

CHAPTER TWO

PREPARATION OF PHOSPHORS AND  
EXPERIMENTAL ASPECTS

CHAPTER TWOPREPARATION OF PHOSPHORS AND EXPERIMENTAL ASPECTS2-1 PREPARATION OF PHOSPHORS:

The phosphors are usually prepared by incorporating traces of impurities (1,2) in a pure semiconductor or insulating crystalline materials. They can be prepared, as per requirement, in the form of single crystals, thin films or microcrystalline powders.

2-1.1 Phosphors in Microcrystalline Powder Form:

Since this is the form in which phosphors are prepared in the present study, the preparation is described in detail.

A) Basic Ingredients of a Phosphor:

The method of obtaining phosphors in powder form, in general, is to start with a pure host material, mix it with a suitable flux along with the activator element added as its salt, preferably in the form of solution. The ingredients are then thoroughly mixed and the charge is finally fired at a suitable temperature for a pre-determined period, in a suitable atmosphere.

a) The Host Material:

Since the transition of electrons responsible for luminescence are within the range of the band gap, for visible luminescence it is necessary that the band gap of the matrix crystal should be greater than 1.5 eV, the energy

of the photon corresponding to the extreme red. For obtaining luminescence in the full visible region it should be greater than 3 eV, the energy corresponding to the extreme violet. Leverenz (3) prescribed the combination of elements of columns I, II, III B, IV A, V, VI A of the periodic table with those of columns VI B and VII B to satisfy the above condition.

b) Activators:

Impurities that provide localised energy levels in the forbidden energy gap of an insulator or semiconductor and which permit radiative transitions are called activators (4). Depending upon the way of functioning, activators are classified as follows:

- i) Originator: It gives rise to new emission lines or bands other than the intrinsic luminescence of the host lattice.
- ii) Intensifier: It intensifies the intrinsic luminescence of the host lattice.
- iii) Dominant and Auxilliary Activators: Some times the intensity of singly activated phosphor is enhanced by adding second activator. The first and the second activators are then known as dominant and auxiliary activators respectively.
- iv) Killer: It provides energy levels because of which radiative transitions are forbidden (4).

v) Co-activator: It provides the balance of charge (5,6) in phosphors activated by monovalent atoms. Moreover, it may also affect the colour of emission, its intensity and the defect structure of the phosphor material.

C) Flux:

There are certain readily fusible salts which when added to the base material, result in good phosphors (7,8). Such salts are known as flux materials or fluxes.

Flux evidently plays different roles in different phosphors. However, it generally,

- i) enhances the rate of reaction at relatively lower temperatures (9,10).
- ii) promotes the crystal growth at lower temperatures;
- iii) facilitates the incorporation of activator and its homogeneous distribution in the host lattice (9,10).
- iv) affects the luminescence intensity (11), and;
- v) serves as a charge compensating against (5,6).

Generally the effective fluxes are oxysalts and sulphates of sodium and potassium (12).

B) Preparative Parameters of Phosphor:

The luminescent properties of a phosphor are usually found to depend on a number of parameters during synthesis. Some of the crucial ones are as follows:

a) Purity of Ingredients:

As luminescence emission is very sensitive to the impurity atoms, a slight trace of any foreign element may cause either activation or poisoning. Hence, the purity of ingredients to be used is an important consideration in making phosphors. A clean laboratory and special attention to maintain purity of ingredients and cleanliness throughout the process are highly essential.

b) Reaction Vessels:

The selection of reaction vessels (crucibles) is to be done on the basis of their chemical inertness, purity, high refractoriness and ability to withstand thermal and mechanical shocks.

c) Firing Temperature and its Duration:

To achieve an optimum brightness, the phosphor is required to be fired for a suitable time at an appropriate temperature(3); empirically determined for each system of phosphor. Also the temperature within the heating chamber of the furnace must be fairly uniform and constant. Variation in the temperature of the furnace sometimes totally changes the crystal structure of the phosphor and thus affects the structural homogeneity of the final product (3,13,14).

d) The Atmosphere of Firing:

The atmosphere in which phosphor ingredients are fired has a pronounced effect on the character of the phosphor (15).

For example, hexagonal CdS, when fired in neutral atmosphere, emits in the infrared region, while it emits in the green region after being heated in H<sub>2</sub>S, atmosphere (16). Also some phosphors (17) which do not show electroluminescence response when fired in H<sub>2</sub>S, become electroluminescent after firing in the presence of water vapour.

e) Grain size of Ingredients:

The grain size of the basic ingredients required for the phosphor preparation has a striking effect on the rate of solid state reaction and thereby upon quality of the phosphor. To have phosphors of good quality, the solid state reaction must be continuous and uniform. This has been achieved when different reacting phases are in intimate contact and therefore the particles of very fine size with large surface to volume ratio are required (3,13,19).

f) Rate of Cooling:

In general rate of cooling affects the luminescent properties such as absorption, spectral emission, the brightness of phosphor and often rate of phosphorescence decay (20). Sudden cooling sometimes even changes the colour of fluorescence (17). Slow cooling rate helps in uniform distribution of imperfections throughout the phosphor (16). On the other hand, rapid cooling preserves the valence state prevalent at high temperature (21).

g) Size of the Charge:

Homogeneity of the final product is affected by the size of the charge (19). Preparation of phosphor in large

quantities may involve different rates of heating due to poor conductivity of the charge. The mixture just in contact with the walls of its container will attain furnace temperature earlier than the central portion, forming a temperature gradient within it. The effect may be minimised by taking small quantity of mixture each time.

