CHAPTER 3

EXPERIMENTAL DETAILS
The present chapter consists of following three portions:

3.1 Preparation of Materials.
3.2 Cell Preparation.
3.3 Measuring Arrangements.

3.1 Preparation of Materials:

3.1.1 PREPARATION OF PHOTOCONDUCTORS:

The different methods employed for the preparation of photoconductors by earlier workers are as follows:

(i) POWDERS

(ia) Powder firing techniques

This method consists of firing a mixture of base, dopants and flux at a particular temperature (comparatively higher) in controlled atmospheres (Rothschild 1956). Powder form is very much useful for those materials for which other techniques are not available.

(ib) HYDROTHERMAL SYNTHESIS

In this technique a mixture of the ingredients is sealed into a quartz vial half filled with water and heated at comparatively lower temperatures. The increased pressure
and temperature increase the solubility of powder in water and during subsequent slow cooling recrystallization occurs (Krahnke and Levine 1957).

(ii) **PC LAYERS**

(iia) **SINTERED LAYERS**

Sintered layers can be prepared from the initial suspension of base material, flux and impurities used for the preparation of photoconductor powders (Thomsen and Sube 1955). The suspension is sprayed on to a substrate and then fired at a particular temperature.

Sintered layers have also been prepared from vapour. For example, sintered layers of CdS and CdSe were prepared by inserting quartz plates into a chamber in which CdS or CdSe was sublimed (Sube 1967).

Sintered layers of metallic oxides can be prepared by the oxidation of corresponding metal. For example, layers of Cu$_2$O were prepared by heating Cu disks very rapidly to oxidation temperature.

(iib) **CHEMICALLY DEPOSITED LAYERS**

A technique of chemical deposition of thin layers
of photoconductors has proved very useful and a number of materials have been prepared by this method. Though this method started being used quite earlier (Moss 1955) but has been of interest recently also (Nair and Nair 1989).

(iic) **EVAPORATED LAYERS** :

Out of a number of methods used for preparing thin layers of photoconductors, evaporations in vacuum has received the most attention. Some important materials prepared by this method are CdS (Kuwabara 1954, Jacobs & Hart 1955, Karpovich & Zvonkov 1965, Kazmerski et al 1972), ZnS (Studer 1955) and PbS (Frank et al 1949).

(iiic) **SOME OTHER METHODS** :

Some of the workers have used sputtering technique for preparing thin film layers of CdS photoconductors (Chamberlin & Skarmann 1966). CdS films have also been prepared by solution sprayed technique (Wu and Bube 1974).

(iii) **SINTERED PELLETS** :

The sintered pellets of PbS were prepared by Putley (1952) who compressed the powder into blocks and
then sintered at 1100 K for several hours in an atmosphere of \( \text{H}_2 \). This method was followed by other workers also (Yoshimast 1955, Gans 1953).

(iv) **Single Crystals**

The various methods used for growing single crystals are:

(a) From the vapour phase (Takahashi and Trillat 1956)
(b) By pulling from the melt (Ainsworth 1956, Harman et al. 1956)
(c) By cooling the melt (Brady 1954, Kröger and Nobel 1955)
(d) From solution (Pankove 1954, Carmant et al. 1954)
(e) Zone melting (Boomgaard 1956, Pfann 1957)

(v) **Other Structures**

Photoconductivity has also been observed from the materials in homo p-n junction forms having p-n, p-i-n- or n-p-n structures (Bube 1967) and hetero junctions of \( \text{Cu}_2\text{S} \) - \( \text{CdS} \) (Lindquist and Bube 1972, Fahrenbruch et al. 1974).
vi. **PRESENT METHOD OF PREPARATION**

Major work included in this thesis is on PC studies of CdSe-ZnS photoconductor. The method of preparation of this material is as given below:

At first base materials CdSe (Ultrapure, E. Merck) and ZnS (Grade 1, Johnson & Matthey Chemicals Ltd.) were mixed in proper proportion. To this mixture appropriate amounts of impurities lanthanum nitrate or dysprosium oxide (both 99.9% from Indian Rare Earths Ltd.) and Sodium fluoride (GR, E. Merck) were added in solution form. The above mixture was slowly heated till dried. The dried mixture was again mixed in an agate pestle and mortar to make it homogeneous. The ratio of CdSe to ZnS was decided as 2:1 on the basis of best photoresponse. The above described mixture was then transferred into a neat and clean silica boat. The boat was suddenly rushed in the hot zone of a silica tube furnace maintained at a constant temperature of 700°C. The mixture was fired for one hour in either air or nitrogen. After firing was completed, the mixture was cooled to room temperature in air or nitrogen. The thus prepared sample was ground in the agate pestle and mortar to a 300 mesh size and then finally sealed. (Fig. 3.1)
1. Metallic Flange
2. Neoprene Rubber
3. Nuts
4. Water Cooling Arrangement
5. Silica Tube
6. Silica Boat (containing the material to be fired)
7. Heating Element
8. Asbestos Coating

FIG. 3.1 THE TUBULAR SILICA FURNACE
The furnace used in the present investigation was fabricated by winding kanthal heating wire on the external surface of a silica tube of 36" length and 2" diameter. This was covered with the layers of asbestos paste to avoid radiation losses. The two ends of the silica tube were sealed by metallic flanges with the help of neoprene rubber gaskets. Arrangements were made to have controlled flow of a gas to maintain the desired atmosphere in the furnace. An arrangement for cooling the ends of the furnace was done by the continuous flow of water, to avoid the damage of the gaskets. The temperature in the furnace was controlled by controlling the current with the help of a dimerstat. The temperature was measured by using a Chromel-Alumel thermocouple and a Toshniwal portable potentiometer (least count 0.01 mv), was used for measuring the thermo e-m-f.

3.1.2 PREPARATION OF EL MATERIALS:

Normally these materials are prepared in any of the following forms:

(1) POWDER PHOSPHORS:

The preparational method of powder phosphors range from the conventional precipitation of activated
(or unactivated) materials e.g. ZnS using hydrogen sulphide or ammonium sulphide to a homogeneous precipitation using organic precipitants like thio-urea (Vecht et al 1970). Other methods include solid state organic reactions & the decomposition of organometallic compounds such as diethyldithiocarbamate. The impurities are introduced by slow addition of their solutions during precipitation or by firing their mixture with base materials (Bhushan 1985, Bhushan et al 1979).

(ii) CRYSTALS:

Single crystals have been grown by vapour phase (Piper and Williams 1952, Girton et al 1969), melt grown (Addamiano et al 1960) and hydrothermal synthesis (Minami et al 1979) etc. methods.

(iii) THIN FILMS:

EL light emission has also been observed from homo p-n junctions (LEDs) prepared by vapour phase epitaxy method or liquid phase epitaxy method (Shargava 1975). In addition to these, other structures include heterojunction (Kirszt et al. 1983), metal semiconductor diodes (Lawther et al. 1980) and metal-insulator-semiconductor diodes (Koroteev et al. 1981).

(v) PRESENT METHOD OF PREPARATION:

For preparation of the EL materials, a mixture of bases (CdSe & ZnS), impurities (La or Dy) and flux (NaF) were fired at a temperature of 950°C in different atmospheres like air, \( N_2 \) and \( H_2S \). The samples prepared in \( N_2 \) however, could only give weak EL emission. Singh and Mohan (1968), however, observed EL in CdSe-ZnS-Cu, Cl up to 50:50 ratio of CdSe and ZnS by firing in an atmosphere of \( N_2 \) atmosphere.

To get EL in this material a new method was attempted. CdSe along with rare earth impurities were mixed with a separately prepared ZnS electroluminor and
fired at a temperature of 700°C for about 40 minutes. By this method CdSe could be mixed up to 10% by weight of ZnS beyond which the emission becomes very low. ZnS electroluminor was separately prepared by firing a mixture of 10g ZnS, 2g ZnO (both luminescent grade), 0.093g CuSO₄, 0.058g NH₄Cl and 0.2g sulphur (All AR grade) at 1000°C for 2.5 hrs. An extra amount of sulphur was poured on the upper part of the vessel and then completely closed. The fired content was washed with 20% acetic acid (to remove excess ZnO), and distilled water and dried. The materials prepared were ground to a 300 mesh size and finally sealed.

