

PREPARATION OF PHOSPHORS AND EXPERIMENTAL ASPECTS:2-1. 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 micro-crystalline powders.

2-1.1 Phosphors in Microcrystalline Powder Form:

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

(A) Basic Ingredients of a Phosphor:

The method of obtaining phosphors in the 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 predetermined period.

(i) The Host Material:

Since the transitions 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

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in the full visible region it should be greater than 3 eV- the energy corresponding to the extreme violet. Combinations of the elements of columns 1,2,3 B,4 A, 5, 6 A of the periodic table with those of columns 6 B and 7 B fulfil this condition(3).

(ii) Activators:

The activators, depending upon their way of functioning, are classified as follows:

- a) Originator: It gives rise to new emission lines or bands other than the intrinsic luminescence of the host lattice.
- b) Intensifier: It intensifies the intrinsic luminescence of the host lattice.
- c) Dominant and Auxiliary Activators: Some times efficiency of singly activated phosphor is enhanced by adding a second activator. The first and second activators are known as dominant and auxiliary activators respectively.
- d) Killer: It provides energy levels between which radiative transitions are forbidden (4).
- e) 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 crystalline structure of the phosphor material.

(iii) Flux:

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

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

- a) increases the speed of reactions at lower temperatures; (9,10).
- b) promotes the crystal growth at lower temperature;
- c) facilitates the incorporation of activator and its homogenous distribution in the host lattice (9,10);
- d) affects the luminescence intensity (11);
- e) serves as charge compensating agent (5,6).

(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:

(i) Purity of Ingredients:

As luminescence emission is very sensitive to the impurity atoms, a slight trace of 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 care to maintain purity and cleanliness throughout the process are essential.

(ii) Reaction Vessels:

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

(iii) Firing Temperature:

To achieve an optimum brightness, the phosphor is required to be fired for a suitable time at an appropriate temperature (3). Also the temperature within the heating chamber of the furnace must be 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 (3,12,13).

(iv) The Atmosphere of Firing:

The atmosphere in which phosphor ingredients are fired has pronounced effect on the character of the phosphor (14). For example hexagonal CdS, when fired in the neutral atmosphere, emits in the infrared region, while it emits in the green region after being heated in H<sub>2</sub>S atmosphere.

(v) Grain Size of Ingredients:

The grain size of the basic ingredients required for phosphor preparation has a striking effect on the rate of solid-state reactions and thereby also on the quality of the phosphor. To have phosphors of good quality, the solid-state reaction must be continuous and uniform. This has been achieved by taking particles of very fine size and having large surface to volume ratio (3,15,16).

(vi) Size of the Charge:

Preparation of phosphors in large quantities involves different rates of heating due to poor conductivity of the charge, and thus affects the homogeneity of the final product



The method involves heating an intimate mixture of the purified  $\text{SrSO}_4$  and carbon, together with the required amount of activator and flux (NaCl). The reduction is carried out at  $900^\circ\text{C}$  by heating the mixture for about  $2\frac{1}{2}$  hours. The details of the procedure followed are as under.

A) Purification of  $\text{SrSO}_4$ :

Strontium sulphate (A.R grade; Belami Flue Chemicals Ltd.,) was used as starting material. In order to remove the metallic impurities, the powder was soaked in 30% nitric acid (AR) for several hours. The settled powder was then boiled for a long time with excess quantity of fresh 30% nitric acid (AR). This ensured complete conversion of metallic impurities into water soluble nitrates. The liquid over the surface of settled powder was decanted. The powder was then repeatedly washed with distilled water till the filtrate gave no 'ring test' for nitrates. The powder was then dried in an oven at  $70^\circ\text{C}$  and stored in clean and tightly sealed bottles.

B) Purification of Carbon:

A.R. grade mark carbon used as reducing agent. To remove any trace of impurities present, it was boiled with excess of distilled water for about half an hour and then filtered. The residue was then washed repeatedly with hot distilled water and finally it was dried in an oven at  $90^\circ\text{C}$ .

