CHAPTER 3

EXPERIMENTAL PROCEDURE

3.1. Chemical reagents and equipments

3.1.1 Chemical reagents

1) Cadmium powder, Cd, M.W.=xxx, purum, analytical grade, Fluka,
2) Zinc powder, Zn, M.W.=65.39, purum, analytical grade, Fluka,
3) Sulphor powder, S, M.W.=xxx, purum, analytical grade, Fluka,
4) Selenium powder, Se, M.W.=xxx, purum, analytical grade, Fluka,
5) Tellurium powder, Te, M.W.=127.60, purum, analytical grade, Fluka,
6) Argon gas, Ar, M.W.=39.948, >99.9%, TIG
7) PEG, (M.W=20,000 g/mol), analytical grade, Fluka
8) Acetonitrile, CH_3CN, M.W.=41.05 g/mol, 99.71%, Lab Scan
9) Litium iodide, LiI, M.W.=166.01 g/mol, purum, analytical grade, BDH
10) Iodine, I2, M.W.=126.9 g/mol, purum, analytical grade, BDH
11) Eosin Y, $C_{20}H_8Br_4O_5$, M.W.=647.92 g/mol, Sigma-Aldrich
12) NaOH
13) $Zn(NO_3)_2.6H_2O$

3.1.2. Equipments and instruments

1) Microwave oven, Electrolux model 2820S
2) Analytical balance, model BP-210S, Sartorius AG. Goettingen, Germany
3) Rotary Vane pump: Edwards, Model RV12
4) Gas flow meter: Cole Parmer scale 0-150
5) Scanning Electron Microscope, and Energy Dispersive X-ray Spectroscopy, Model JEM-6335, JEOL, Japan
6) Scanning Electron Microscope, and Energy Dispersive X-ray Spectroscopy, Model S2600H, Hitachi, Japan
7) Transmission Electron Microscope, Model JEM-2010, JEOL, Japan
8) X-ray Diffractometer, Model Xpert MPD, Philips, Netherlands
9) Raman spectroscopy, Model T64000 JY, Horiba Jobin Yvon, France
10) Luminescence spectrometer, Model LS50B, Perkin Elmer
11) UV-Vis-NIR Spectrophotometer, Model Lamdda 19, Perkin Elmer
12) Hotplate & magnetic stirrer, model 502P-2, PMC Industries, Inc., San Diego, America

3.2 Synthesized methods

3.2.1 Synthesis of CdS using microwave plasma

To produce ZnTe, Zn and Te powders (purum, analytical grade, Fluka) were used without further purification. Two solid mixtures with 1:1, 1:2 and 1:3 molar ratios of Cd:S were mixed by rotation for 1 hr at room temperature and loaded into silica tube (11 mm I.D. x 100 mm long), each of which was placed in a horizontal (H) quartz tube (Figure 3.1). The tube was tightly closed and evacuated to absolute pressure of 4.3±1 kPa for removal of air. Subsequently, argon was gradually fed into this H tube. The procedure was repeated three times. Finally, argon in the H tube was evacuated to a constant value of 4.3±1 kPa absolute pressure. Simultaneously, each solid mixture was treated by 900 W irradiated microwave plasma for 10 min, and left to cool down in the vacuum to room temperature. The solid was milled and mixed by rotation at room temperature for 5 min. Microwave heating was repeated under the same condition for 10 min at a time, until at the finished of the process. The microwave was heated the sample of 1:1 and 1:3 molar ratio products for 20 min, and 1:3 molar ratio product for 20, 40, 60, 80, 100, 120, and 140 min, respectively. The final products were characterized using X-ray powder diffractometer (XRD) with a 1.5406 Å wavelength of Cu-Kα line, scanning electron microscope (SEM) operated at 15 kV and selected area electron diffractometer (SAED) equipped with a transmission electron microscope (TEM) operated at 200 kV, Raman spectrometer using 30 mW He-Ne laser with 632.8 nm (red) wavelength, photoluminescence (PL) spectrometer using 450 W Xe-lamp with the 0.2 nm resolution and 325 nm excitation wavelength at room temperature, and UV-visible spectrometer operated at the 300-850 nm wavelength range with the 0.5 $nm.s^{-1}$ scanning rate.