#### 2-1.2 Preparation of Alkaline Earth Sulphide Phosphors:

Since the time of Lenard (2), a number of attempts have been made to prepare efficient alkaline earth sulphide phosphors incorporating different activators. The usual method of preparing alkaline earth sulphide phosphors is due to Wells (22), and is the firing of the mixture of alkaline earth carbonates, oxides or hydroxides with sulphur along with a suitable flux such as  $\text{Na}_2\text{SO}_4$ ,  $\text{NaCl}$ ,  $\text{CaF}_2$  etc. together with a desired impurity at a temperature well above the melting point of flux. This process involved the simultaneous reduction and activation of phosphors. There are other methods, in which first, the different alkaline earth compounds are converted to the respective sulphides by heating them in an atmosphere like  $\text{H}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{NH}_3$ ,  $\text{CS}_2$ , water gas etc., and are activated with different impurities, thus making reduction and activation by two different processes. A brief survey of preparative method is done by Sumio Sakka (23).

#### 2-1.3 Preparation of CaS Phosphors:

A literature survey presents number of methods for the preparation of CaS phosphors. However, the following methods are widely used.

A) Method due to Wachtel (24):

According to this method, the salts of calcium are converted into calcium sulphate which on reduction by  $H_2$  at  $1000^\circ C$  gives CaS as  $CaSO_4 + 4H_2 = CaS + 4H_2O$ . The activation is done separately during the firing of the phosphors in an inert atmosphere like  $N_2$ ,  $H_2S$  etc. A method developed by Wachtel has been used by Lehmann (25) for his extensive study on CaS phosphors.

B) Method Due to Bhawalkar (26):

According to this method, phosphor samples of CaS are prepared from Indian material, Gypsum, and activated simultaneously. This method of phosphor preparation is a speciality of solid state physics laboratory of Sagar and is widely followed in these days in other laboratories in India (27,28,29).

Now-a-days, preparation of single crystals of alkaline earth sulphide phosphors is achieved. Reals and Jack (30) have studied the reflectance and absorption spectra of calcium sulphide single crystals near the edge of the fundamental absorption. Thin films of these phosphors have been prepared and studied by many workers (31,32).

2-1.4 Details of the Method Followed:

The method followed in preparing CaS phosphors in the present investigation, is the one developed by Bhawalkar (26). The method involved the heating of an intimate mixture of purified gypsum ( $CaSO_4 \cdot 2H_2O$ ) and carbon together with the



required amount of activator and flux ( $\text{Na}_2\text{SO}_4$ ). The prepared charge was fired at  $900^\circ\text{C}$  for  $2\frac{1}{2}$  hours and was cooled slowly in the furnace itself.

The details of the procedure followed in the present investigation may be divided into two stages. The first stage involves the purification and preparation of basic ingredients while second one deals with preparation and firing of the charge at suitable temperature.

A) First Stage:

a) Host Material in Pure Form:

In Bhawalkar's method, an Indian mineral gypsum is used as starting material. However, in the present investigation, use is made of ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), AR, BDH, with maximum limits of following impurities as labelled by manufacture:

Calcium sulphate (Dihydrate)  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} = 172.17$

(As say not less than 99%  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ).

Maximum limits of impurities,

HCl insoluble matter 0.01%, Free acid ( $\text{H}_2\text{SO}_4$ ) 0.01%

Carbonate 0.1%, Chloride 0.002%,

Nitrate 0.002%, Arsenic 0.00004%,

Iron 0.0005%, Lead 0.001%

Magnesium 0.01%, Potassium 0.01%

Sodium 0.01%.

b) Purification of Carbon:

A.R. grade E. mark carbon was used as a reducing agent.

To remove any trace of impurities present, it was boiled with

excess of double distilled water for about half an hour and then filtered. The residue was then repeatedly washed with hot double distilled water. Finally it was oven-dried (Kleertone, Model KA01) at  $60^{\circ}\text{C}$  and stored in clean bottle.

c) Activator Solution: (Zn):

The activator was added in the form of solution of its salt. The weighed quantity of the salt zinc acetate  $[(\text{CH}_3\text{COO})_2\text{Zn}, 2\text{H}_2\text{O}]$ , A.R. grade, was dissolved in measured amount of double distilled water. The solution was then diluted subsequently to suit various concentrations of the activator to be added.

d) Purification of the Reaction Vessels:

Graphite crucibles were used as reaction vessels. These were soaked in 30% Nitric acid for several hours to ensure the complete conversion of contaminating impurities into ~~w-a~~ water soluble nitrates. These were then repeatedly washed with distilled water and oven-dried at  $80^{\circ}\text{C}$ . The crucibles were then fired at  $900^{\circ}\text{C}$  for three hours so as to remove any contaminating gases. It also tested their ability to withstand the thermal and mechanical shocks.

e) Flux:

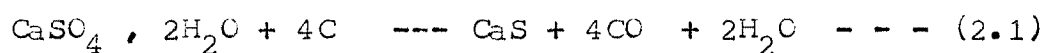
In every phosphor, the efficient flux (12)  $\text{Na}_2\text{SO}_4$  was added, 5% by weight.

