

Chapter-2

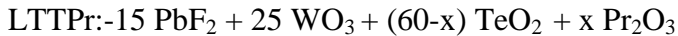
Experimental Techniques

2.1. Introduction

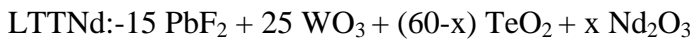
This chapter deals with the experimental techniques used for the preparation of glasses, X-ray diffraction (XRD), physical characterization, absorption, photoluminescence and decay spectral measurements of Pr^{3+} , Nd^{3+} , Ho^{3+} and Tm^{3+} ions doped in lead tungsten tellurite (LTT) glasses. Selection of the glass composition for a desired optical application is a comprehensive task as the optical performance of the glass can be influenced by the glass structure, glass composition, optical quality, chemical durability and thermo-mechanical properties of the glass. Knowledge of energy level positions, intensities and the transitions involved helps to understand the optical response of rare earth ion in any particular host. These optical responses will provide necessary information pertaining to various interactions that takes place between lanthanide-ligand-radiation, ion-ion and ion-host interaction.

2.2. Glass Preparation

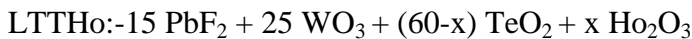
The most common method used to prepare glasses is by using melt quenching in which fusion of one or more crystalline substances are used. When the cooling rate is sufficiently fast to bypass the crystallization process, then the disordered state of the liquid becomes a solid by retaining its disorderness. After several trails, the author could prepared LTT glasses using the chemical composition (in mol %) of $15 \text{PbF}_2 + 25 \text{WO}_3 + (60-x) \text{TeO}_2 + x \text{RE}_2\text{O}_3$, where $x = 0.1, 0.5, 1.0, 1.5, 2.0$ and 2.5 (RE = Pr, Nd, Ho and Tm).



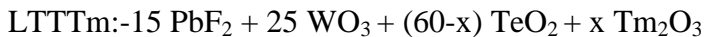
(Where $x=0.01, 0.1, 0.5, 1.0$ and 1.5 mol %)



(Where $x=0.1, 0.5, 1.0$ and 1.5 mol %)



(Where $x=0.1, 0.5, 1.0, 1.5, 2.0$ and 2.5 mol %)



(Where $x=0.1, 0.5, 1.0, 1.5, 2.0$ and 2.5 mol %)

The High purity starting materials are used to prepare the glasses needed for the present work. About 10 g batches of pre-weighed chemical quantities were collected in an agate mortar and thoroughly mixed to obtain homogenized fine powder. Such powder mixture taken in a silica crucible was heated in an electric furnace at a temperature of 700-730⁰C for half an hour. The melt was then quenched in air by pouring on to a pre-heated brass mould and pressed with another brass mould. The glasses so obtained were annealed at 350⁰C for about 4 hours to remove thermal strains produced inside during sudden quenching process. The samples were found to be stable at ambient conditions and were polished using emery paper before measuring their optical properties. Analar reagent grade chemicals such as TeO₂, WO₃, PbF₂, Pr₂O₃, Nd₂O₃, Ho₂O₃ and Tm₂O₃ were used as starting materials to prepare these glasses. These glasses are represented according to the doped rare earth ions Pr³⁺, Nd³⁺, Ho³⁺ and Tm³⁺ as LTTPr, LTTNd, LTTHo and LTTTm respectively.

2.3. Physical Parameters

Certain physical properties such as thickness, density, concentration of the RE ions and refractive index are important to characterize the RE ion doped glasses.

Thickness: The thicknesses (l) of the given samples were measured using a screw gauge of least count 0.01mm.

Density: The densities (d) of the glass samples were determined by conventional Archimedes's method, using distilled water as an immersion liquid at room temperature by using the following formula

$$d = \left(\frac{a}{a-b} \right) \text{ gm/cc} \quad (2.1)$$

where 'a' is the sample weight in air, 'b' is the sample weight in distilled water

Refractive index: For refractive index measurements, the Brewster's angle method has been adopted using a 2 mW He-Ne polarized laser (632 nm) as light source.

