CHAPTER - II
Experimental Studies

This chapter describes the preparation and characterization of three different types of borophosphate glasses containing certain rare earth ions (Pr$^{3+}$, Sm$^{3+}$, Eu$^{3+}$, Tb$^{3+}$, Dy$^{3+}$ and Ho$^{3+}$) as the dopants in the following two chemical compositions.

a) $44.5B_2O_3 + 44.5P_2O_5 + 10R_2SO_4$ (where R=Li, Na & K)  
   (with Eu$^{3+}$, Tb$^{3+}$, Sm$^{3+}$, Dy$^{3+}$)

b) $44.75B_2O_3 + 44.75P_2O_5 + 10R_2SO_4$ (where R=Li, Na & K)  
   (with Pr$^{3+}$ & Ho$^{3+}$)

Like in the case of Eu$^{3+}$, Tb$^{3+}$, Sm$^{3+}$, Dy$^{3+}$ glasses, an attempt was first made to incorporate 1M% Pr$^{3+}$, but these praseodymium glasses could not be made in good transparency, therefore the dopant ion (Pr$^{3+}$) concentration was subsequently reduced to 0.5M% in order to obtain bubble free and transparent Pr$^{3+}$-glasses. In a similar situation, Ho$^{3+}$-glasses were also made with 0.5M% as the dopant ion (Ho$^{3+}$) concentration. For our reference convenience, the glass containing Li$_2$SO$_4$ has been labelled as Glass-A, Na$_2$SO$_4$ as Glass-B and K$_2$SO$_4$ as Glass-C. The chemicals used in the present work are NaH$_2$PO$_4$, 2H$_2$O, H$_3$BO$_3$, Li$_2$SO$_4$, H$_2$O, Na$_2$SO$_4$, K$_2$SO$_4$. The rare earth salts (99.99% purity) have been purchased from M/s Indian Rare-Earths Ltd., Udyogamandal, Kerala State. Each of the above chemical batches weighing about 8g, was taken into an agate mortar to obtain fine powder with a homogeneous mixing. Every time, both the mortar and the pestle were properly cleaned. Finely powdered samples were collected into porcelain crucibles for melting them in the temperature range of 900-950°C for about 30 min. Electrical furnace used in the preparation of the glass samples has been shown in Fig 2.1. The
Fig. 2.1: Experimental set up for preparation of glasses
melts were subsequently quenched between a couple of smooth surfaced plates in order to obtain the glass samples in circular windows (3-4 cm in diameter and thickness of 0.41 cm). Thus by employing the ‘quenching technique’, transparent rare earth doped borophosphate glasses were obtained [1-3]. All these glasses did show extended UV and IR transmission ability.

**Physical properties**

By employing the traditional methods, both glass density (d) and refractive index (n_d at 589.3 nm) were determined and the same were used to evaluate other related physical quantities that are obtained from the following expressions.

(i) Molar refractivity (R_M) is calculated from [4]

\[
R_M \ (cm^3) = \left( \frac{n_d^2 - 1}{n_d^2 - 2} \right) \cdot \frac{\bar{M}}{d}
\]

The quantity ‘R_M’ has the unit of volume. The term \(\frac{\bar{M}}{d}\) represents the molar volume, the term \(\left(\frac{n_d^2 - 1}{n_d^2 - 2}\right)\) represents the optical degree of efficiency of spacial packing. The molar refractivity, moreover is directly proportional to the polarizability \(\alpha_e\). \(R_M = (4\pi N_A / 3) \alpha_e\) with \(N_A\) as Avogadro number. Thus, larger the polarizability of an ion, the larger its contribution to molar refractivity, which at the same time means a larger contribution to the refractive index. Since the anions have a substantially greater polarizability than the cation, they chiefly determine the index of refraction.

(ii) Mean atomic volume (V) [3]

\[
V (g \ cm^{-3} \ \text{at}^{-1}) = \left[ \frac{\bar{M}}{\text{Total no. of atoms} \times d} \right]
\]
(iii) Molecular electronic polarizability ($\alpha_e$) [5]

$$\alpha_e (cm^3) = \frac{(n_d^2 - 1)/(n_d^2 + 2)}{4\pi \left( d \cdot \frac{N_A}{M} \right)}$$

(iv) The rare earth ion concentration ($N$) [6]

$$N (10^{22} \text{ ions} \cdot cm^{-3}) = \frac{N_A \cdot (M\% \text{ RE}) d}{M}$$

where $M\%$ is the molarity of the ions available in the glass matrix. With these values ($N$), the ionic radius ($r_p$) and interionic distance ($r_i$) could be evaluated from [7].