B) Second Stage:a) Preparation of Charge for Firing:

Calcium sulphate (10 grams.) and Carbon (2.5 grams) were mixed intimately to give a uniform mixture. The activator solution in requisite amount, alongwith flux solution was added and the charge was again mixed thoroughly. Few drops of absolute alcohol was added which facilitated dispersion and diffusion of activator throughout the charge. It was then allowed to dry in a dust free chamber (electric oven) at 60°C.

b) Firing of the Charge:

The mixed and dried charge was thoroughly grinded to a fine particle size and then packed in one of the pre-fired crucibles. A thin layer of purified carbon (in fixed quantity) was spread over the surface of the filled charge to keep the atmosphere reducing, and a second crucible was fitted over it to act as lid. A little quantity of carbon was also put in the lid. The crucible was then fired in an electric muffle furnace (Okey Electric Furnace- By Sakh and Co., Calcutta-6) maintained at 900°C for a duration of two and half hours. The current in the furnace then switched off and the charge was allowed to cool slowly. The cooled charge was powdered and collected as a phosphor. The reduction of calcium sulphate into calcium sulphide occurs according to the reaction:



As alkaline earth sulphides are hygroscopic, the prepared samples were stored in sealed and numbered test tubes.

#### 2-1.5 Prepared Phosphors:

Prepared CaS:Zn phosphors contained the activator Zn in amounts 0.00, 0.2, 0.4, 0.6, 0.8, 1.0, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.5 wt.% by weight of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ . A list of prepared samples is given in Table 2.1.

Amongst the samples prepared, the pure CaS was white while other containing Zn, were faint gray, showing fading in colour with decrease of Zn content. Moreover, the uniformity of solid solution was checked through photoluminescence. A uniform colour under UV excitation suggests the formation of the homogeneous compound structure.

#### 2-1.6 X-Ray Analysis of Synthesised Phosphor:

X-ray powder diffraction technique was adopted to check the completion of reaction. The X-ray diffraction studies are useful not only to examine the phase of the prepared samples but also to study their crystal structure. CaS takes the cubic structure of NaCl type (Fig.2.1-a). The Bravais lattice is face centred cubic; the basis consists of one Ca atom and one S atom separated by one half the body diagonal of a unit cube. There are four units of CaS in each unit cube, with atoms in the positions

$$\begin{aligned} \text{Ca} &: 000, \frac{1}{2} \frac{1}{2} 0, \frac{1}{2} 0 \frac{1}{2}, 0 \frac{1}{2} \frac{1}{2} \\ \text{S} &: \frac{1}{2} \frac{1}{2} \frac{1}{2}, 0 0 \frac{1}{2}, 0 \frac{1}{2} 0, \frac{1}{2} 0 0 \end{aligned}$$

Each Ca atom has six equidistant S atoms at nearest sites and vice versa. The ionic radii of Ca and S are  $0.99^{\circ}\text{A}$  and  $1.84^{\circ}\text{A}$ . The ionic radial distance Ca-S is  $2.83^{\circ}\text{A}$ . The space group symmetry of CaS is Fm  $3m$ .

Fig.2.1-b shows a typical Debye-Scherrer powder pattern for sample No.F6. The patterns were taken on a Philips X-ray diffraction unit using copper target (using filtered Cu-K radiation). It is found that the phosphors are of FCC type with lattice constant  $5.7^{\circ}\text{A}$ . This agrees well with the results of other workers (33.34).

## 2-2 EXPERIMENTAL ASPECTS:

The details of the experimental techniques followed in electroluminescence and electro-thermoluminescence are as follows:

### 2-2.1 Electroluminescence Measurements:

The electroluminescent response of the phosphors has been studied with a particular reference to voltage and frequency dependance of brightness. The experimental arrangement and the procedure followed are as described below:

#### A) Experimental Set-up:

A block diagram of experimental set-up for the study is shown in Fig.2.2 while Fig.2.3 presents a photograph of it. The set-up mainly consists of a source of excitation, on electroluminescent cell and a brightness measuring system.

a) Source of Excitation:

The exciting source used was an audio frequency generator (Philips, type GM 2308/90) with a frequency range of 50 Hz to 16 KHz and having maximum output voltage of 90 volts. As this voltage was not sufficient to excite the phosphors, a wide band amplifier (Telmex, type SF-100) was used in conjunction with the frequency generator (Fig.2.4). The maximum voltage thus available was upto 2.0  $KV_{rms}$  in the frequency range of 50Hz to 2KHz. At higher frequencies, output voltage dropped significantly and was insufficient to excite the phosphor.

b) Electroluminescent Cell:

An usual type electroluminescent cell (EL cell) consists of a phosphor layer embedded in a dielectric. The phosphor layer thus formed is sandwiched between two parallel electrodes. One of the electrodes must necessarily be transparent so as to observe light produced by the application of electric field. In literature, an EL Cell is also referred to as "Luminescent condenser". An efficient EL Cell should possess low resistance of transparent electrodes, appropriate thickness of the phosphor layer and a suitable dielectric medium.

Different types of EL cells have been described by several workers (35,36,37) with different designs and different dielectric media for the phosphor. The dielectric medium used should possess high dielectric constant and breakdown strength. The dielectrics usually used are castor oil,

silicon grease, araldite, polysterene in benzene, polymethyl methacrylate in ethylene dichloride, cyanoethyl cellulose, plasticized polyvinal chloride etc. The details of the cell used in the present investigation are as under:

Fig.2.5-a shows a schematic view of the EL cell used. The cell consisted of a bakelite sheet of size 9 X 5 X 0.7 cms. and a cavity of size 5 X 2.5 X 0.2 cms. groved in it. In a cavity a conducting glass (resistance 150 Ohm.  $\text{cm}^{-1}$  and transmittance 80%) of appropriate size was fitted. The conducting glass served as one of the electrodes and electrical contact with it was made through a metal plate. Another bakelite sheet, of the same size, was rigidly screwed with the previous one and holds an aluminium plate of appropriate size which acts as another electrode. The first bakelite plate carriers a rectangular window of size 2.2 X 1.3 cms. to observe the emitted light. With the cell thus formed, a thin layer of phosphor-embedded in a dielectric medium and of desired size and thickness-along with a thin and uniform mica sheet could be sandwiched between the two electrodes. A thin mica sheet, having high dielectric constant and sufficient breakdown strength, excludes the possibility of carrier injection at the electrode contacts (38).