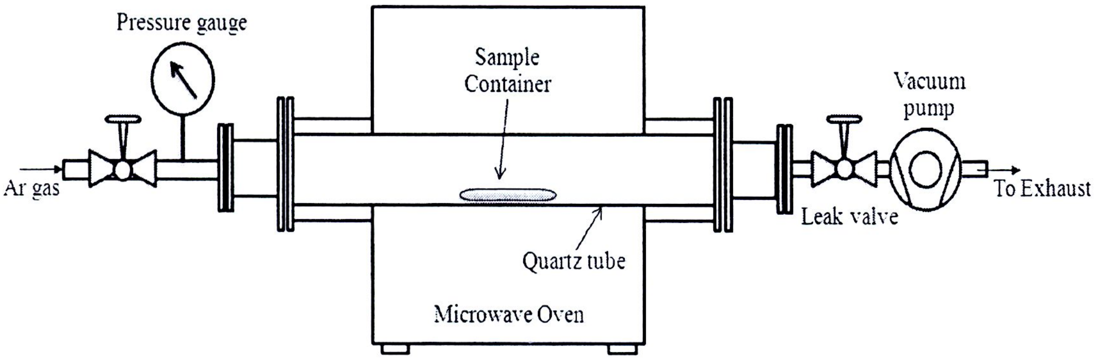

Figure 3.1 Schematic diagram of microwave induced plasma system.

3.2.2 Synthesis of CdTe using microwave plasma

To produce CdTe, Cd and Te powders (purum, analytical grade, Fluka) were used without further purification. Two solid mixtures with 1:1 molar ratios of Cd:Te were mixed by rotation for 1 hr at room temperature and loaded into silica tube (11 mm I.D. x 100 mm long), each of which was placed in a horizontal (H) quartz tube. The tube was tightly closed and evacuated to absolute pressure of 4.3±1 kPa for removal of air. Subsequently, argon was gradually fed into this H tube. The procedure was repeated three times. Finally, argon in the H tube was evacuated to a constant value of 4.3±1 kPa absolute pressure. Simultaneously, each solid mixture was treated by 900 W irradiated microwave plasma for 10 min, and left to cool down in the vacuum to room temperature. The solid was milled and mixed by rotation at room temperature for 30 min. Microwave heating was repeated under the same condition for 10 min, until at the finished of the process. The microwave was heated the sample of 1:1 molar ration products for 10, 20 and 30 min. The products were then characterized using X-ray powder diffractometer (XRD) with a 1.5406 Å wavelength of Cu-Kα line, scanning electron microscope (SEM) operated at 15 kV and selected area electron diffractometer (SAED) equipped with a transmission electron microscope (TEM) operated at 200 kV, Raman spectrometer using 30 mW He-Ne laser with 632.8 nm (red) wavelength, photoluminescence (PL) spectrometer using 450 W Xe-lamp with the 0.2 nm resolution and 325 nm excitation wavelength at room temperature, and UV-visible spectrometer operated at the 300-850 nm wavelength range with the 0.5 nm.s^{-1} scanning rate.

3.2.3 Synthesis of ZnTe using microwave plasma

To produce ZnTe, Zn and Te powders (purum, analytical grade, Fluka) were used without further purification. Two solid mixtures with 1:1 molar ratios of Zn:Te were mixed by rotation for 1 hr at room temperature and loaded into silica tube (11 mm I.D. x 100 mm long), each of which was placed in a horizontal (H) quartz tube. The tube was tightly closed and evacuated to absolute pressure of 4.3±1 kPa for removal of air. Subsequently, argon was gradually fed into this H tube. The procedure was repeated three times. Finally, argon in the H tube was evacuated to a constant value of 4.3±1 kPa absolute pressure. Simultaneously, each solid mixture was heated in a manner of batch run by a 2,450 MHz microwave using 300, 450, 600 and 900W microwave plasma. Each batch, the solids were heated for 30 min, left to cool down in vacuum to room temperature, and thoroughly mixed. The process was repeated under the same condition until at the completion of 300, 450, 600 and 900 W. The products were then analyzed using X-ray powder diffractometer (XRD) with a 1.5406 Å wavelength of Cu-Kα line, scanning electron microscope (SEM) operated at 15 kV, Photoluminescence spectroscopy operated at 30 kV, and selected area electron diffractometer (SAED) operated at 200 kV, Raman spectrometer using 30 mW He-Ne laser with 632.8 nm (red) wavelength, and UV-visible spectrometer operated at the 300-850 nm wavelength range with the 0.5 $nm.sec^{-1}$ scanning rate.