C) Activator:

The activator, Zn, was added in the form of solution of its acetate. The weighed quantity of zinc acetate (A.R.) was

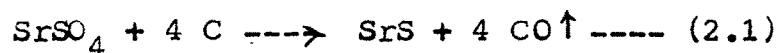
taken and solution was prepared by dissolving it in double distilled water. This solution was then diluted subsequently to suit various concentrations of the activator to be added.

D) Preparation of Charge:

Following Bhawalkar (21), the required amounts of strontium sulphate (5 gms.), carbon (1.310 gms.) and flux NaCl in desired quantity were mixed intemetely to give a uniform mixture. The activator solution along with a few drops of absolute alchol were then added and the charge was thoroughly mixed. The addition of a few drops of alchol facilitated dispersion of the activator throughout the charge. The charge was then allowed to dry in a dust free chamber.

E) Firing:

For firing the charge graphite crucibles were used. The crucibles were perfired at  $900^{\circ}\text{c}$  for four hours so as to remove any contaminating gases. The mixed and dried charge was then packed in one of the crucibles. A thin layer of pure carbon (fixed quantity) was spread over the filled charge to keep the atmosphere reducing, and the second crucible was fitted over it to act as a lid. Finally a little quantify of carbon was also put in the lid. The charged crucible was then fired in an electric muffle furnace at  $900^{\circ}\text{c}$  for a duration of  $2\frac{1}{2}$  hours. After firing, the charge was removed from the furnace and pulverized rapidly while red hot. The reduction of strontium sulphate in to sulphide occurs according to the reaction.



The prepared phosphors were stored in test tubes.

#### 2-1.4 Prepared Phosphors:

The details of samples prepared are given in Table 2-1. In all three series of phosphors were prepared. For first series, concentration of Zn was varied from 0.00 to 2.0 wt %  $\text{SrSO}_4$  and flux, NaCl, was not added. The second series contained only flux and its amount was varied from 0.62 to 40 Wt % of  $\text{SrSO}_4$ . The third one contained fixed amount of NaCl and varying concentration of Zn.

#### 2-2 EXPERIMENTAL ASPECTS:

The details of the experimental techniques followed in studying phosphorescence decay and thermoluminescence are as follows:

##### 2-2.1 Phosphorescence decay Measurements:

###### A) Experimental Set-up:

Phosphorescence decay measurements were carried out at room temperature. The photograph of the experiment arrangement is shown in Fig.2.1, while it is illustrated schematically in Fig.2.2. The arrangement consists of:

- a) Source of excitation;
- b) sample holder, and
- c) intensity measuring unit.

###### a) Source of excitation:

The excitation source used was an ultraviolet lamp ( UV products, U.S.A.type UVS-12) emitting predominantly the



3650<sup>o</sup>A Hg doublet. A stabilizer was used in conjunction with the lamp to maintain exciting energy constant.

b) Sample holder:

A sample holder consists of a metal frame supporting a cassette inclined at 45<sup>o</sup>. A cassette carries a slide pointed with phosphor material applying silicon grease. A beam of UV light projected on the inclined slide excites the phosphor. The emission intensity, at right angles to the incident beam, is to be recorded by intensity measuring unit.

c) Intensity Measuring Unit:

The intensity measuring unit consists of a photomultiplier tube, its power supply and potentiometric recorder. The photomultiplier tube used was RCA 931 A. The tube was operated at 900 volts obtained from a well stabilized D.C. power supply. To measure output of PM tube a potentiometric strip chart recorder (type ECIL CR 5855) was used.

b) Experimental Procedure:

The phosphor in the form of thin layer was painted on slide by using silicon grease; a non-luminescent adhesive material. The constancy in layer thickness was ensured by taking fixed volume of phosphor spread over the fixed area. It was then placed in cassette and adjusted in such a way that excitation and emission could be achieved at right angles to each other. To measure the emission intensity, a photomultiplier tube was placed underneath the assembly protecting it from extraneous light by a mechanical shutter.

The output of PM tube was fed to a potentiometric recorder.

The phosphor was excited to saturation level (5 minutes) using an ultraviolet lamp. During excitation, the shutter was closed and dark current was compensated. After excitation, the UV lamp was switched off and at the same time the shutter was opened. The decaying intensity was recorded on the potentiometric recorder.