The excitation of the phosphor could be achieved by applying electric field across the electrodes. The strength of the field was measured using A.C. voltmeter (Ruttonsha Simpson AC/DC VTVM 321-I).

C) Brightness Measuring System:

Brightness measuring system consists of a D.C. microvoltmeter (Philips, type PP 9004), a photomultiplier tube and its power supply. The photomultiplier tube used was "RCA 931 A" having Sb-Cs cathode (cathode sensitivity of  $10 \mu\text{A}/\text{mm}$  and spectral response in the range  $3000-7000^{\circ}\text{A}$  (Fig.2.6). The tube was operated at 900 volts obtained from a well stabilized D.C. power supply (Fig.2.7). The output of the PM tube was measured by D.C. microvoltmeter.

B) Experimental Procedure:

It was observed that the phosphors under present investigation give poor emission when embedded in dielectric materials such as castor oil, polysterene in benzene, chlorinated rubber in xylene etc. However, with silicon grease as dielectric material, the phosphors gave better luminescence and hence was used as a dielectric matrix in further studies.

a) Preparation of EL Cell:

A thin layer of phosphor was applied to the aluminium plate using silicon grease. The constancy in layer thickness was maintained by taking a fixed volume of phosphor and spreading it over a fixed area. To guard the cell against electrical breakdown a thin sheet of mica (thickness about  $50 \mu$ ) was placed over the phosphor layer. The conducting glass was then mounted over the mica sheet. A screw arrangement helped in adjusting the interelectrode distance and pressure.



b) Voltage and Frequency Dependence of EL Brightness:

The prepared cell was mounted on a platform and below it was placed a PM tube. The output of the PM tube was connected to D.C. microvoltmeter (Philips 9004). The phosphor was then excited by applying voltage from the exciting source and brightness variations with voltage and frequency were noted. The observations were carried out first varying the voltage from 0 to 1.5 KV<sub>rms</sub> and keeping frequency constant, and latter by varying the frequency from 50 Hz to 2.0 KHz and maintaining the voltage constant.

2-2.2 Electro-Thermoluminescence Measurements:

The electro-thermoluminescence (EL-TL) measurements of phosphors are nothing but thermoluminescence measurements under the action of an applied sinusoidal voltage.

A) Experimental Set-Up:

The experimental set-up used essentially consists of (a) source of excitation (b) suitable (EL-TL) cell and (c) the intensity measuring unit.

a) Source of Excitation:

Set-up consisting of an audio frequency generator in conjunction with a wide band amplifier (as already described in Section 2-2.1(A) under electroluminescence measurements) was used as a source of excitation.

b) Electro-Thermoluminescent Cell:

Suitable EL-TL cell, fabricated in the laboratory, consists of an usual condenser type EL cell, provided with an arrangement of heating the sample at a uniform heating rate. The schematic view of the EL-TL cell is illustrated in Fig.2-5-b. The system was capable of raising the temperature of phosphor at a convenient heating rate.

c) Intensity Measuring Unit:

It is the same unit as that used in electroluminescence measurements.

Fig.2-8 shows a block diagram of the complete set-up used in EL-TL measurements.

B) Experimental Procedure:

An EL-TL cell prepared with silicon grease as a dielectric gets interrupted on heating. Also a success in preparation of permanent type (39) of cell could not be achieved. Hence no dielectric medium was used for the studies.

A thin layer of phosphor spread on a brass plate was covered with a mica sheet. A conducting glass plate placed over the mica sheet served the purpose of one electrode, while the brass plate that of the other. The prepared cell was mounted on a platform. The photomultiplier tube was positioned so as to receive the emission from the cell. The cell was energised by an a.c. voltage derived from the audio

frequency generator in conjunction with a wide band amplifier; and simultaneously heated with a constant heating rate. The intensity was measured as a function of temperature using D.C. microvoltmeter. The measurements were carried out by varying one of the parameters; i.e. either voltage or frequency or the heating rate and keeping others to remain constant. The measurements were made above the threshold voltages and frequency.

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Table 2.1:

A Matrix of Prepared Samples

( 10 gms of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  + 2.5 gms of activated charcoal + Solution of the flux  $\text{Na}_2\text{SO}_4$  (containing 0.5 gm. of  $\text{Na}_2\text{SO}_4$ ) + requisite amount of activator (Zn)  $\frac{860^\circ\text{C}}{2.5 \text{ Hrs.}}$  Phosphor).

Sample Number	Concentration of activator (Zn) by weight in $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	Sample Number	Concentration of activator (Zn) by weight in $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
P <sub>1</sub>	0.0%	P <sub>7</sub>	1.2%
P <sub>2</sub>	0.2%	P <sub>8</sub>	1.4%
P <sub>3</sub>	0.4%	P <sub>9</sub>	1.6%
P <sub>4</sub>	0.6%	P <sub>10</sub>	1.8%
P <sub>5</sub>	0.8%	P <sub>11</sub>	2.0%
P <sub>6</sub>	1.0%	P <sub>12</sub>	2.5%

Every sample contains the flux  $\text{Na}_2\text{SO}_4$  , 5% by weight of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ .

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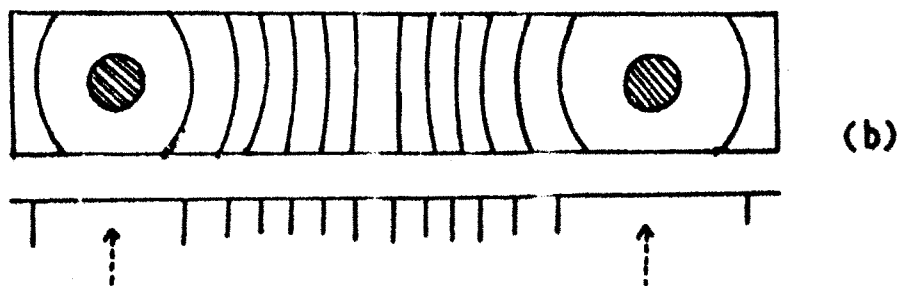
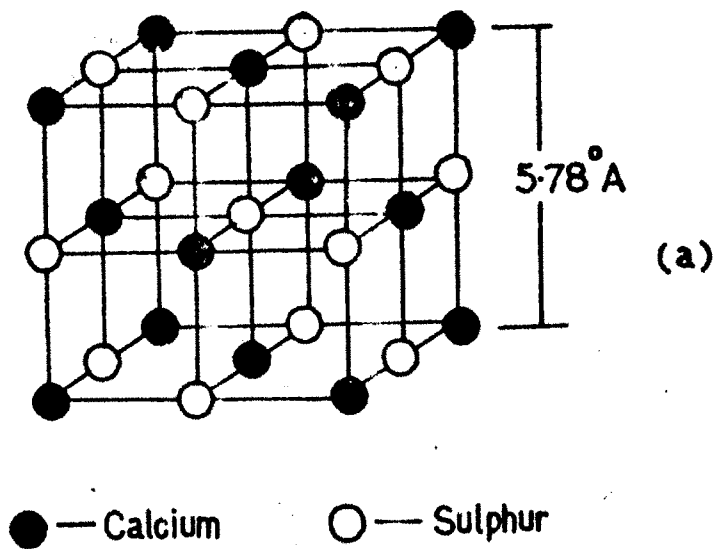


FIG. 2-1 (a) CRYSTAL STRUCTURE OF CaS.  
(b) X-RAY DIFFRACTION PATTERN.