3.2.4 Synthesis of ZnO using microwave plasma

To produce ZnO, Zn powder (analytical grade, Fluka) were used without further purification and loaded into silica tube (11 mm I.D. x 100 mm long), each of which was placed in a horizontal (H) quartz tube. The tube was tightly closed and evacuated to absolute pressure of 4.3±1 kPa for removal of air. Simultaneously, each solid powder was treated by 900 W irradiated microwave plasma for 5 min, and left to cool down in the vacuum to room temperature. The solid was milled and mixed by rotation at room temperature for 30 min. Microwave heating was repeated under the same condition for 5 min, until at the finished of the process. The products were then analyzed using X-ray powder diffractometer (XRD) with a 1.5406 Å wavelength of Cu-Kα line, scanning electron microscope (SEM) operated at 15 kV, Photoluminescence spectroscopy operated at 30 kV, and selected area electron diffractometer (SAED) operated at 200 kV, Raman spectrometer using 30 mW He-Ne laser with 632.8 nm (red) wavelength, and UV-visible spectrometer operated at the 300-850 nm wavelength range with the 0.5 nm.sec-1 scanning rate.

3.2.5 Synthesis of long nanorods ZnO using sonochemical process

To produce nanostructured ZnO, 0.005 mole $Zn(NO_3)_2.6H_2O$ and 0.05 mole NaOH were dissolved in 100 ml water containing 10 g polyethylene glycol (PEG20,000) and stirred for 15 min. The mixtures were sonicated at 80°C (sonothermally processed) for 5 h to produce precipitates. Then products were washed with water and ethanol, dried at 70°C for 24 h, and characterized using an X-ray diffractometer (XRD) operated at 20 kV, 15 mA and using Cu Ka radiation with a 1.5406 Å wavelength in the 2θ angular range of 10 - 60 deg, a scanning electron microscope (SEM) operated at 15 kV, and a transmission electron microscope (TEM) including the selected area electron diffraction (SAED) technique operated at 200 kV, and compared with the electron diffraction patterns obtained by simulation

3.3. Characterization

This section describes the characterization technique on samples in term of phases, chemicals, morphologies, microstructure, optical properties and photovoltaic properties.

3.3.1 X-Ray Diffraction (XRD)

The crystallinity and phase purity of the products were analyzed by using X-ray diffractometry (XRD) with Cu K_{α} radiation (λ = 1.5406 ´) operating at 20 kV-15mA, at a scanning rate of 5°/min in the 2θ range of 10°-60°. The identification samples were assisted by Philips X'Pert Highscore Computer Software (search-match program) on the database of JCPDS software.

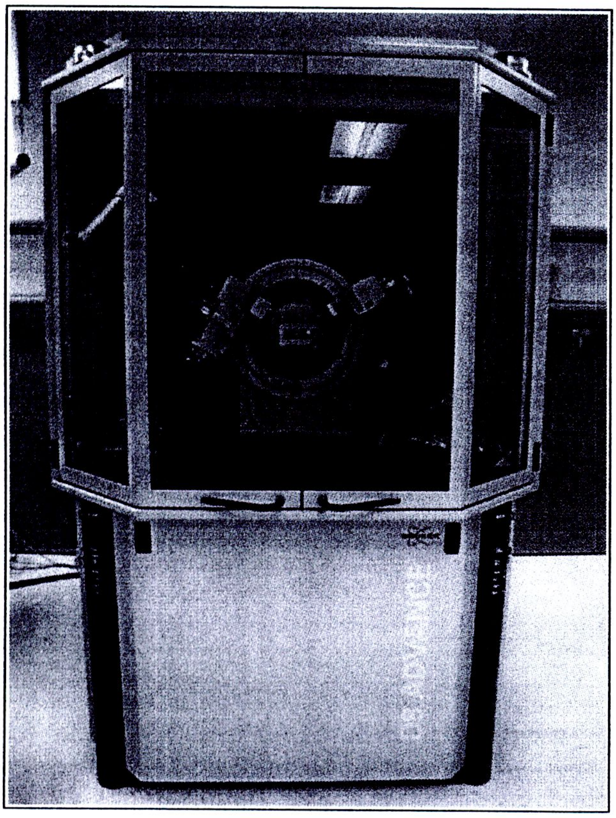

Figure 3.2 X-ray diffractometer.