Rare Earth (RE³⁺) Ion Concentration (C)

The concentrations (C) (mole liter⁻¹) of RE³⁺ ion were measured by using the below formula. [90]

$$C = \frac{M_{RE}}{M_{tot}} \times \frac{d}{MW} \times 100 \quad (2.2)$$

Here M_{RE} is the rare earth salt mass, M_{tot} is the total weight of the chemical composition, d is the density of the glass and MW is the molecular weight of the rare earth salt. The concentration determined in mole litre⁻¹ can be converted into ions cm⁻³ by multiplying with the Avogadro's number (N).

From the experimentally measured densities and refractive indices, different physical properties such as Average molecular weight, $(\bar{M})(g)$, Molar Volume (V_m) (cm³/mol), Mean atomic volume (g/cm³/atom), Dielectric constant (ϵ), Optical dielectric constant ($\epsilon - 1 = P \frac{\partial t}{\partial P}$), Reflection losses (R %), Molar refraction (R_m) (cm⁻³), Polaron radius (r_p) (Å), Interionic distance (r_i) (Å), Molecular electronic polarizability (α) (10⁻²³cm³), Field strength (F) (10¹⁵cm⁻²) and Optical basicity (Λ_{th}) of LTT glasses have been evaluated by using the following relevant equations [90].

$$\text{Polaron radius, } r_p = \frac{1}{2(\pi/6N)^{1/3}} \quad (2.3)$$

$$\text{Interionic distance, } r_i = \left(\frac{1}{N}\right)^{1/3} \quad (2.4)$$

$$\text{Field strength, } F = \frac{Z}{r_p^2} \quad (2.5)$$

The reflection loss from the glass surface was computed from the refractive index by using Fresnel's formula [90]

$$R = \left[\frac{n_d - 1}{n_d + 1}\right]^2 \quad (2.6)$$

The dielectric constant was calculated from the refractive index of the glass using the following expression [90]

$$\epsilon = n_d^2 \quad (2.7)$$

The molar refractivity (R_M) for each glass was calculated from the following relationship [90]

$$R_M = \left[\frac{(n_d^2 - 1)}{(n_d^2 + 1)} \right]^2 \frac{\bar{M}}{d} \quad (2.8)$$

Here n_d is the refractive index of the glass at 632 nm, \bar{M} is the average molecular weight of the glass and d is the density of the glass.

The optical dielectric constant ($\epsilon - 1 = P \frac{\partial t}{\partial P}$) was calculated from the measured refractive index at 632 nm using the following expression [90]

$$P \frac{\partial t}{\partial P} = \epsilon - 1 = n_d^2 - 1 \quad (2.9)$$

Here ϵ is the dielectric constant.

The molecular electronic polarizability factor (α) was determined using the formula [95]

$$\alpha = \frac{1}{\left(\frac{4\pi N}{3}\right)} \left[\frac{n_d^2 - 1}{n_d^2 + 1} \right] \quad (2.10)$$

Here n_d is the refractive index and N is the rare earth ion concentration. Refractive index is a critical parameter in the control of mode profile and can affect the performance of optical fiber amplifiers [91].

Using average molecular weight and densities of the prepared glasses, the total number of ions, the mean atomic volume ($\text{g}/\text{cm}^3/\text{atom}$) can be determined. It is possible to calculate the theoretical value of optical basicity, which is given by [92]

$$\Lambda_{th} = \sum_i \frac{Z_i r_i}{2\gamma_i}, \text{ Where } \gamma_i = 1.36(x_i - 0.26) \quad (2.11)$$

Here Z_i is the oxidation number of the cation i , r_i is the ionic ratio with respect to the total number of oxides γ_i is the basicity moderating parameter and is given from the Pauling electro negativity x_i . The optical basicity denotes the average electron donating power of the medium to the oxide atoms present in that medium. Increasing/decreasing in optical basicity values indicate increasing/decreasing covalency in the cation-oxygen bonding.

