Chapter II
II EXPERIMENTAL TECHNIQUES

2.1 Glass preparation

The procedure for the preparation of various binary and ternary borate glasses has been reported by several authors [1-6]. Rare earth doped mixed alkali borate glasses were prepared using analar grade \( \text{H}_3\text{BO}_3 \), \( \text{Li}_2\text{CO}_3 \), \( \text{Na}_2\text{CO}_3 \), \( \text{K}_2\text{CO}_3 \), \( \text{Cs}_2\text{CO}_3 \), Sm\(_2\)O\(_3\), Dy\(_2\)O\(_3\), Ho\(_2\)O\(_3\) and Tm\(_2\)O\(_3\). Rare earth chemicals were obtained from Indian rare earths limited, Kerala and Himedia Laboratories, Bombay. All these chemicals have 99.9% purity. The appropriate chemicals were weighed (±15g) and mixed thoroughly with the help of mortar and pestle. Each composition was taken into porcelain crucible and kept in a muffle furnace to heat up to 950-1050\(^{\circ}\)C, depending on the composition and maintained this temperature for an half-an hour. The crucible was shaken frequently for homogeneous mixing. Then the melt was quenched at room temperature in air by pouring between two well-polished brass plates. The samples were annealed at 300-350\(^{\circ}\)C for 2 hrs to remove thermal strains. Glasses were cut into proper shape and polished for further characterization. Samples are characterized by X-Ray technique and are found to be amorphous. The samples are found to be stable at room temperature and atmospheric pressure. The glass systems studied in the present work are given below.

1. Samarium doped mixed alkali borate glasses (x in mol%)

\[
\begin{align*}
67\text{H}_3\text{BO}_3.x\text{Li}_2\text{CO}_3.(32-x) \text{Na}_2\text{CO}_3.1\text{Sm}_2\text{O}_3 & \quad (x=8, 12, 16, 20 \text{ and } 24) \\
67\text{H}_3\text{BO}_3.x\text{Li}_2\text{CO}_3.(32-x) \text{K}_2\text{CO}_3.1\text{Sm}_2\text{O}_3 & \quad (x=8, 12, 16, 20 \text{ and } 24) \\
67\text{H}_3\text{BO}_3.x\text{Li}_2\text{CO}_3.(32-x) \text{Cs}_2\text{CO}_3.1\text{Sm}_2\text{O}_3 & \quad (x=8, 12, 16, 20 \text{ and } 24) \\
67\text{H}_3\text{BO}_3.x\text{Na}_2\text{CO}_3.(32-x) \text{K}_2\text{CO}_3.1\text{Sm}_2\text{O}_3 & \quad (x=8, 12, 16, 20 \text{ and } 24)
\end{align*}
\]
II. Dysprosium doped mixed alkali borate glasses (x in mol%)

- 67.5 H$_3$BO$_3$.xLi$_2$CO$_3$. (32-x) Na$_2$CO$_3$.0.5Dy$_2$O$_3$  \( (x= 8, 12, 16, 20 \text{ and } 24) \)
- 67.5 H$_3$BO$_3$.xLi$_2$CO$_3$. (32-x) K$_2$CO$_3$. 0.5Dy$_2$O$_3$  \( (x= 8, 12, 16, 20 \text{ and } 24) \)
- 67.5 H$_3$BO$_3$.xLi$_2$CO$_3$. (32-x) Cs$_2$CO$_3$. 0.5Dy$_2$O$_3$  \( (x= 8, 12, 16, 20 \text{ and } 24) \)
- 67.5 H$_3$BO$_3$.xNa$_2$CO$_3$. (32-x) K$_2$CO$_3$. 0.5Dy$_2$O$_3$  \( (x= 8, 12, 16, 20 \text{ and } 24) \)

III. Holmium doped mixed alkali borate glasses (x in mol%)

- 67H$_3$BO$_3$.xLi$_2$CO$_3$. (32-x) Na$_2$CO$_3$.1Ho$_2$O$_3$  \( (x= 8, 12, 16, 20 \text{ and } 24) \)
- 67H$_3$BO$_3$.xLi$_2$CO$_3$. (32-x) K$_2$CO$_3$. 1Ho$_2$O$_3$  \( (x= 8, 12, 16, 20 \text{ and } 24) \)
- 67H$_3$BO$_3$.xLi$_2$CO$_3$. (32-x) Cs$_2$CO$_3$. 1Ho$_2$O$_3$  \( (x= 8, 12, 16, 20 \text{ and } 24) \)