3.2 Preparation of Cell:

The cells used in the PC and EL studies were prepared as described below:

3.2.1 PC Cell:

The PC cell was prepared by pressing photoconductors between a conducting glass plate (resistivity 200 ohm/cm²) and an aluminium plate at a gap of 70 m (except
for thickness dependent studies). The area of the cell was kept about 1cm². This is shown in Fig. 3.2.

3.2.2. **EL CELL**

As shown in Fig. 3.3, this type of cell was prepared by pressing a mixture of electroluminor and binder between a conducting glass plate (resistivity 200~Ω/cm²) and an aluminium plate at a gap of 250 μm.

For comparison purposes and having knowledge about the origin of emission bands results of PL are also presented in this thesis. Construction of PL Cell is as follows:

**PL Cell**: The Pl cell was prepared by depositing the phosphors on a quartz plate with the help of a volatile organic liquid. The organic liquid neither showed any fluorescence in the range of study nor could damage the phosphor.

3.2.3 **PREPARATION OF CONDUCTING GLASS PLATE**

In the preparation of PC or EL Cell conducting glass plate is required as one of the electrodes. The same was prepared in this laboratory by the method given
CONDUCTING GLASS PLATE

MICA SHEET

SAMPLE

ALUMINIUM PLATE

FIG. 3.2 CONSTRUCTION OF PC CELL

1 SCREW 2 SPRING 3 PROJECTED METALLIC ANNULAR BASE 4 CONDUCTING GLASS PLATE 5 ELECTRODES 6 EBONITE BASE 7 MICA SHEET 8 STAINLESS STEEL PLATE 9 ELM MATERIAL

FIG. 3.3 CONSTRUCTION OF ELM CELL
Thin glass plates of proper size were placed on a thick metallic plate and heated slowly up to a temperature of about 600°C. When appropriate temperature was attained, vapours of stannous chloride were sprayed on the heated glass plate. In the presence of air this vapour got deposited as stannous oxide. Plates of resistivity of the order of 100 ohm/cm² with sufficient transparency were successfully prepared. The spraying apparatus is shown in Fig. 3.4.

3.3 MEASURING ARRANGEMENTS:

This thesis concerns with the studies on PC and EL along with PL of the samples. The details of the experimental arrangements required for these studies are as follows:

3.3.1 PC STUDIES:

Set up used in different PC studies may be summarized as given below

(1) RISE AND DECAY STUDIES:

For rise and decay studies as a function of different controlling parameters a general set up described in Fig. 3.5 was used. A 60 watt commercial bulb was taken
FIG. 3.4 ARRANGEMENT FOR PREPARATION OF CONDUCTING GLASS PLATE
FIG. 3.5 BLOCK DIAGRAM FOR PC RISE AND DECAY STUDIES.
as an excitation source. Biasing was done by using a regulated power supply (INCO) and the photocurrent was recorded by a nanometer (sensitivity 0.1 nA, NM 122 W/S scientific equipment, Roorkee). The intensity of excitation was changed by the distance between the cell and the excitation source. For changing ambient temperature a calibrated heating element was placed below the cell. For studies at lower pressure a setup fabricated in the department was used. To create low pressure a rotary vacuum pump (W/S Hind Vacuum Co., Hyderabad) was used and pressure created was measured with the help of a McLeod Gauge (Sensitivity 0.001 mm Hg).

This setup is described in Fig. 3.6. It consists of a cast iron tube having 4 cm. length and about 8 cm. diameter. Another cylinder having the cell mount on its lower part was welded to this cylinder. At the junctions O-rings were used. A glass plate was kept in the window. The window was made on the top for excitation purpose and electrodes were taken out for biasing and current measurement.