## 2-2.2 Thermoluminescence Measurements:

### A) Experimental Set-Up:

The thermoluminescence measurements were carried out above room temperature within a range of  $300^{\circ}$  K to  $443^{\circ}$  K. The experimental set-up and the procedure followed is as below:

The experimental arrangement essentially consists of a source of excitation, the heating chamber and an intensity measuring unit.

#### a) Source of excitation:

The source of excitation used is the same as that used in phosphorescence decay measurement study.

#### b) Heating Chamber:

It consists of a small brass cup holding a phosphor powder for the purpose of exciting and heating it. The brass cup is placed in contact with copper cylinder over which a heating coil (Kanthal wire 22 SWG) embedded in an insulating material was closely wound. The whole assembly is enclosed in a dewar flask to ensure thermal equilibrium. An electrical

energy supplied to heating coil through a dimmerstat with an ammeter in series, heats up the phosphor at a convenient heating rate. The assembly was capable of controlling uniform heating rate within 2.5 % at lower temperatures and 3.5 % at higher temperatures. A typical plot of temperature versus time is shown in Fig.2.3.

c) Intensity Measuring Unit:

It is the same unit that used in the phosphorescence decay measurement study.

The experimental arrangement of TL set up is shown in Fig.2.4 and a photograph in Fig.2.5.

B) Experimental Procedure:

A phosphor layer of nearly equal thickness was spread in a brass cup by taking equal volume of phosphor each time. It was then excited to saturation level (for five minutes). After excitation, the sample was allowed to decay for five minutes. At the termination of five minutes, the current in the heating coil (which was originally adjusted to desired value) was switched on and the thermoluminescent emission was recorded on the recorder.

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TABLE - 2.1

Details of the Samples Prepared

Series No	Sample No	Concentration of Zn, Wt.% of $\text{SrSO}_4$	Concentration of flux NaCl, Wt.% of $\text{SrSO}_4$
I	B <sub>1</sub>	0.0000	Nil
	B <sub>2</sub>	0.01	-do-
	B <sub>3</sub>	0.02	-do-
	B <sub>4</sub>	0.05	-do-
	B <sub>5</sub>	0.10	-do-
	B <sub>6</sub>	0.15	-do-
	B <sub>7</sub>	0.20	-do-
	B <sub>8</sub>	0.50	-do-
	B <sub>9</sub>	1.00	-do-
	B <sub>10</sub>	1.50	-do-
	B <sub>11</sub>	2.00	-do-



TABLE- 2.1 (Contd)

Series No	Sample No	Concentration of flux NaCl Wt.% of $\text{SrSO}_4$	Concentration of $Z_n$ , Wt.% of $\text{SrSO}_4$
II	B <sub>12</sub>	0.62	Nil
	B <sub>13</sub>	1.25	-do-
	B <sub>14</sub>	2.50	-do-
	B <sub>15</sub>	5.00	-do-
	B <sub>17</sub>	20.00	-do-
	B <sub>18</sub>	30.00	-do-
	B <sub>19</sub>	40.00	-do-