IV. Thulium doped mixed alkali borate glasses (x in mol%)

- 69.5H$_3$BO$_3$.xNa$_2$CO$_3$. (30-x) K$_2$CO$_3$. 0.5Tm$_2$O$_3$  \( (x= 5, 10, 15, 20 \text{ and } 25) \)

The author has not studied the spectroscopic investigations of holmium doped sodium potassium mixed alkali borate glasses because they are already studied and reported in the literature. Similarly, due to lack of thulium oxide chemical, spectral investigations of Tm$^{3+}$ ion in the other three mixed alkali borate glasses were not done.

The glass compositions are the formal glass compositions although for the calculation of concentration, the actual composition was taken into account. The actual composition was calculated from the exact masses of the components in glass batch. The refractive indices were measured using an Abbe refractometer with sodium vapor lamp and using 1-monobromonaphthalene as an adhesive coating with an accuracy of $\pm 0.001$. The density measurements of all the glasses
were carried out with an accuracy of ±0.02 (g/cm³) by using the Archimedis principle with the following formula:

\[ D \ (g/cm^3) = \frac{a}{(a - b)} \]  

(1)

where 'a' is the weight of the glass in air, 'b' is the weight of the glass in xylene and 0.86 (g/cm³) is the density of xylene. The thickness of the sample used for absorption measurements was determined with a micrometer (±0.01 mm) at different points on the sample surface along the slit image of the spectrometer. Using the measured glass densities and refractive indices, concentration values are obtained using the formula:

Concentration of the lanthanide ions, \( N(\text{ions/cm}^3) = \)

\[ \frac{N_A \times (\text{mol}\% \text{ of the rare earth ion}) \times D}{M} \]  

(2)

where \( N_A \) is the Avogadro's number, \( D \) is density and \( M \), the average molecular weight. The rms deviation between experimental and calculated values are obtained using the formula:

\[ \delta_{\text{rms}} = \sqrt{\frac{\sum \Delta^2}{M' - N}} \]  

(3)

where \( \Delta^2 \) is the sum of the squares of deviation, \( M' \) the number of levels used for fitting and \( N \) is the number of parameters.
2.2 Absorption spectra

The room temperature optical absorption spectra of the polished samples in ultraviolet, visible and near infrared regions of Sm$^{3+}$, Dy$^{3+}$, Ho$^{3+}$ and Tm$^{3+}$ ions in all the mixed alkali borate glasses were obtained using a JASCO V-570 UV-VIS-NIR spectrophotometer and a Hitachi U-3400 spectrophotometer. Principle of the operation and some of the specifications of the two instruments are given below.

(i) JASCO V-570 UV-VIS-NIR Spectrophotometer

Fig. 2.1 shows the photograph of a JASCO V-570 UV-VIS-NIR spectrophotometer. This double beam spectrophotometer is capable of recording the optical absorption spectra in the wavelength region of 190 to 2500 nm at room temperature. A deuterium discharge tube in the wavelength region of 190 to 350 nm and a tungsten iodine lamp in the wavelength region of 330 to 2500 nm are used as light sources. The light from the source lamp is reflected by a mirror into a slit to fall onto the monochromator. It is dispersed by the grating in the monochromator and a light passing through the exit slit is monochromated. This light is split into two light paths by a sector mirror, one incident on the sample to be measured and the other on the reference sample such as solvent or other. The light that has passed through the sample or the reference sample is incident on a photomultiplier tube or a PbS photoconducting cell and converted into an electrical signal and, after being synchronously refracted, is converted into a digital form and enters a personal computer. The signal processed by the personal computer is displayed on an output device as spectrum. Light source change over, wavelength drive, slit drive, filter drive, etc. are controlled by the personal computer. The optical alignment of the JASCO V-570 UV-VIS-NIR Spectrophotometer is shown in Fig. 2.2 [7].
Fig. 2.1. Photograph of JASCO V-570 UV-VIS-NIR spectrophotometer.
Fig. 2.2. Optical alignment of JASCO V-570 UV-VIS-NIR spectrophotometer.
(ii) Hitachi U-3400 Spectrophotometer