Table 2.1. Measured density and refractive indices of Nd³⁺, Pr³⁺, Ho³⁺ and Tm³⁺ ions doped LTT glasses.

S. No	Name of the Glass System	Density (d) (g/cm³)	Refractive index (n_d)
LTTPr Glasses			
1	LTTPr001	6.606	2.305
2	LTTPr01	6.607	2.306
3	LTTPr05	6.612	2.307
4	LTTPr10	6.619	2.308
5	LTTPr15	6.626	2.309
LTTNd Glasses			
6	LTTNd01	6.607	2.190
7	LTTNd05	6.612	2.201
9	LTTNd10	6.619	2.213
10	LTTNd15	6.626	2.221
LTTHo Glasses			
11	LTTHo01	6.608	2.400
12	LTTHo05	6.618	2.404
13	LTTHo10	6.631	2.407
14	LTTHo15	6.643	2.415
15	LTTHo20	6.656	2.435
16	LTTHo25	6.668	2.437
LTTTm Glasses			
17	LTTTm01	6.608	2.481
18	LTTTm05	6.619	2.510
19	LTTTm10	6.623	2.543
20	LTTTm15	6.645	2.548
21	LTTTm20	6.660	2.554
22	LTTTm25	6.673	2.572

2.4. XRD Spectral Analysis

The glassy nature of the samples prepared for the present work was confirmed by the X-ray diffraction (XRD) patterns. The XRD measurement were taken up by using Bruker X-ray diffractometer (model D8 Advance) which operates at 40 KV and 40 mA with CuK α radiation ($k=1.54\text{\AA}$) in the 2θ angle range $0^\circ - 80^\circ$ with step size $0.02^\circ \text{ s}^{-1}$. Fig. 2.1 shows the XRD pattern of an un-doped LTT glass. Absence of sharp peaks in the XRD pattern represents that there is no long range structural order, which confirms the glassy nature of the sample.

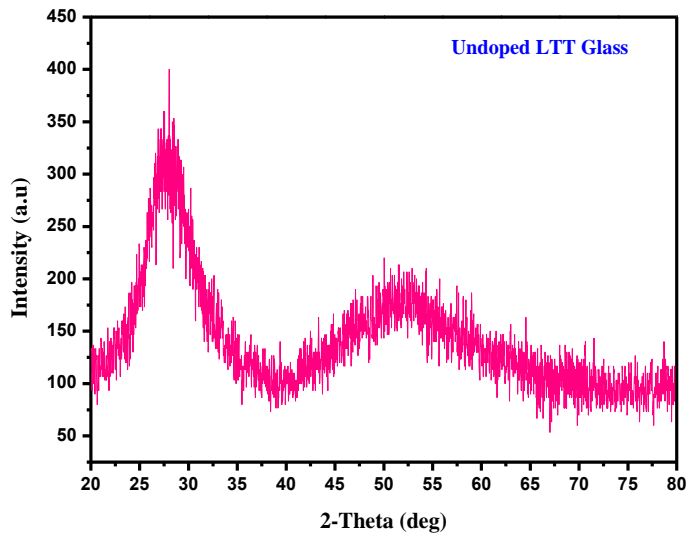


Fig. 2.1. XRD spectrum of an un-doped LTT glass

2.5. FT-IR Spectral Analysis (For Un-doped LTT Glass)

The FT-IR spectrum for an un-doped LTT glass has been recorded with a spectral resolution of 4 cm^{-1} using Perkin-Elmer Spectrum II FT-IR spectrophotometer in the wave number range $400\text{-}4000 \text{ cm}^{-1}$ following KBr Pellet technique to know the various functional groups present in the prepared glasses. Fig.2.2 shows the FT-IR spectrum recorded for an un-doped LTT glass. The OH^- content present in a glassy material can be estimated using the following equation

$$\alpha_{\text{OH}} = \ln\left(\frac{T_0}{T_D}\right) / l \quad (2.12)$$

Here ' T_o ' is the highest transmission, ' T_D ' is the transmission of the glass at 3000 cm^{-1} and ' l ' is the thickness of the glass sample. The OH^- content estimated for LTT host glass using the above expression is 50.17 ppm.