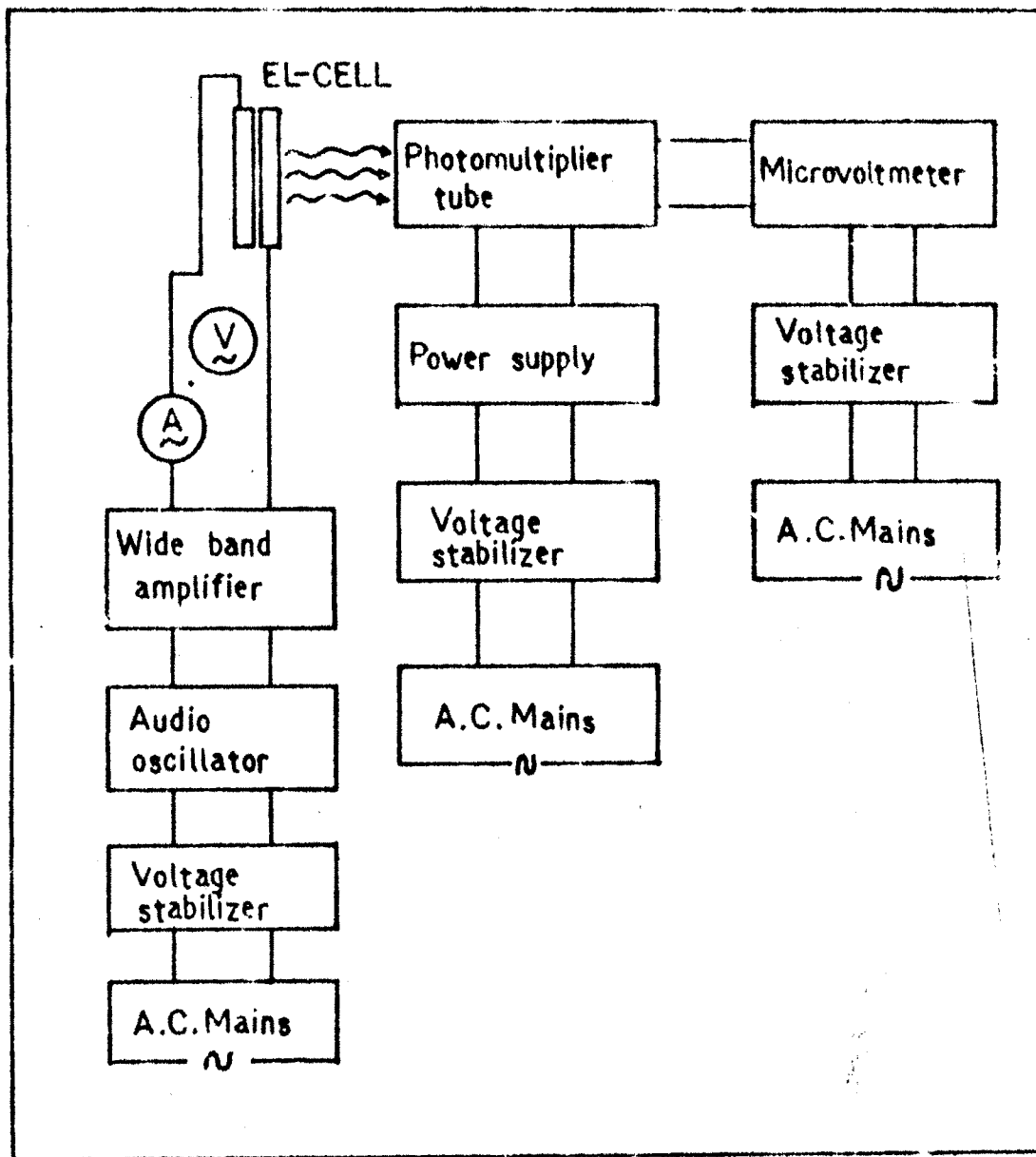


Fig. 2-2—Experimental set up for electroluminescence studies.

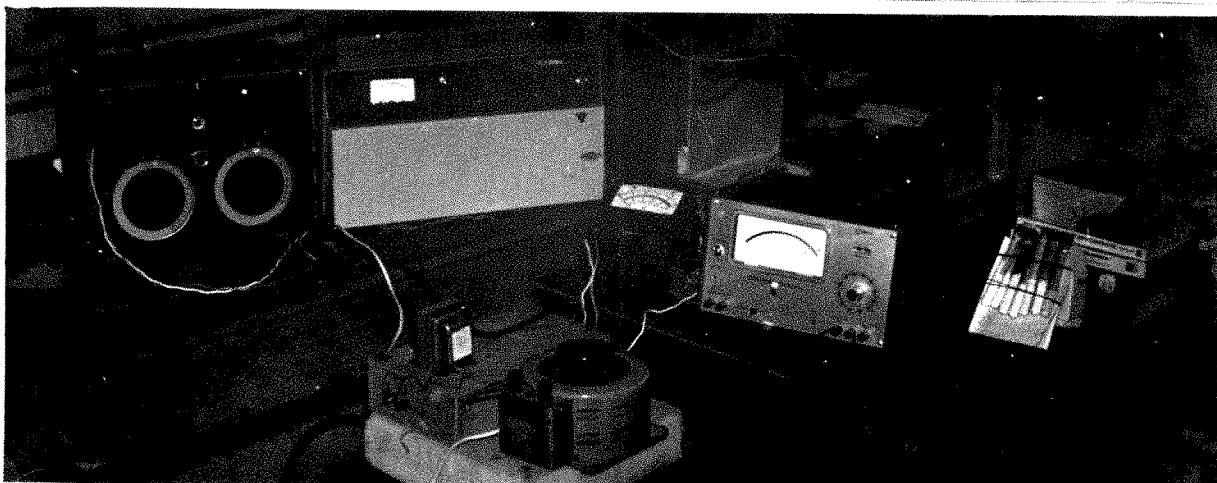


Fig. 2.3 Photograph of the experimental set up used in electroluminescence studies.