(a) Optical Layout

Fig. 2.3 shows the photograph of a Hitachi U-3400 spectrophotometer. Optical layout of the Model U-3400 spectrophotometer is shown in Fig. 2.4 [8]. The white light emitted from the light source (Tungsten iodine lamp or Deuterium lamp) passes through a mechanical chopper CH to minimise the deviation in zero signal and to a first monochromator slit S₁. From S₁ it passes through a toroidal mirror M₂ to the littrow mount monochromator, which adopts a model 340 prism. The light from plane mirrors M₄ and M₅ passes through a second slit S₂ to the second monochromator which adopts a grating double monochromator system G₁ and G₂. The lenses used in the conventional monochromator have all been replaced with mirrors to eliminate any deviation due to chromatic aberration. This monochromator has a grating constant G₁ of 1440 lines/mm which can scan the wavelength range of 190 - 850 nm and G₂ of 600 lines/mm (800-2600 nm). In the monochromator, the light is converted into monochromatic light. It passes through an exit slit S₃ and a cylindrical mirror M₇ and reaches a rotating mirror M₈ where it is divided into two light beams; one is used for reference and the other is for sample. These two light beams, after passing through the sample compartment, alternately irradiate the photomultiplier R928, an ultra high sensitive detector for UV-VIS region and a PbS detector for near IR region. There they are converted into two electric signals.
Fig. 2.3. Photograph of Hitachi U-3400 UV-VIS-NIR double beam spectrophotometer.
Fig. 2.4. Optical layout of Hitachi spectrophotometer (model U-3400).
In Fig. 2.4

- $M_1$: Concave mirror
- $M_2$: Toroidal mirror
- $M_3$: Concave mirror
- $M_4$: Plane mirror
- $M_5$: Plane mirror
- $M_6$: Toroidal mirror
- $P$: Prism
- $P_{\text{M1}}$: Prism
- $S_1$: 1st monochromator slit
- $S_2$: 2nd monochromator entrance slit
- $S_3$: 3rd monochromator exit slit
- $P_{\text{M2}}$: Detector for UV-VIS (R928)
- PbS: Detector for near infrared ray
- $G_1$: Plane grating 1440 lines/mm (190-850 nm)
- $G_2$: Plane grating 600 lines/mm (800-2600 nm)
b) Specifications

<table>
<thead>
<tr>
<th>Item</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monochromater</td>
<td>Prism/grating double monochromator Littrow mount</td>
</tr>
<tr>
<td>Wavelength range</td>
<td>187 nm to 2600 nm</td>
</tr>
<tr>
<td>Resolution</td>
<td>0.07 nm (at bandpass of between 0.08 nm and 0.04 nm)</td>
</tr>
<tr>
<td>Spectral band pass</td>
<td>UV-VIS : 0.07 to 6 nm</td>
</tr>
<tr>
<td></td>
<td>NIR : 0.17 nm to 14 nm</td>
</tr>
<tr>
<td>Stray light</td>
<td>0.0001% max</td>
</tr>
<tr>
<td></td>
<td>(NaI 220nm, NaN02 340nm)</td>
</tr>
<tr>
<td>Wavelength accuracy</td>
<td>UV-VIS : ±0.2 nm</td>
</tr>
<tr>
<td></td>
<td>NIR : ±1 nm</td>
</tr>
<tr>
<td></td>
<td>Automatic wavelength calibrating function built in.</td>
</tr>
<tr>
<td>Wavelength setting</td>
<td>UV-VIS : ±0.1 nm</td>
</tr>
<tr>
<td>Repeatability</td>
<td>NIR : ±0.5 nm</td>
</tr>
<tr>
<td>Baseline stability</td>
<td>Better than 0.0004 Abs/h (at 340 nm)</td>
</tr>
<tr>
<td>Baseline flatness</td>
<td>Better than ±0.001 Abs (UV-VIS)</td>
</tr>
<tr>
<td></td>
<td>Better than 0.002 Abs (NIR)</td>
</tr>
<tr>
<td>Light source</td>
<td>Adjustment – free deuterium lamp</td>
</tr>
<tr>
<td></td>
<td>Adjustment – free iodine tungsten lamp (50 W)</td>
</tr>
<tr>
<td>Sample compartment</td>
<td>Beam spacing 100 mm</td>
</tr>
<tr>
<td>Detector</td>
<td>Photomultiplier R 928 (UV-VIS) PbS (NIR)</td>
</tr>
<tr>
<td>Display</td>
<td>12-inch monochromatic display</td>
</tr>
<tr>
<td>Recorder</td>
<td>Thermosensitive graphic</td>
</tr>
</tbody>
</table>
In the present work, the optical absorption spectra of glass samples were recorded in absorbance mode. The absorption spectrum gives optical density (arbitrary units) versus wavelength in UV-VIS-NIR regions. The measured wavelengths of the corresponding transitions have been converted into wave numbers (in cm⁻¹).

