Chapter 2

Experimental Methods

THIS CHAPTER GIVES THE DESCRIPTION OF EXPERIMENTAL METHODS EMPLOYED IN THE PREPARATION AND CHARACTERIZATION OF Li_{2}O–Y_{2}O_{3}–SiO_{2} GLASSES. THE DETAILS OF THE APPARATUS USED AND THE TECHNIQUES ADOPTED FOR MEASURING ELECTRICAL PROPERTIES, IR, OPTICAL ABSORPTION, ESR AND
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 samples are also discussed. The description of the apparatus used and detailed procedure adopted for studying dielectric properties, Infrared, optical absorption, electron spin resonance, and photoluminescence spectra of transition metal ions and rare earth ions doped Li$_2$O–Y$_2$O$_3$–SiO$_2$ glasses are also included.

2.2 Glass preparation

2.2.1 Composition of the glass

Within the glass forming region of Li$_2$O–Y$_2$O$_3$–SiO$_2$ system the following compositions are chosen for the present study.

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

7. (40−x) Li$_2$O−10 Y$_2$O$_3$−50 SiO$_2$: x Fe$_2$O$_3$ (0 ≤ x ≤ 1.5 mol%)

8. (49−x) Li$_2$O− x Y$_2$O$_3$−50 SiO$_2$: 1.0 Ce$_2$O$_3$/Yb$_2$O$_3$ and
   (49−x) Li$_2$O−x Y$_2$O$_3$−50SiO$_2$: 0.5Ce$_2$O$_3$+0.5Yb$_2$O$_3$ (0 ≤ x ≤ 15.0 mol%)

9. (49−x) Li$_2$O− x Y$_2$O$_3$−50 SiO$_2$: 1.0 Yb$_2$O$_3$/Tm$_2$O$_3$ and
   (49−x) Li$_2$O−x Y$_2$O$_3$−50SiO$_2$: 0.5Yb$_2$O$_3$+0.5Tm$_2$O$_3$ (0 ≤ x ≤ 5.0 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 of Li$_2$CO$_3$, Y$_2$O$_3$, SiO$_2$, Fe$_2$O$_3$, Ce$_2$O$_3$, Yb$_2$O$_3$ and Tm$_2$O$_3$ (METALL, China, 3N pure). The compounds of required compositions were thoroughly mixed in an agate mortar and melted in a platinum crucible. The furnace used was a proportional–integral–derivative (PID) temperature controlled furnace (Fig. 2.1). The glasses were melted at about 1400–1450 °C for an hour till a bubble free liquid was formed. The resultant melt was then poured in a brass mould (containing smooth polished inner surface) and subsequently annealed from 350 °C with a cooling rate of 1°C/min. 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.
2.3 Characterization of the samples

2.3.1 Physical parameters

The density (d) of the glasses and glass ceramics was determined by the standard principle of Archimedes’ using O-xylene (99.99 % pure) as the buoyant liquid. The mass of the samples was measured to an accuracy of 0.1 mg using Ohaus digital balance Model AR2140. The density of the samples was determined by weighing the bulk glasses in the liquid and in air. 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 glasses was measured (at $\lambda = 589.3$ nm) at room temperature using Abbe refractometer (Fig. 2.2) with monobromo naphthalene as the contact layer between the glass and the refractometer prism.

**Fig. 2.2** Abbe refractometer (Model NAR-4T)

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/cm$^3$)</td>
<td>±0.0001</td>
</tr>
<tr>
<td>Dopant ion concentration, $N_i$ ($10^{20}$/cm$^3$)</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>
<tr>
<td>Field strength, $F_i$ ($10^{15}$ cm$^{-2}$)</td>
<td>±0.01</td>
</tr>
<tr>
<td>Refractive index</td>
<td>±0.001</td>
</tr>
</tbody>
</table>
2.4 Analytical techniques

2.4.1 Dielectric measurements

The dielectric measurements of the samples used in the present investigation by using Agilent 4294A precision impedance analyzer in the frequency range 40 Hz to 2 MHz in the temperature range 100 K – 360 K.