(ii) PC SPECTRAL STUDIES:

For spectral studies the photocurrent was recorded as a function of wavelength of incident light. Light from
Fig. 3.6 Sketch of set up for low pressure studies.
the exciting source was first passed through the monochromator and a cell was kept in front of light coming out of monochromator. The photocurrent thus produced was measured with the help of a digital multimeter (Keithley model 160). A 1000W commercial bulb was used as the excitation source, the wavelength of which was changed by rotating drum of the monochromator. The monochromator used was a constant deviation spectroscopy (model 17050 from W/S Andhra Scientific Co., Machilipatnam). It uses glass prisms as dispersing medium and can be used in the spectral region from 400 to 700 nm. The monochromator was standardised with the help of prominent lines from mercury discharge tube. Then it was finally adjusted for its optimum performance by keeping the width of entrance and exit slits equal (Parker 1968). The spectra reported are after proper correction (described in section 3.3.5). The experimental setup for such studies are shown in Fig. 3.7.

3.3.2 EL STUDIES:

Setup used in different EL studies are as follows:

(1) EL BRIGHTNESS STUDIES:

The experimental arrangement for this is shown in
FIG. 3.7 BLOCK DIAGRAM FOR PC SPECTRAL STUDIES.
Fig. 3.9. The AC excitation source was an audio oscillator (R and A r t) coupled with a wide band amplifier (Electronic Appliances, Roorkee) which could provide 0-1000 volts for a frequency range 50-20 kHz. The detecting unit consists of a photomultiplier tube (RCA 6217) operated by a regulated power supply (BHT-11 Scientific Equipment, Roorkee). The integrated light output was recorded in the form of current by the digital multimeter (Keithley 160). The photomultiplier 6217 tube has 3-10 spectral response so it can be safely used within the range 400 to 700 nm.

(i1) EL SPECTRAL STUDIES

The experimental arrangement is shown in Fig. 3.9. Light from EL cell was first passed through the monochromator and the dispersed light was allowed to fall on the photomultiplier (RCA-6217) tube and the corresponding current was recorded by digital multimeter (Keithley 160). The monochromator was the same as used in FC studies, the spectra recorded are after proper corrections (described in section 3.3.4).

3.3.3. PL STUDIES

PL studies comprise of the brightness and spectral studies as a function of various additions in preparing the samples. For spectral studies the setup shown in Fig. 3.15
FIG. 3.8 BLOCK DIAGRAM FOR EL BRIGHTNESS STUDIES.
FIG. 3.9 BLOCK DIAGRAM FOR SPECTRAL STUDIES.
FIG. 3.10 BLOCK DIAGRAM FOR PL BRIGHTNESS STUDIES.
FIG. 11 BLOCK DIAGRAM FOR SPECTRAL STUDIES OF PL EMISSION.
was used. The PL excitation source was a high pressure Hg source. The 365 nm line was selected by using a Carl Zeiss interference filter. Other arrangements are the same as described in EL studies. For brightness, the PL cell was directly placed in front of the photomultiplier at an angle of 45°. Glass plates were used in between these two to avoid any uv radiation.

3.3.4 CORRECTION OF EL AND PL SPECTRA:

The plot of luminescent intensity, measured in quanta per unit frequency (or wave number) interval, against frequency or wave number represents the emission spectrum. If \( \Delta \) represents the total number of quanta (of all wave numbers) emitted per unit time, then \( \frac{\Delta \omega}{\Delta \omega} \) represents the intensity at a wave number, and the plot of \( \frac{\Delta \omega}{\Delta \omega} \) against \( \frac{\Delta \omega}{\Delta \omega} \) is the true spectrum. In practice, the spectrum is normally plotted in relative rather than absolute units.