2.3 Emission spectra

The room temperature emission spectra of the polished samples in their respective wavelength regions of Sm³⁺, Dy³⁺ and Ho³⁺ ions in all the mixed alkali borate glasses were obtained using SPEX Fluoro Max-3 spectro-fluorometer and Hitachi U-4700 spectrophotometer under suitable excitation wavelength. The photograph of the SPEX Fluoro Max-3 spectro-fluorometer is shown in Fig. 2.5. Some of the specifications of the SPEX Fluoro Max-3 spectro-fluorometer are given below [9].

(i) Model SPEX Fluoro Max-3 spectro-fluorometer

(a) Specifications

<table>
<thead>
<tr>
<th>Item</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Excitation light source</td>
<td>150-W xenon CW ozone-free lamp</td>
</tr>
<tr>
<td>Optics system</td>
<td>Total reflection</td>
</tr>
<tr>
<td>Dispersion</td>
<td>4.25 nm/mm</td>
</tr>
<tr>
<td>Resolution</td>
<td>0.3 nm</td>
</tr>
<tr>
<td>Maximum scanning speed</td>
<td>200 nm/s</td>
</tr>
<tr>
<td>Wavelength accuracy</td>
<td>±0.5 nm</td>
</tr>
<tr>
<td>Step size</td>
<td>0.0625 - 100 nm</td>
</tr>
<tr>
<td>Range</td>
<td>0 - 950 nm</td>
</tr>
<tr>
<td>Gratings Excitation side</td>
<td>330 nm</td>
</tr>
</tbody>
</table>
Fig. 2.5. Photograph of SPEX Fluoro Max-3 spectro-fluorometer.
<table>
<thead>
<tr>
<th>Blaze (spectral range)</th>
<th>220 - 600 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emission side</td>
<td>500 nm</td>
</tr>
<tr>
<td>Blaze (spectral range)</td>
<td>290 - 850 nm</td>
</tr>
<tr>
<td>Detector:</td>
<td>Supports 200 - 980 nm; photodiode for excitation reference correction, Supports 180-850 nm; emission side detector; highly sensitive PMT (R928P) in the photon-counting mode</td>
</tr>
<tr>
<td>High voltage</td>
<td>950 V</td>
</tr>
<tr>
<td>Emission intensity</td>
<td>2x10^6 cps &lt;1,000 cps (dark noise level)</td>
</tr>
<tr>
<td>Bandpass range</td>
<td>0 - 30 nm</td>
</tr>
<tr>
<td>Sample compartment dimensions</td>
<td>140 width x 178 length x 178 height mm)</td>
</tr>
<tr>
<td>Environmental temperature</td>
<td>15 - 30 °C</td>
</tr>
<tr>
<td>Maximum humidity</td>
<td>75%</td>
</tr>
<tr>
<td>Power system</td>
<td>5 A; 100 V;</td>
</tr>
<tr>
<td></td>
<td>(standard specification for Japan) 50 Hz</td>
</tr>
</tbody>
</table>
References


9. Instruction manual of SPEX Fluoro Max-3 spectro-fluorometer (manufactured by JOBIN YVON, Japan).