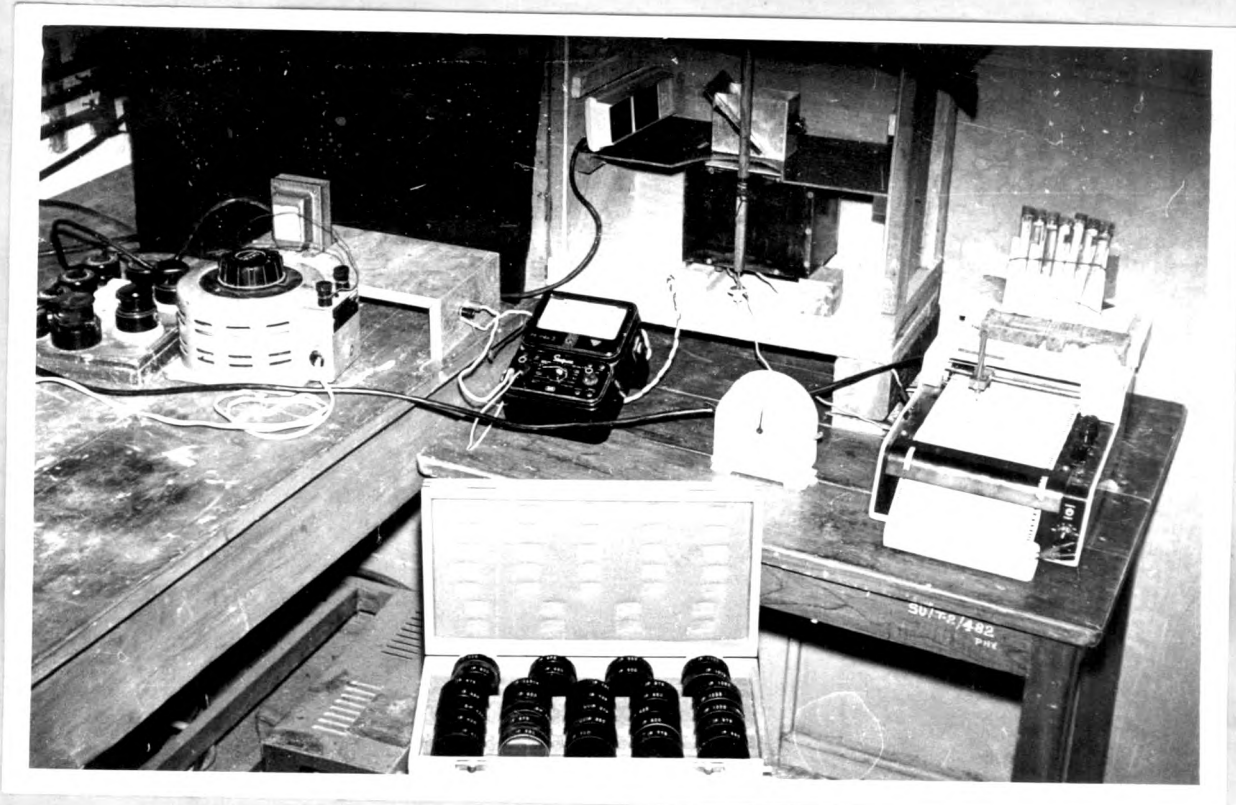
Series No	Sample No	Concentration of $Z_n$ Wt.% of $\text{SrSO}_4$	Concentration of flux NaCl Wt.% of $\text{SrSO}_4$
III	B <sub>20</sub>	0.02	1.25
	B <sub>21</sub>	0.1	1.25
	B <sub>22</sub>	0.2	1.25
	B <sub>23</sub>	1.0	1.25
	B <sub>24</sub>	2.00	1.25

2-3 REFERENCES:

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2.1 Photograph of Experimental Set-up  
used for decay measurements