3.3.2 Scanning Electron Microscope (SEM) and Energy Dispersive X-ray Spectroscopy

The morphology and particle sizes of as-obtained samples were determined by a Field emission-scanning electron microscope (SEM, JSM-6335F) operated at 15 kV accelerating voltage. The chemical composition can be investigated by energy dispersive x-ray (EDX) analyzer equipped to SEM and controlled by Inca program used to determine the chemical composition.

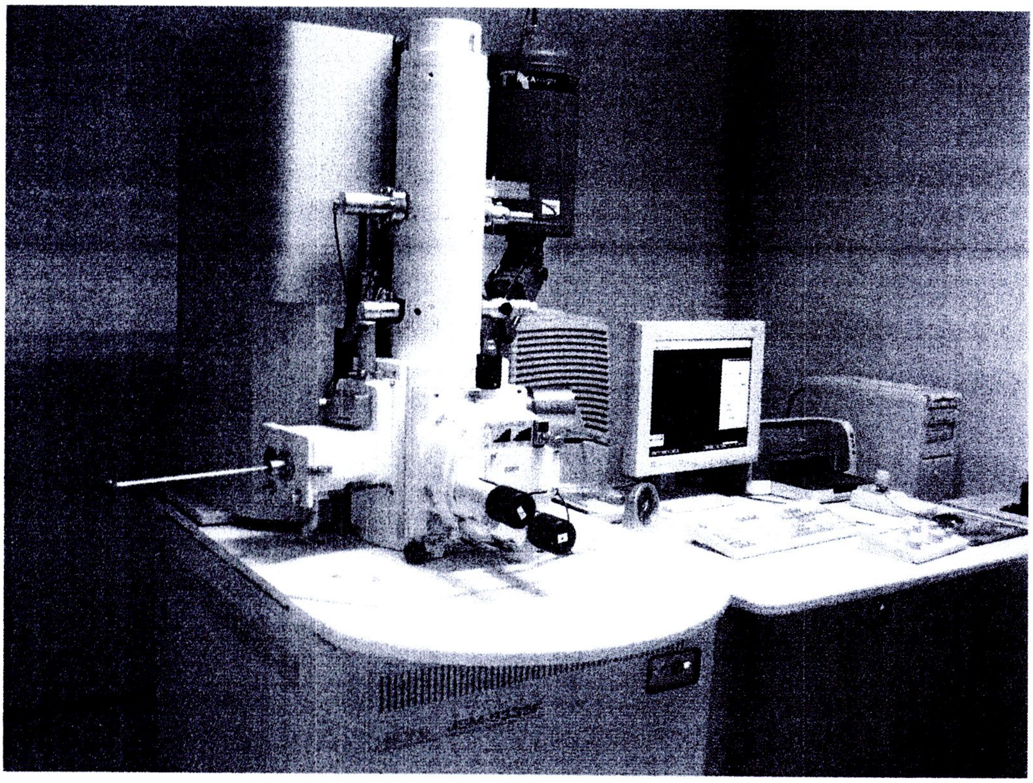

Figure 3.3 Scanning electron microscope.

3.3.3 Transmission Electron Microscope (TEM)

The particle size and morphology was also observed by transmission electron microscope (TEM, JEOL JEM-2010) operating at 20 kV. The samples for TEM analysis were prepared by dispersing small amount of the powder in absolute ethanol and placing a drop of the solution onto a copper grid coated with holey carbon film and letting the ethanol evaporate slowly in air.