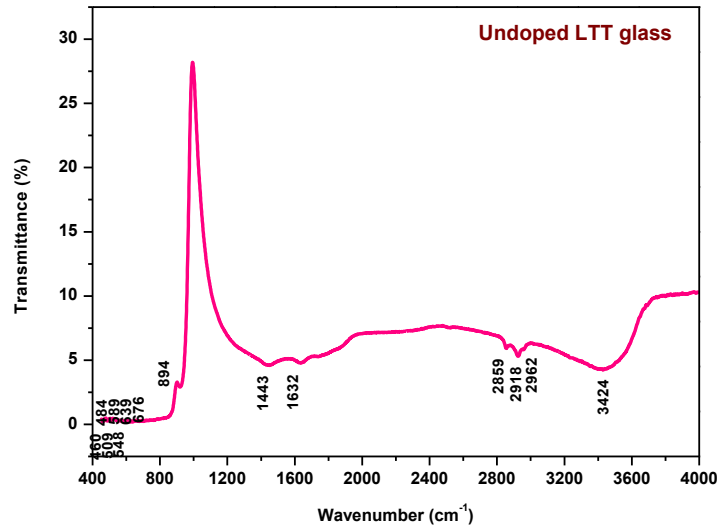


Fig. 2.2. FT-IR spectrum of an un-doped LTT glass

This figure shows the characteristic IR absorption band at 3424 cm^{-1} , which is due to the fundamental vibrations of OH group. It is a known fact that, larger the amount of OH content in a glass, lesser will be the quantum efficiency of the prepared glasses. This is obvious because the OH groups present in glass will increase the non-radiative decay loss and affects the quantum efficiency of the prepared luminescent materials. The low intensity of OH band observed for LTT glasses indicates the presence of less OH content. The coefficient of OH vibration (α_{OH}) at 3000 cm^{-1} is used as a measure of the OH content [93]. Such OH content present in a glassy material can be estimated using the equation given in the literature [99]. The OH content estimated for the present un-doped LTT glass is 50.17 ppm (1.67 cm^{-1}), which is smaller than ZnAlBiB (65.48 ppm) [94], LBTAf (123.00 ppm) [95], GeS₂ (175.5 ppm) [96] and LHG-8L (128 ppm) glasses [97]. Relatively less OH content obtained for the present glasses under investigation signifies that the rare earth doped LTT glasses are relatively good for efficient lasers with low non-radiative losses.

The peaks identified in the region 1600-3000 cm^{-1} are mainly attributed to hydrogen bonding. The vibrations observed at 894 cm^{-1} is attributed to the ν_1 vibrations of WO_4 groups & stretching vibrations of W-O^- and W-O bonds in WO_4 or WO_6 units [98]. From the literature, tellurite glasses show $\alpha\text{-TeO}_2$ (para tellurite) crystallization which is created by (TeO_4) Trigonal bipyramids (TBP) [99]. When glass modifiers are added into the tellurite glass network, the network will be more open and non-bridging oxygen's were formed by allowing the TeO_{3+1} and TeO_3 structural units. The peak observed at 676 cm^{-1} is due to the stretching vibrations TeO_4 trigonal bipyramid units [100]. The peak observed at 639 is due to the $\nu_s - \text{TeO}_{2\text{ax}}$ vibrations with C_{2v} symmetry. The peak observed at 589 cm^{-1} due to the stretching vibrations of TeO_{3+1} units [101]. The peaks observed at 548 and 509 cm^{-1} are due to the stretching vibrations of PbOF_4 and PbO_4 units. The peaks observed in the region 460 and 484 cm^{-1} are due to the stretching vibrations of Te-O-Te or Te-O-W linkages. All the band assigned from the FT-IR spectrum of an un-doped LTT glass are given in Table 2.2.