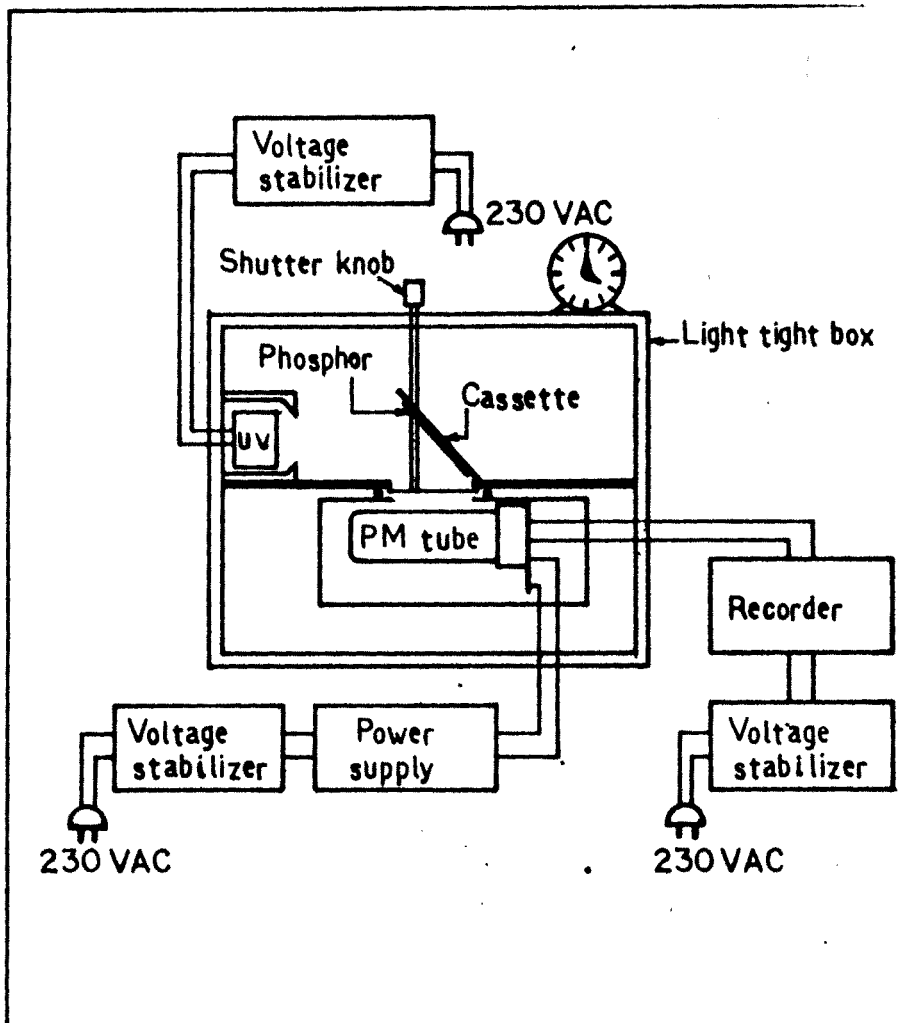


Fig. 2-2 Experimental set up for phosphorescence decay measurements.