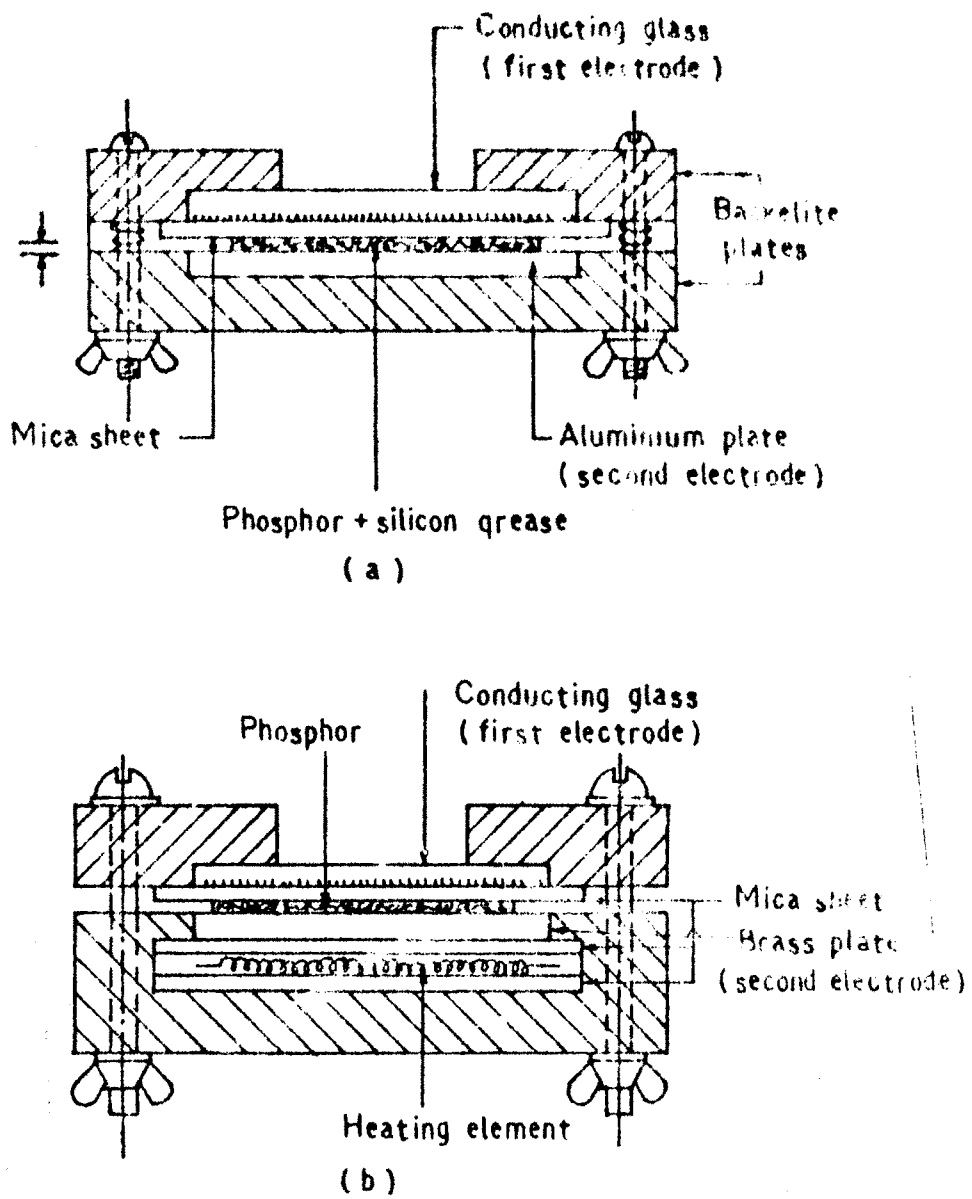


Fig. 2.5 (a) Electroluminescence (EL) cell.  
 (b) Electrothermoluminescence (EL-TL) cell.

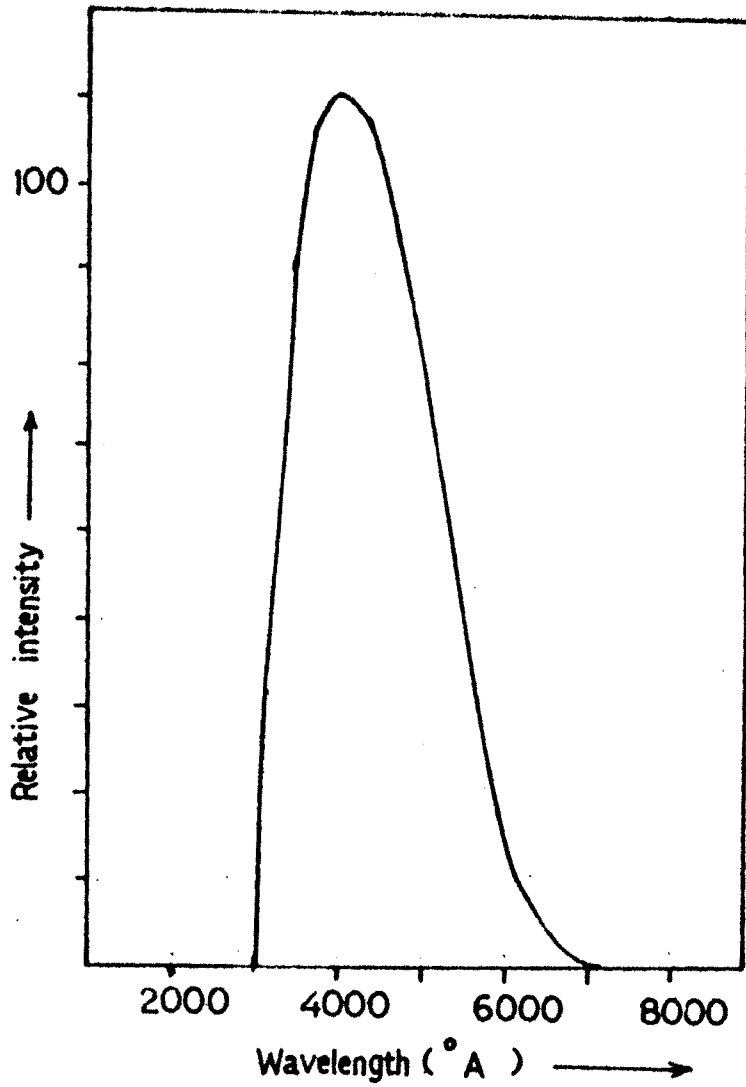


FIG. 2.6 —SPECTRAL RESPONSE CURVE FOR  
RCA 931 A PM TUBE.

