CHAPTER II

Experimental Studies
Methods of preparation of different glasses with and without dopant transition metal (Cu$^{2+}$, Mn$^{2+}$, Ni$^{2+}$, Co$^{2+}$) and rare-earth (Eu$^{3+}$, Tb$^{3+}$, Sm$^{3+}$, Dy$^{3+}$) ions have been described in respective Chapters (III-VI) of this thesis. Based on measurement of glass densities and refractive indices, several other related physical characteristic properties have been computed and the results are documented for all the selected luminescent ions in the heavy metal oxide (HMO) glasses in the chapters concerned. Since the details of measurements carried out for different glass are already described in the Chapters. Therefore to avoid repetition of the information, it is not dealt with in this Chapter. The necessary mathematical formulae [1-4] in evaluating other physical properties of the glass is borrowed from the literature.

2.1 Refractive Indices

Glass densities were measured by using toluene as an immersion liquid based on the Archimedes principle. Glass refractive indices were measured on a Precision Refractometer (Kalnew, Model GMR-1) and also an Abbe – refractometer with mono-bromo napthalene as the immersion liquid by using the minimum deviation method between the wavelength of 0.4 μm and 1.1 μm.

2.2 XRD – Spectra

The XRD spectra were recorded on Shimadzu - XD 3A diffractometer with a Ni-filter and CuKα (1.5418Å) radiation using a tube with Cu anode with Ni filter at the room temperature with the operating conditions 30KV and 20 mA with Si at the 2θ values at two degrees per minute, resulting in with CuKα as 1.5418 Å.

2.3 Absorption Spectra

The absorption spectra were measured on Varian – Cary 5E win UV-VIS-NIR spectrophotometer. The UV-VIS spectrum is due to the electronic transitions of the molecule. This is characteristic of a compound. Qualitative and quantitative estimations of compounds are possible by this non destructive technique.
The absorption ($A$) of a sample at a particular wavelength is given by Beer-Lambert's law $\epsilon c t = A$ where $c$ is the concentration of the compound, $t$ is the thickness of the cell and $\epsilon$ is the molar extinction coefficient characteristic of the compound at a given wavelength. This principle is used for quantitative measurements.

Cary 5E is a high resolution spectrophotometer to study the electronic absorption spectra of glass samples in the range of 3150-185 nm. This is a double beam instrument controlled by a microprocessor. Base line correction, repetitive scan, kinetics, derivative and concentration modes are possible. Diffuse reflectance is available for solid samples. VT accessory in the range 5-90 degrees Centigrade is available. The absorption spectrum gives optical density (arbitrary units) versus wavelength in UV-NIR region. The measured wavelengths of the corresponding transitions have been converted into wavenumbers ($\text{cm}^{-1}$) by using the wavenumber Tables published in the literature earlier (5-6).

2.4 FTIR – Spectra

The FTIR spectra of the samples were recorded between the range 400-4000 cm$^{-1}$ on BRUKER IFS66v FT-IR SPECTROMETER. The interference pattern obtained from a two beam interferometer as the path difference between the two beams is altered, when Fourier transformed, gives rise to the spectrum. The transformation of the interferogram into spectrum is carried out mathematically with a dedicated on-line computer.

The Bruker IFS66v FT-IR instrument consists of globar and mercury vapor lamp as sources, an interferometer chamber comprising of KBr and mylar beam splitters followed by a sample chamber and detector. Entire region of 10-10000 cm$^{-1}$ is covered by this instrument. The spectrometer works under vacuum conditions. Solid samples are dispersed in KBr or polyethylene pellets depending on the region of interest. This instrument has a resolution of 0.1 cm$^{-1}$. Signal averaging, signal enhancement, base line correction and other spectral manipulations are possible with multitasking OPUS software on the dedicated PC/AT 486. Spectra are plotted on a HP plotter and data can be printed or saved on a 3.5" floppy.
2.5 Photoluminescence Spectra

SPEX FLUOROLOG-2 (MODEL-II) with a data max software was used for recording the photoluminescence spectra of the samples. The spectrometer provides optimum performance for highly scattering samples such as proteins, Membranes and Solid samples. Both Excitation radiation and emitted radiation can be scanned.

Source -Xenon Lamp 450W

Range 180-1550 nm

Detector PMT for UV & Visible (180 to 850 nm) region and Cooled detector for IR region 800-1550 nm.

Resolution 0.2 nm (maximum at specific wave lengths)

Software DATA MAX / GRAMS/31

Types of samples Small volume samples, Solids, dissolved solids and Biological samples, Thin films etc.

2.6 DSC – Measurement

The DSC measurements were carried out on a Netzsch Thermal Analyzer in the temperature range of 30-1200°C at the rate of 10°C/min under nitrogen atmosphere. Thermal analysis is a group of techniques in which the physical property of a substance is measured as a function of temperature, while the substance is subjected to a controlled temperature program. These include change in weight [(Thermogravimetry (TG)], temperature difference [(Differential Thermal Analysis (DTA)] and heat flux difference [(Differential Scanning Calorimetry (DSC)].
References

1. J.E. Shelby and J. Ruller

2. G. Fuxi, G. Huang and S. Chen


5. C.D. Coleman, W.R. Bozman and W.F. Meggers
   Tables of Wavenumbers
   (National Bureau of Standards, Washington, DC 1960)

6. S.V.J. Lakshman and S. Srinivas
   Wavenumber Tables (2000-9000 Å)
   (Maruthi Book Depot, Guntur, India, 1988)