(v) $r_p (\AA) = \frac{1}{2} \left[ \frac{\pi}{6N} \right]^{1/3}$

(vi) $r_i (\AA) = \left[ \frac{1}{N} \right]^{1/3}$

(vii) The field strength ($F$) can be calculated by using the oxidation number ($Z$) and the ionic radii ($r_p$) [7]

$$F (cm^2) = \frac{Z}{r_p^2}$$

The conventional nomenclature given to the spectral lines with their corresponding wavelengths and sources of illuminations are presented in Table 1. As $n$ rises, $\nu$ falls which is a general phenomenon. Glasses with low $n$ and $\nu > 55$ are called crown glasses and glasses with high $n$ and $\nu < 50$ are called flint glasses.
Table 1

Nomenclature of different wavelengths (\( \lambda \) nm) with appropriate letters as the subscripts depending upon the source of light used

<table>
<thead>
<tr>
<th>Wavelength</th>
<th>Symbol</th>
<th>Spectral line</th>
</tr>
</thead>
<tbody>
<tr>
<td>479.99</td>
<td>( n_F )</td>
<td>Blue Cd line</td>
</tr>
<tr>
<td>486.13</td>
<td>( n_F' )</td>
<td>Blue H line H_\beta</td>
</tr>
<tr>
<td>546.07</td>
<td>( n_D )</td>
<td>Green Hg line</td>
</tr>
<tr>
<td>587.56</td>
<td>( n'_D )</td>
<td>Yellow He line</td>
</tr>
<tr>
<td>589.30</td>
<td>( n_C )</td>
<td>Yellow Na line</td>
</tr>
<tr>
<td>643.85</td>
<td>( n_C' )</td>
<td>Red Cd line</td>
</tr>
<tr>
<td>656.28</td>
<td>( n_D' = n_D = n'_D )</td>
<td>Red H line H_a</td>
</tr>
</tbody>
</table>

Abbe number \( \nu_c = \frac{n_s - 1}{n'_F \cdot n'_C} \left( \frac{n_D - 1}{n'_F \cdot n'_C} \right) \)

\( n'_F - n'_C \) = principal dispersion
\( n_c \) = principal refractive index
\( n_c = n_d = n_d' = n_D \)
Absorption Spectra in the UV-Visible Region

In this region, the absorption spectra of the RE$^{3+}$-doped glasses have been recorded on a Perkin-Elmer 551 Spectrophotometer. It is a double beam spectrophotometer. It is designed for measuring solid, liquid and gaseous samples in the range 195-920 nm. The block diagram of this instrument has been shown in Fig.2.2 and the simplified diagram of the optical system in Fig.2.3. Light from the source lamp is reflected by the source mirror onto the entrance slit. In the visible range 350-800 nm, light from the tungsten halogen lamp (W-lamp) is pre-filtered and reflected onto the slit, while in the UV range, 195-350 nm an automatic lamp change mirror swings into the beam path to reflect light from the dueterium lamp (D$_2$-lamp) onto the slit. The light is spectrally dispersed by a grating monochromator in littrow configuration and a beam of monochromatic light with a band-pass corresponding to the selected slit setting (0.4 nm, 1.0 nm, 2.0 nm & 4.0 nm), emerges from the exit slit. The image of the exit slit is focussed by a spherical mirror onto a rotating chopper and it in turn reflects the image alternatively into sample and reference beams. A pair of matched cylindrical mirrors focus the image in each beam onto the cell plane. In the cell, the beam has a cross section of 1.6 nm wide by 11 nm height at a band-pass of 2 nm. Further two spherical mirrors and a plane mirror reflect the radiation onto the photomultiplier tube. The number of reflections, the angle of reflection, and the optical path-length are identical in both the beams. Light energy through the sample and reference cells fall onto the photomultiplier tube and is suitably converted into electrical energy. The photomultiplier signal is amplified by a pre-amplifier and fed to a demodulator and this is so regulated in the correct phase relationship by a light barrier on the chopper that the reference signal is fed to one channel and the sample signal to another. The reference signal is compared in a comparator with a fixed reference value to regulate
Fig. 2.2: Perkin-Elmer 551 Recording Spectrophotometer (Block Diagram)
Fig.2.3: Perkin-Elmer 551 Recording Spectrophotometer (Optical Alignment)
the high voltage for the photomultiplier such that the electrical reference signal always assumes a fixed value. This multiplier voltage is also effective for the sample phase which immediately follows. The electrical sample signal is thus directly proportional to the ratio of the sample signal to the reference signal i.e., proportional to the optical transmission / absorption / reflection / concentration of a sample studied. In absorbance mode (as has been appropriately indicated on the operating knobs of the instrument), first the signal is routed through a logarithmic amplifier (T/A converter) and then routed through one branch directly to the recorder output terminals and through a second branch via a dynamic filter to an analogue to digital converter where it is displayed digitally.