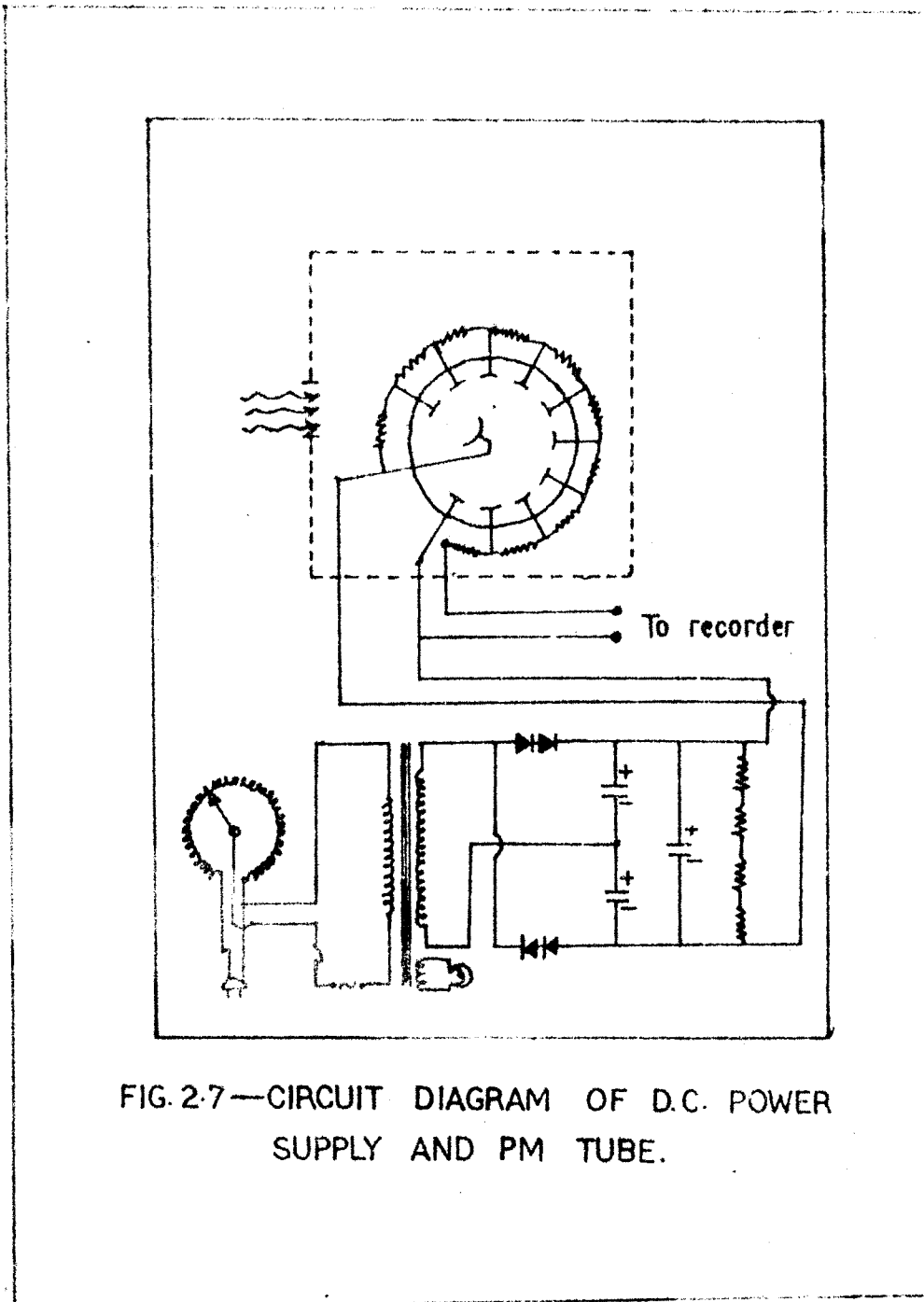


FIG. 2.7—CIRCUIT DIAGRAM OF D.C. POWER SUPPLY AND PM TUBE.

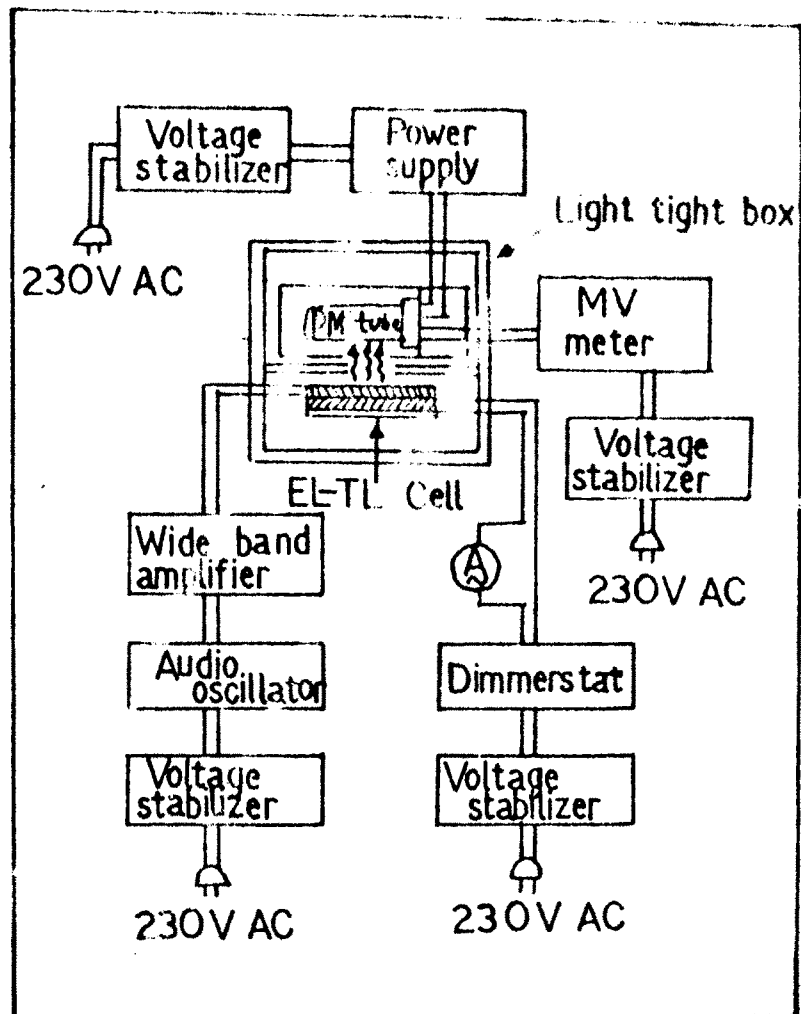


FIG. 2.8— EXPERIMENTAL SET UP FOR THE ELECTRO - THERMOLUMINESCENCE STUDIES.