Table 2.2. Band positions (cm^{-1}) of FT-IR spectrum of an un-doped LTT glass

Band positions cm^{-1})	Assignments	
460 } 484 }	Stretching vibrations of Te-O-Te or Te-O-W linkages	
509		
548	Stretching vibrations of PbO_4 units	
589	Stretching vibrations of PbOF_4 units	
639	Stretching vibrations of TeO_{3+1} units	
676	$\nu_s - \text{TeO}_{2\text{ax}}$ vibrations with C_{2v} symmetry	
894	Stretching vibrations TeO_4 trigonal bipyramid units	
1443 } 1632 } 2859 } 2918 } 2962 }	ν_1 vibrations of WO_4 groups / stretching vibrations of W-O^- and W-O bonds in WO_4 or WO_6 units	
3424		
		Hydrogen bonding and stretching vibrations of OH groups
		Stretching vibrations of OH Content

2.6. Optical Absorption Spectral Measurements

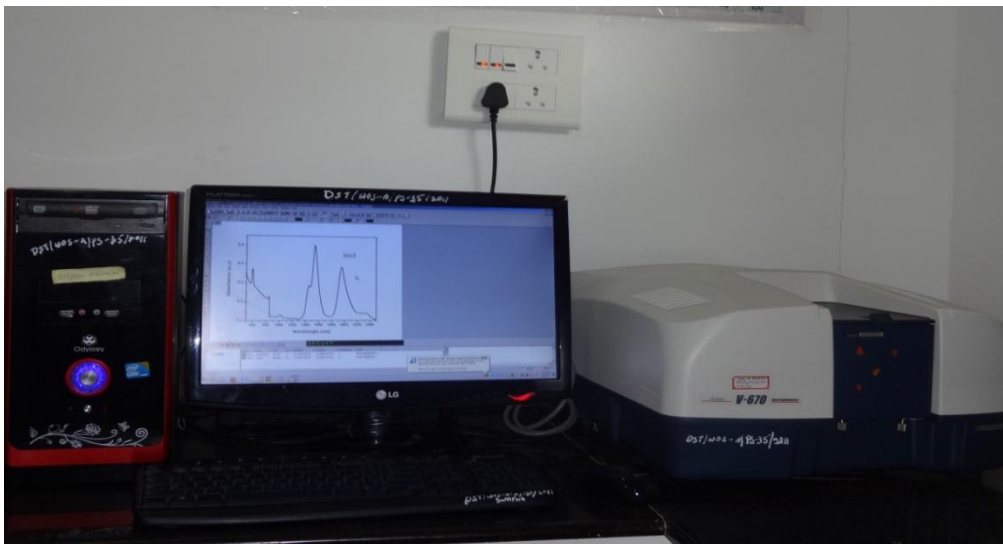


Plate 2.1: Photograph of Jasco Model V-670 UV-vis-NIR spectrophotometer

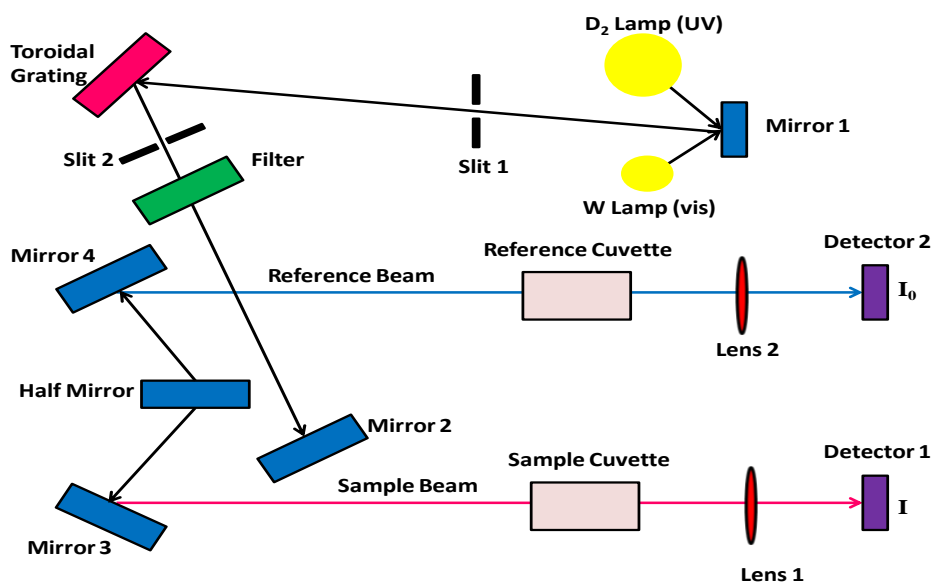


Fig. 2.3: Schematic diagram of the optical system of the JASCO model V-670 UV-vis-NIR spectrophotometer

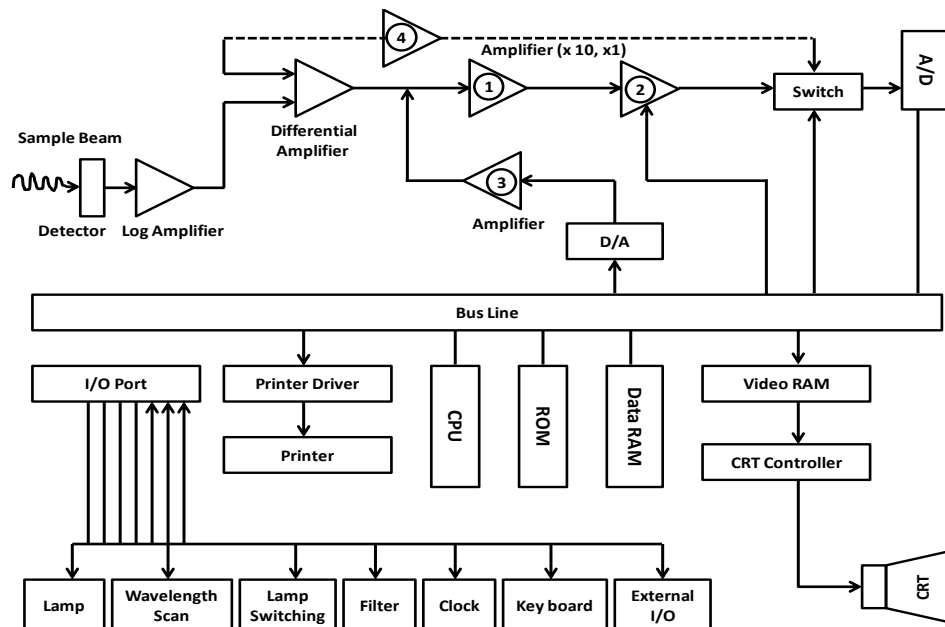


Fig. 2.4. Schematic diagram of electrical system of the JASCO model V-670 UV-vis-NIR spectrometer

The optical absorption spectra of the glasses prepared in the present work glass were recorded at room temperature in the spectral wavelength range covering 300-2700 nm with a spectral resolution of 0.1 nm using JASCO Model V-670 UV-vis-NIR spectrophotometer (Plate 2.1). A schematic diagram of the optical spectrophotometer arrangement in the equipment is shown in Fig. 2.3. 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 W from light source switching wavelength 1100 nm. Deuterium lamp and halogen lamp are interchanged automatically according to the wavelength range. The light beam originating from the monochromator is passed through a stray-light cut off filter F, reflected by mirror M2 and then split by the half mirror M3 into two beams namely sample and reference beams. Each beam directly passes through the respective cell and reach the photo diode detector. Fig. 2.4 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. A little amount of the signal is 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.