**Operating principle of the recorder**

The signal potential from the spectrophotometer is then compared to the voltage provided by the potentiometric measuring circuit. When there is a potential difference between the two, this difference voltage is applied to the FET chopper resulting in an alternating voltage applied to the amplifier. The amplifier drives the balancing motor, which is mechanically coupled with the control slide wire contact in the potentiometric measuring circuit. The control slide wire contact is moved until the difference voltage is reduced to zero. The recording pen, which is mechanically connected with the control slide wire contact, records the pen position on the recording chart. A value proportional to the input voltage is recorded on the chart while the recording chart is driven in one direction at the uniform speed (chart speed 5, 10, 20, 60, 120 & 240 nm/minute) provided by the synchronous motor. The input voltage selector has a minimum 1.0 mv, to maximum 10 v (1 mv, 2 mv, 5 mv, 10 mv, 20 mv, 50 mv, 0.1 v, 0.2 v, 0.5 v, 1.0 v & 10 v) which limits the movement along the Y-axis. Six selectable scanning speeds are provided to vary
dispersion of the wavelength. The slowest scanning speed of the wavelength is 5 nm/minute and the fastest is 480 nm/minute (5, 20, 60, 120, 240, 480 nm/minute).

The presentation on the chart is

\[
\text{Presentation (nm/cm)} = \frac{\text{Spectrophotometer scan speed (nm/min)}}{\text{Recorder chart advance (cm/min)}} \times 10
\]

The wavelength scale is accurate to better than 0.4 nm throughout its range. The wavelengths (nm) of the spectral features (absorption and photoluminescence) have been converted into wavenumbers (cm\(^{-1}\)) by using the wavenumber tables [8-9].

**Photoluminescence Spectra**

The photoluminescence spectra of the glasses have been carried out on a F-3010 Hitachi Fluorescence Spectrophotometer. This facility was made available to us by the Central Instruments Laboratory, University of Hyderabad. Fig.2.4 is a functional block diagram of the Model F-3010. The light emitted from the Xe-lamp enters the excitation monochromator. The light emerging from the excitation monochromator is split by the beam splitter and a fraction is directed to the monitor detector. A shutter is provided between the excitation monochromator and sample, and it is placed into the optical path as commanded from the operation panel. All the driving components, i.e., the wavelength drive motors, slit control motors and rotary solenoid for shutter are operated by signals sent from the computer.

**Optical system**

Fig 2.5 presents the optical system configuration of the Model F-3010 Spectrophotometer. The radiation coming from the Xe lamp is converged at entrance.
Fig. 2.4: Functional block diagram of Hitachi F-3010 Fluorescence Spectrophotometer

RS
535.84
A84
Fig. 2.5: Optical system configuration of Hitachi F-3010 Fluorescence Spectrophotometer
slit S1 of the excitation monochromator through lenses L1 and L2. Only the light
dispersed by the excitation concave grating (excitation beam) enters exit slit S2.
The excitation beam from exit slit S2 is split by a beam splitter BS, and part of the
split beam is given to the monitor detector via lens L3 and diffusion plate for
measurement of its intensity. On the other hand, most of the split beam after BS
is reflected by mirror M1 and converged at the sample cell through lens L4. The
fluorescence coming out of the sample is restricted into entrance slit S3 of the
emission monochromator through lenses L5 and L6. The fluorescence dispersed by
the emission concave grating passes through the exit slit S4 and is converged at the
photomultiplier via concave mirror M2 for intensity measurement. The emission
shutter is provided in order to protect the photomultiplier. It automatically closes
upon opening the lid of the sample compartment.

a) Monochromators: Large stigmatic concave grating having 900 lines/mm used
on both excitation and emission sides.

Eagle mount : F : 3
Blaze wavelength : 300 nm on excitation side, 400 nm on emission side

b) Measuring wavelength range: 220 to 730 nm and 0-order light on both
excitation and emission sides (though wavelength display is possible within 220
to 800 nm including 0-order light)

c) Resolution 15 nm (with minimum bandpass)

d) Wavelength accuracy Better than ±2 nm

e) Wavelength scan rate: 2, 5, 15, 30, 60, 120, 240 & 600 nm/min (8-step
selection) (1200 nm/min in GO TO or prescan mode).

f) Bandpass:

Excitation side : 1.5, 3, 5, 10, 20 nm (5 steps)
Emission side : 1.5, 3, 5, 10, 20, 40 nm (6 steps)
(accuracy better than ±20% at 1.5, 3, 5 and 10 nm)
g) Light source: 150 W xenon lamp with ozone self-dissociation function.

h) Lamp power supply: built in the main unit with high frequency switching system

i) Detectors: Photomultiplier tube - R372F for measurement

Photoelectric tube - R518 for monitoring

j) Recorder: graphic plotter (thermosensitive type) used for printing out measuring conditions, recording spectrum, making hard copy of CRT display and so on.
References

[1] M. Poulain, M. Poulain, J. Lucas and P. Brun


    *Tables of Wavenumbers*
    (National Bureau of Standards, Washington, DC 1960)

    *Wavenumber Tables (2000-9000 Å)*
    (Maruthi Book Depot, Guntur, India, 1988).