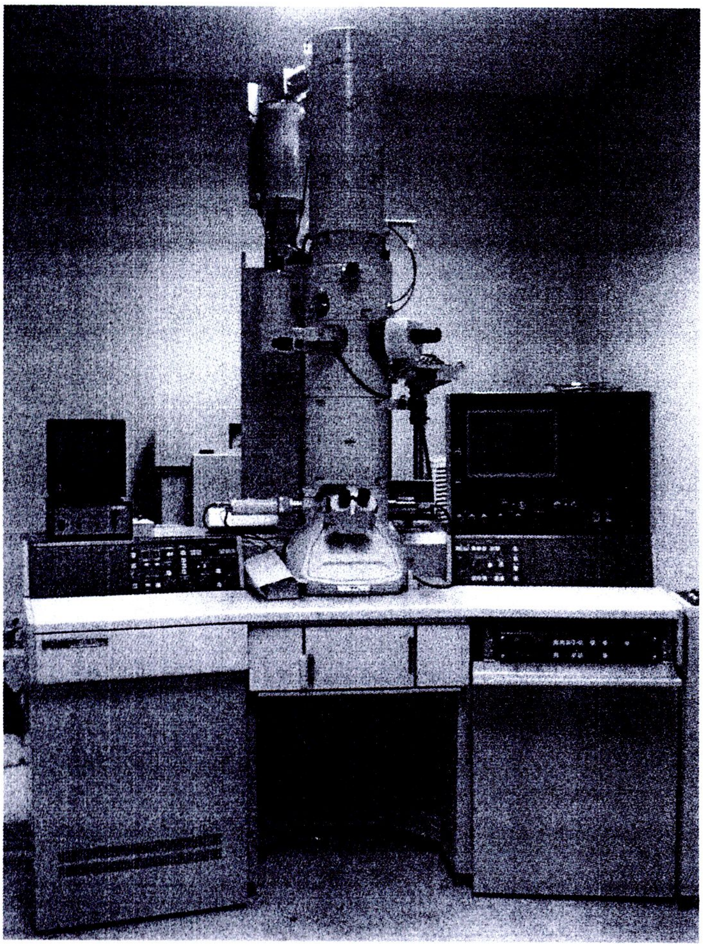

Figure 3.4 Transmission electron microscope.

3.3.4 Luminescence Spectrometer

The luminescence emission spectra of the samples were investigated using Perkin Elmer Luminescence spectrometer LS50B at room temperature. It is a very versatile instrument that allows measurement of fluorescence, phosphorescence, and chemiluminescence or bioluminescence of a liquid, solid, powder, or thin film sample. The sample is illuminated in the wavelength range of 200 to 800 nm and the emission spectra recorded from 200 to 900 nm. Excitation and emission monochromators can be independently or synchronously scanned, while the Prescan mode is ideal for method development and locating of peak excitation and emission maxima.

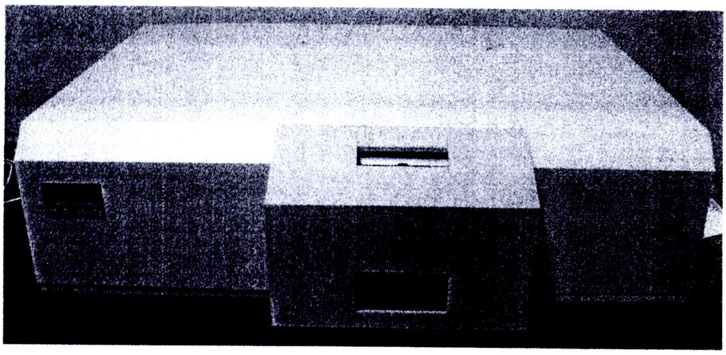

Figure 3.5 Luminescence spectrometer.

3.3.5 UV-Vis-NIR spectrophotometer

The transmission and absorption spectra of the samples were investigated using UV-Vis-NIR Spectrophotometer, model Lambda 19, Perkin Elmer (Figure 3.6) at room temperature.

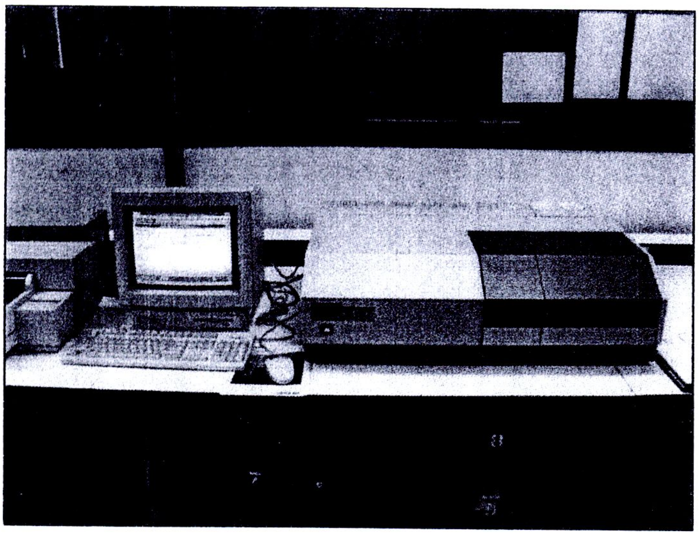

Figure 3.6 UV-Vis-NIR Spectrophotometer.