When the monochromator is scanned at constant slit width and constant photomultiplier sensitivity, the observed spectrum must be corrected for following factors (i) the quantum efficiency of the photomultiplier (ii) the band width of the monochromator and (iii) the transmission factor of the monochromator. Thus the observed photomultiplier output
A at wave number corresponding to the apparent emission spectrum is given by -

\[ A \approx (\frac{dJ}{d\nu}) (P_{\nu} B \nu L_{\nu}) = \frac{dJ}{d\nu} S_{\nu} \]

Where \( P_{\nu} \) is the relative quantum efficiency of the photomultiplier, \( B_{\nu} \) is the relative bandwidth at constant slit width of the monochromator and \( L_{\nu} \) is the fraction of light transmitted by the monochromator. The true spectrum can thus be calculated from the observed curve by dividing each ordinate by corresponding value of \( S_{\nu} \).

The quantity \( S_{\nu} \) is proportional to the photomultiplier output that would be observed if the entrance slit were illuminated by a source having constant spectral distribution. If, therefore, a diffuse source of known spectral distribution is used to illuminate the entrance slit of the monochromator in such a way that the collimator is filled with light and the photomultiplier response \( R_{SL} \) recorded as a function of wave number, then \( S_{\nu} \) can be determined from (Parker 1968)

\[ S_{\nu} = \frac{R_{SL}}{(dJ/d\nu)_{SL}} \]

For calibration in the visible region a tungsten lamp of known colour temperature was used. The lamp was
calibrated at NPL, New Delhi and its details are as follows:

at test voltage 250 V and current 0.064 A, Colour temperature was 2080°K. This was used to illuminate MgO screen placed at an angle in front of the entrance slit. The entrance and exit slits were adjusted for optimum performance. Photomultiplier response RSL was then recorded for the whole spectrum. Using Plank's law according to which the spectral distribution of emitted radiation is:

\[
(\frac{d\Phi}{d\nu})_{SL} = \frac{0.3127 \nu^2}{\exp \left( \frac{1.1384 \nu}{T} \right) - 1}
\]
einstein sec^{-1} per \mu m^{-1} interval where \(\nu\) is expressed in \mu m^{-1} and \(T\) is the colour temperature of the tungsten lamp used. Each calculated value of \((\frac{d\Phi}{d\nu})_{SL}\) was then corrected by multiplying it with reflectivity of magnesium oxide for that particular frequency range.

Value of \(R_{SL}\) and corrected \((\frac{d\Phi}{d\nu})_{SL}\) are plotted against \(\nu\) (Curves B and A respectively in fig. 3.11) after normalising them for common wave \(\nu\) number at 0.56 \mu m. Curve C is the spectral sensitivity curve. The corrected spectra were obtained by dividing each value of observed spectrum by ordinate of curve C.
FIG. 3.12 SPECTRAL SENSITIVITY CURVE
3.3.5 **CORRECTION OF PC EXCITATION SPECTRA**

The PC excitation spectrum was obtained by recording the photoresponse for different excitation wavelength obtained from the monochromator at a constant slit width. The excitation spectra so obtained is uncorrected and depends on the characteristics of the instruments used in this process and thus is a grossly distorted version of the true spectrum. The correction method used in the present investigation has been the one suggested by Bhushan and Sharma (1988). The method is as follows:

First the uncorrected emission spectrum of the excitation source (incandescent bulb of 1000 W) has been recorded by using a prism monochromator and a RCA 6217 photomultiplier tube operated by a highly regulated power supply. This spectrum has then been corrected for the efficiency of photomultiplier tube and the band width and transmission factor of the monochromator. The true emission spectrum has been obtained from the observed curve by dividing each ordinate by the corresponding values of a sensitivity factor derived from the product of relative quantum efficiency of photomultiplier, relative band width of monochromator and the fraction of light transmitted by the monochromator.
The sensitivity factor has been determined from the ratio of observed photomultiplier response and the intensity at different wavelengths calculated from Plank's law for the colour temperature of the source and multiplying by the reflectivity of MgO used for illuminating the entrance slit.

The corrected intensity as a function of wave number has been used to correct the PC excitation spectrum. Bhushan and Sharma (1988) have claimed that the method presents very accurate results for CdS.