes through the respective cell to photodiode detector. Fig. 2.11 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.
2.4.2 (b) Electron spin resonance spectra

The electron spin resonance spectra of Li$_2$O–PbO–P$_2$O$_5$ glasses doped with tin and gadolinium ions were recorded using E11Z Varian X-band ($\nu = 9.5 \, \text{GHz}$) JEOL JES-TES100 X-band ESR spectrometer (Fig. 2.12) of 100 kHz field modulation that works.

![Fig. 2.11 Schematic diagram of electrical system of the spectrophotometer.](image)

![Fig. 2.12 JEOL ESR spectrometer](image)
The principle of microwave spectrometer used for Electron Spin Resonance and the schematic diagram of the JEOL ESR spectrometer are shown in Figs. 2.13 & 2.14. 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.

![Diagram of microwave spectrometer](image1)

**Fig. 2.13** Principle of a microwave spectrometer used for recording ESR signal.

![Diagram of JEOL ESR spectrometer](image2)

**Fig. 2.14** Schematic diagram of the JEOL ESR spectrometer.
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 a circulator 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 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 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. 2.15.
2.4.2 (c) Infrared transmission spectra

Infrared transmission spectra were recorded on a (Fig. 2.16) 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 \(~680\text{MPa}\). The spectra were recorded on Jasco-FT/IR-5300 spectrophotometer.
2.4.2 (d) *Excitation and Photoluminescence spectra*

The photoluminescence spectra of the samples were recorded at room temperature on a FLS920 Spectrofluorometer (Fig. 2.17). All steady state luminescence and lifetime measurements were carried out using an Edinburgh Instruments FLSP 920 system, with 450 W Xe lamp, nanosecond and microsecond flash lamps as excitation sources. All emission spectra were corrected for the detector response and all excitation spectra for the lamp profile. All emission measurements were carried out with a resolution of 3 nm. Decay curves were recorded based on multi channel scaling mode using a microsecond flash lamp as the excitation source.
The FLS920-s is a modular, computer controlled spectrofluorimeter for measuring steady state luminescence spectra in the ultraviolet to near infrared spectral range with single photon counting sensitivity. It combines ultimate sensitivity with high spectral resolution and excellent stray light rejection.

The FLS920-s uses Czerny-Turner monochromators with high quality diffraction gratings for high dispersion and excellent imaging quality. Wavelength tuning is micro-stepper motor driven with a minimum step size of 0.05nm. Spectral details as close as 0.1nm can be resolved over the spectral range from UV to NIR.

Fig. 2.17 FLS920 Spectrofluorometer
The brief sketch of the methods employed in recording the absorption, excitation and photoluminescence spectra are shown in Fig 2.18.

Fig. 2.18 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–PbO–P$_2$O$_5$ glasses and glasses doped with tin oxide and rare earth ions are found to be reproducible within the accuracies mentioned.
References