The optical property of the sample was studied using UV-Vis-NIR spectrophotometer with the aid of the following equations [3,19]:

$$(\alpha h\nu) = A^{*}(h\nu - E_{g})^{n} \tag{3.1}$$

$$\alpha = -\frac{\log T}{t} \tag{3.2}$$

$$t = \frac{bC}{d} \tag{3.3}$$

where α is the total absorption coefficient, $h\nu$ is the photon energy, A^{*} is a constant, E_g is the energy gap of material, n is a number associated with the different types of electronic transitions: n = 1/2, 2, 3/2 or 3 for direct-allowed, indirect-allowed, direct-forbidden and indirect-forbidden transitions, respectively. T is the transmittance of photon through the suspension in ethanol (concentration, $C = 0.001$ g/cm^3) containing in the cuvettes (spectroscopy cells) with the path length (b) of 10.00 mm, t is the effective thickness, and d is the density of sample. The curves of $(\alpha h\nu)^2$ vs $h\nu$ for direct allowed transition were plotted, and extrapolated to $\alpha = 0$. The absorption edge energies, corresponding to the energy gap of the samples.

3.3.6 Raman Spectrometer

Raman spectroscopy is a spectroscopic technique used to study vibrational, rotational, and other low-frequency modes in a system. It relies on inelastic scattering, or Raman scattering, of monochromatic light, usually from a laser in the visible, near infrared, or near ultraviolet range. The laser light interacts with molecular vibrations, phonons or other excitations in the system, resulting in the energy of the laser photons being shifted up or down. The shift in energy gives information about the vibrational modes in the system. A T64000 Raman spectrometer Triple monochromator with Ar laser 514.32 nm and 50 mW by Jobin Yvon Horiba was also used.

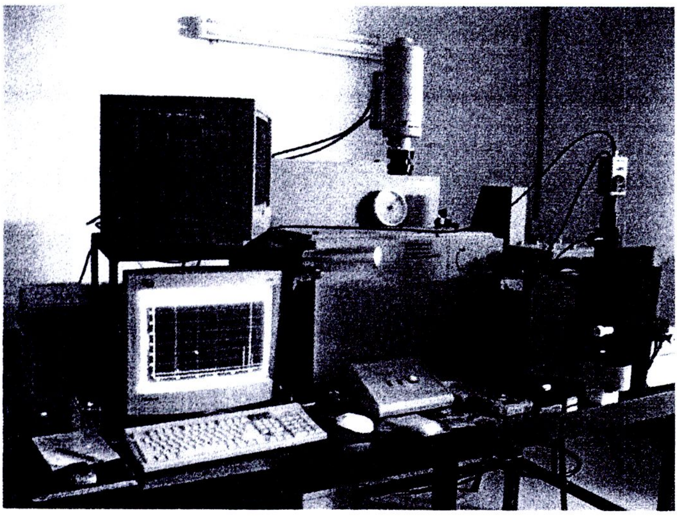

Figure 3.7 Raman spectrometer.

3.3.7 Solar Simulator

A solar simulator is a device that provides illumination approximating natural sunlight. The purpose of the solar simulator is to provide a controllable indoor test facility under laboratory conditions, used for the testing of solar cells, sun screen, plastics, and other materials and devices.

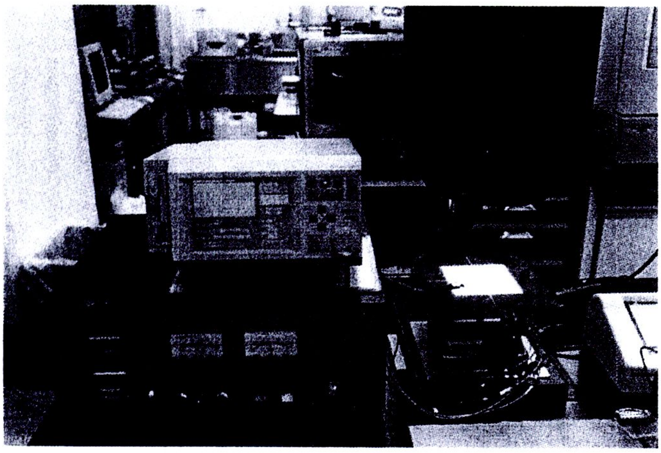

Figure 3.8 Solar simulator.