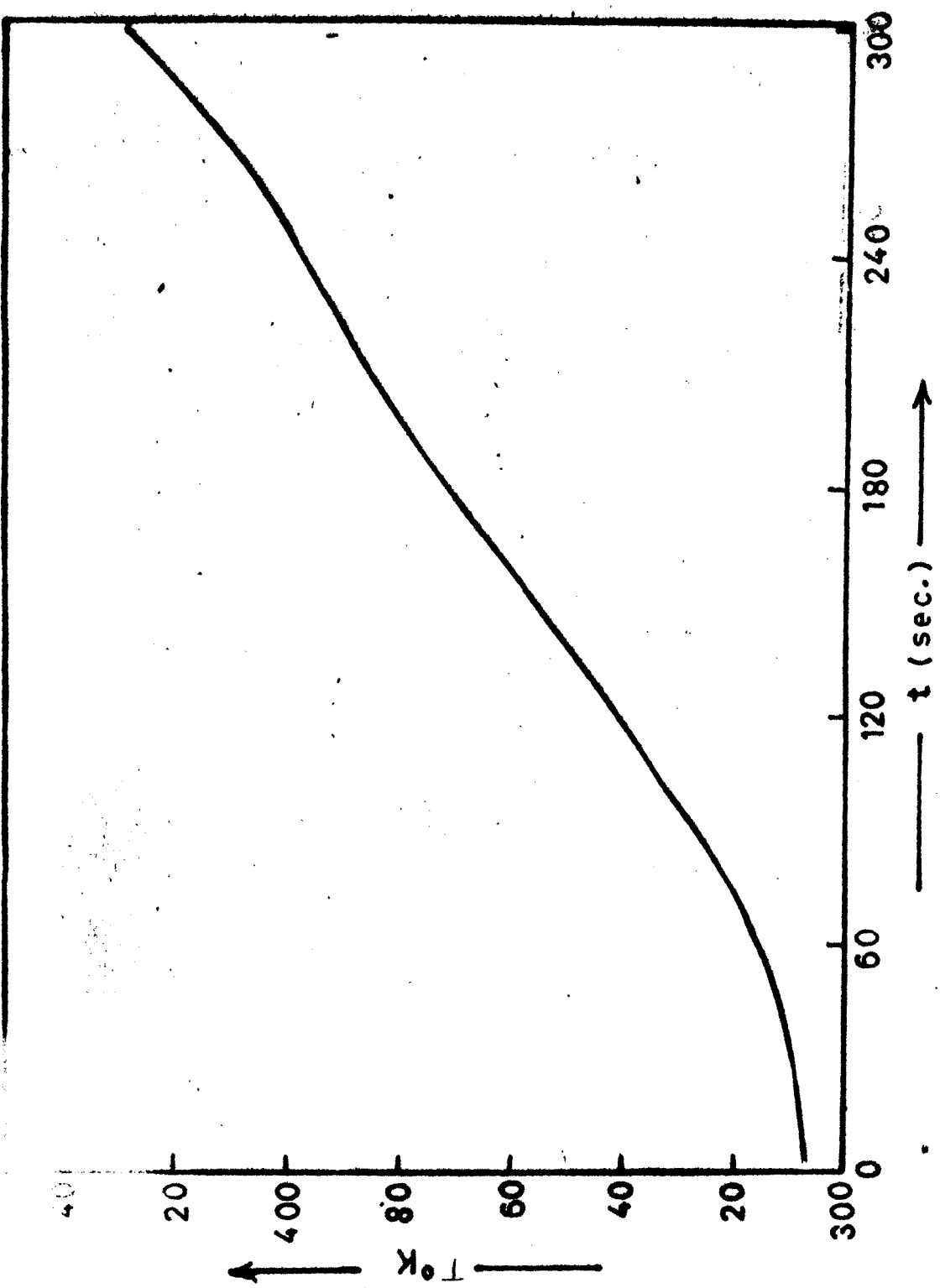


Fig. 2.3.