2.7. Excitation, Emission and Lifetime Spectral Measurements

2.7.1. For LTTPr Glasses:

The luminescence spectra for Pr³⁺ doped LTT glasses were recorded using Perkin-Elmer spectrophotometer at room temperature by exciting the samples with 470 nm wavelength using xenon lamp as an excitation source.

2.7.2. For LTTNd Glasses

For LTTNd glasses the luminescence spectral measurements were carried out at room temperature using emission from the sample coupled in to a monochromator (Acton SP2300) coupled CCD (Charge Coupled Detector) through appropriate lens and filters. With the help of a 6 W power diode laser (SDL-980-LM-6000T) with CW operating mode as radiation source with wavelength 808 nm. The beam divergence of the diode laser used is < 2.5 mrad. The emission signals in NIR region were detected by using InGaAs detector equipped with electronic data storage assembly (Plate 2.2).

2.7.3. LTTHo, LTTTm Glasses:

The Shimadzu RF-5301 PC Spectrofluorophotometer (Plate 2.3) is used to record the excitation and emission spectra for all LTTHo glasses at room temperature.

2.7.4. LTTTm Glasses:

The emission and excitation spectra for all LTTTm glasses investigated in the present work were recorded on Shimadzu RF-5301 PC Spectrofluorophotometer (Plate 2.3) at room temperature.

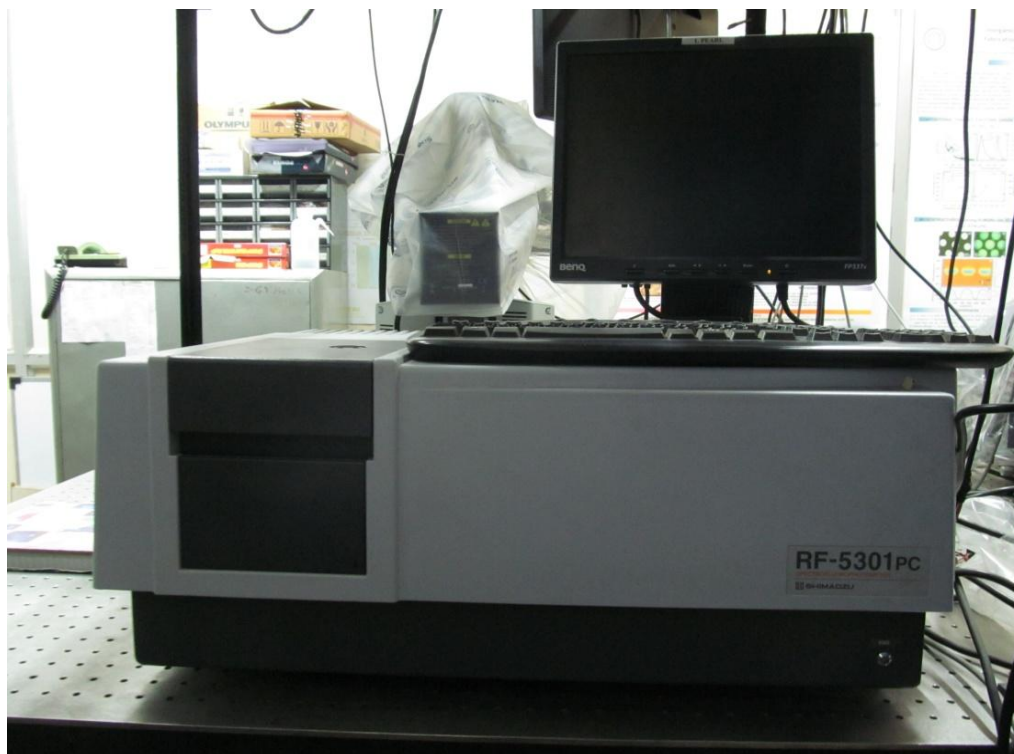


Plate 2.2: Photograph of Shimadzu RF-5301 PC Spectrofluorometer



Plate 2.3: Photograph of Acton SP2300 coupled with lenses and photomultiplier tube