2.4.1 (a) 4294A precision impedance analyzer

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 2.3 shows the simplified diagram of the 4294A analog section.

Fig. 2.3. Agilent 4294A precision impedance analyzer
Table 2.1. Agilent 4294A precision impedance analyzer key specifications

<table>
<thead>
<tr>
<th>Test signal</th>
<th>Frequency: 40 Hz to 110 MHz, 1 MHz resolution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Signal level: 5 mV to 1 V rms</td>
</tr>
<tr>
<td>Impedance measurement parameters</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[Z], [Y], θ, R, X, G, B, L, C, D, Q</td>
</tr>
<tr>
<td>Impedance measurement range</td>
<td>3 mΩ to 500 MΩ</td>
</tr>
<tr>
<td>Basic measurement</td>
<td>0.08% of reading</td>
</tr>
<tr>
<td>Accuracy</td>
<td>Color graphic display, 6 digits</td>
</tr>
<tr>
<td>Display</td>
<td>0 V to ±40 V, 0 mA to ±100 mA</td>
</tr>
</tbody>
</table>

### 2.4.2 Spectroscopic properties

Under the spectroscopic properties (a) optical absorption, (b) electron spin resonance spectra (c) infrared transmission spectra (d) photoluminescence spectra Li$_2$O−Y$_2$O$_3$−SiO$_2$ glasses doped with different concentrations of Fe$_2$O$_3$ and Ln$_2$O$_3$ 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. 2.4(a)).
Fig. 2.4 (a) Jasco Model V-670 UV–vis–NIR spectrophotometer.

A schematic diagram of the optical spectrophotometer arrangement in the equipment is shown in Fig. 2.4 (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. 2.4 (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 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. 2.5 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.
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.

**Fig. 2.5** 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–Y$_2$O$_3$–SiO$_2$ glasses doped with iron ions were recorded at liquid nitrogen temperature using E11Z Varian X-band (ν = 9.5 GHz) JEOL JES-TES100 X-band ESR spectrometer (Fig. 2.6) of 100 kHz field modulation that works.

![JEOL ESR spectrometer](image)

Fig. 2.6 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. 2.7 & 2.8. 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. 2.7 Principle of a microwave spectrometer used for recording ESR signal.

Fig. 2.8 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 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 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. 2.9.
Infrared transmission spectra were recorded on a (Fig. 2.10) 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 \(\sim 680\) MPa. The spectra were recorded on JASCO-FT/IR-5300 spectrophotometer.
2.4.2 (d) Photoluminescence spectra

The photoluminescence spectra of the samples were recorded at room temperature on a Photon Technology International (PTI) Spectrofluorometer (Fig. 2.11). This instrument contains autocalibrated quadrascopic monochromator for wavelength selection and quadracentric sample compartment. The light source is high intensity continuous xenon lamp with high sensitivity TE-cooled InGaAs detector with lock-in amplifier and chopper for noise suppression and an additional emission mono with a 600 groove grating blazed at 1.2 microns. The system provides unmatched NIR luminescence recording capability from 500 nm–2.2 µm. The spectral resolution is 0.1 nm.
Fig. 2.11 Photon Technology International fluorescence spectrophotometer
The brief sketch of the methods employed in recording the absorption, excitation and photoluminescence spectra are shown in Fig 2.12.

The fluorescence decay curves were recorded for rare earth ions doped glasses and glass ceramics using Jobinyvon spectrofluorolog-3 with pulsed xenon lamp of 450 W.

In general it is to be pointed out the data have been taken with the several Li$_2$O–Y$_2$O$_3$–SiO$_2$ glasses mixed with different concentrations of iron oxide and rare earth oxides are found to be reproducible with in the accuracies mentioned.
References