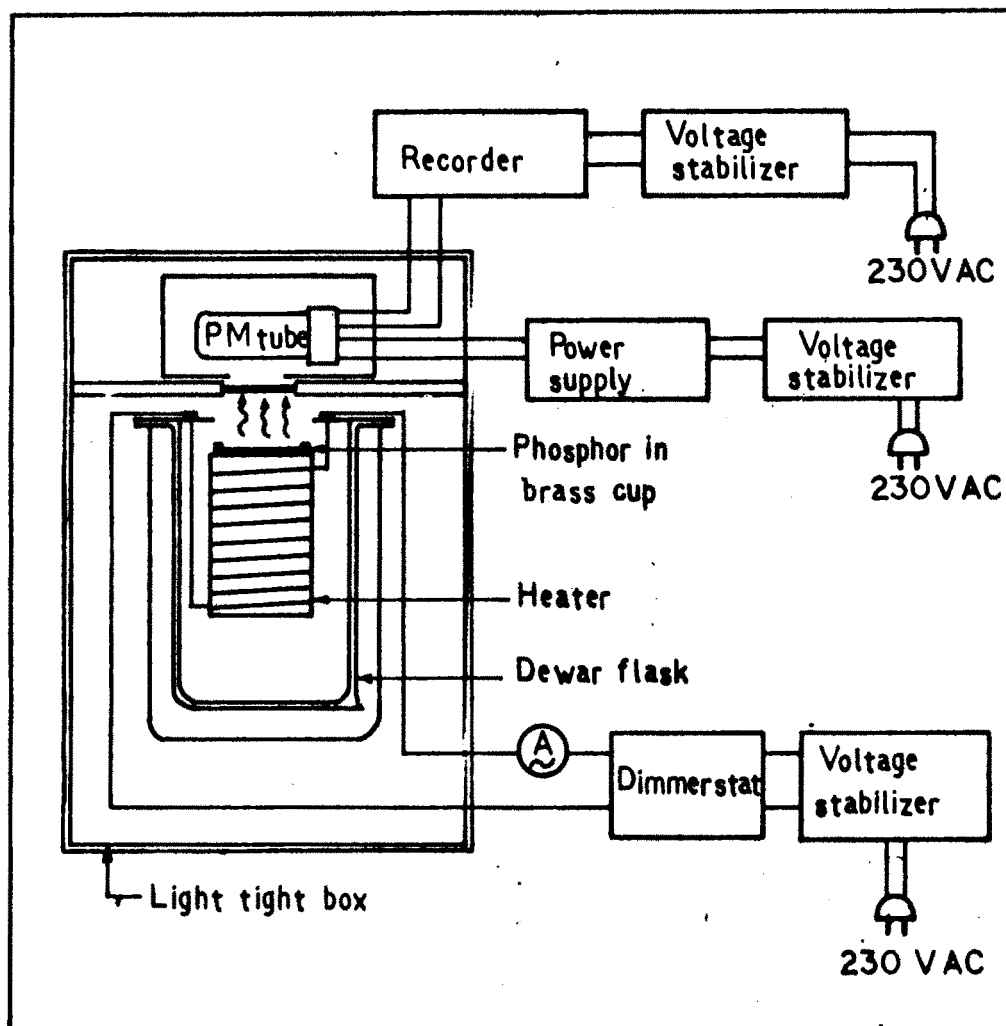
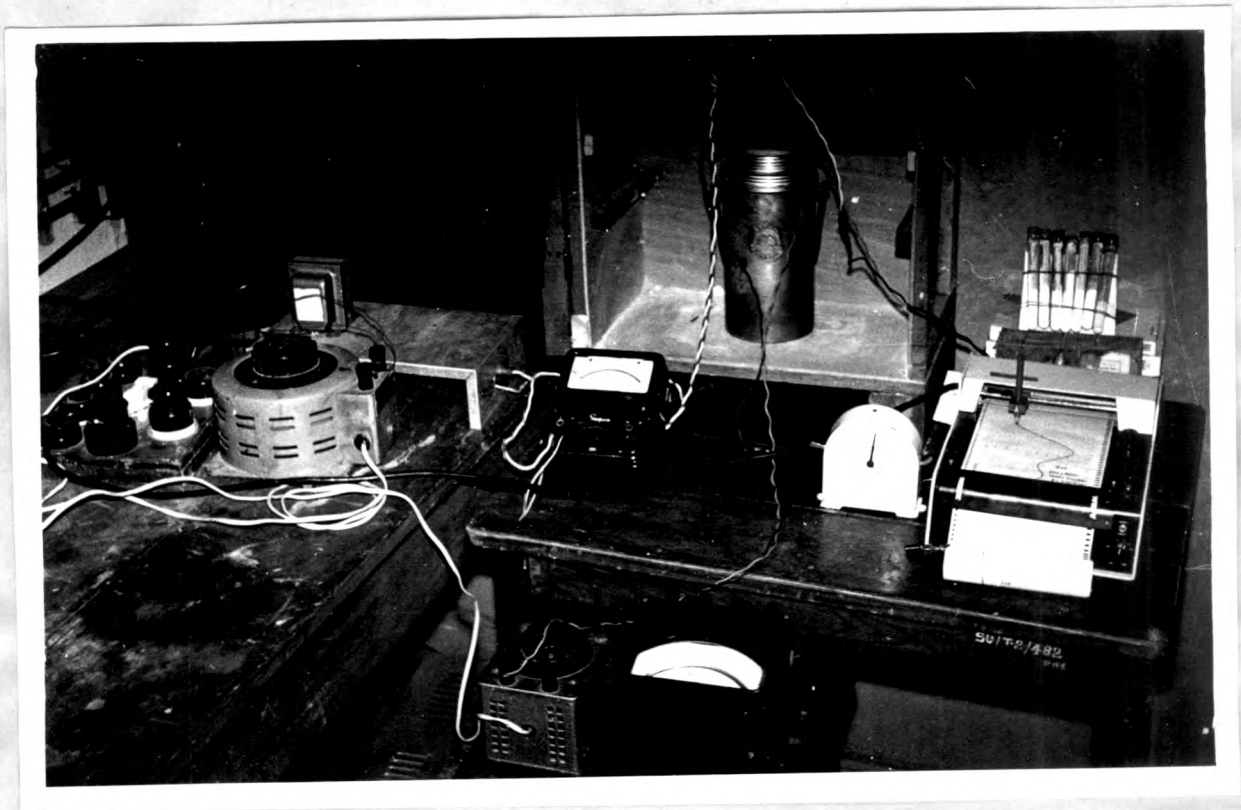


Fig. 2.4. Experimental set up for thermoluminescence studies.

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2.5 Photograph of Experimental Arrangement  
used for studying thermoluminescence