CHAPTER II

PREPARATION OF PHOSPHORS AND EXPERIMENTAL ASPECTS

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2.1 INTRODUCTION

Phosphors can be prepared in the following forms -

i) Single Crystal

ii) Thin Film

iii) Microcrystalline Powder.

It is not possible to grow a single crystal of alkaline earth sulphide, because it decomposes before they melt. These sulphide phosphors can be prepared in the form of thin film or microcrystalline powder.

In the present investigation, these sulphide phosphors are prepared in the microcrystalline powder form. To prepare the phosphor atom percentage method is used.

2.2 GENERAL CONSIDERATION DURING PREPARATION OF PHOSPHORS

2.2.1 Basic in-gradients of a Phosphor :

The method of obtaining phosphors in the powder form starts with a pure host material. Mix with a suitable flux along with an activator element added in the form of solution. The ingradients are mixed and the charge is finally fired at a suitable temperature for a pre determined period, in a suitable atmosphere.

a) The Host Material

The base material in which we add impurities so as to produce luminescnece is called as host material or matrix element. The transitions of electrons responsible for luminescence are within the range of band gap, for visible luminescence. The band gap for host material should be greater than 3 eV, the energy corresponding to extreme violet. Leverenz (1) prescribed the combination of elements of columns I, II, III B, IV A, V, VIA of the periodic table with those of columns VI B and VII B to satisfy the above consideration.

b) Activators :

Activator is one which provides localized energy levels, in the forbidden gap of the host material and which permits radiative transitions (2) Activators are classified into following groups :

i) Originator,
ii) Intensifier,
iii) Dominant and auxiliary activator,
iv) Killer
v) Co-activator,

i) Originator gives new emission lines or bands other than the intrinsic luminescence of the host lattice.

ii) Intensifier intensifies the intrinsic luminescence of host lattice.

iii) Auxiliary activator is a second activator used to enhance the intensity of activated phosphor. The first activator is called dominant activator and second one as auxilliary activator.

iv) Killers are the impurities which decrease the luminescnece intensity. These activators introduce energy levels between which radiative transitions are forbidden (2).

v) Co-activator provides balance of charge (3,4,) in phosphors activated by monovalent atom. It will also affect the colour of emission, its intensity and the defect structure of the phosphor material.

c) Flux :

These are the materials which when added to the base material, result in good phosphors (5,6), such salts are known as fluxes.

Flux plays different roles in different phosphors.

1) It serves as charge compensator (3, 4)

2) It promotes the crystal growth at lower temperature.

3) It enchances the rate of reaction at relatively low temp. (7, 8).

4) If facilitates the homogenous distribution of activator in the host material (7, 8).

5) Affects the luminescence intensity (9).

Generally effective fluxes are oxysalts and sulphates of sodium and potassium (10).

The role of flux as -

Charge Compensator

The role of flux (Na_2SO_4) as charge compensator in the enhancement of fluorescence intensity can be understood as follows :

The charge neutrality in the preparation of CaS:Bi:Dy or CaS:Mn:Dy phosphors demands the removal of three Ca^{2+} ions, to incorporate two Dy^{3+} (or Bi^{3+}) ions. This prompts Ca^{2+} ions vacancies in the host lattice. The host lattice defects produced during the preparation of phospphors due to such Ca^{2+} ion vacancies, restricts the entry of Dy^{3+} (or Bi^{3+}) activator ions in the lattice structure. This is because a good deal of energy is required to create a vacancy. The simultaneous doping of Na^+, the charge compensator ion from Na_2SO_4 along with Dy^{3+} (or Bi^{3+}) wipes the host lattice defects arising due to Ca^{2+} ion vacancies, bringing about an appropriate charge compensation (Pawar 1978)

$$2\ Ca^{2+} \longrightarrow Dy^{3+} + Na^{+}$$

$$2\ Ca^{2+} \longrightarrow Bi^{3+} + Na^{+}$$

This is according to charge compensation theory of Kroger and Hellingman (1949), such a charge balancing offers an easy way for the incorporation of trivalent activator ions without creating vacancies. The ionic radius of Dy^{3+} is more close to the ionic radius of Ca^{2+} ion of the host lattice compared to that of Bi^{3+} ion. Therefore Dy^{3+} ions enter the host lattice more easily than Bi^{3+} ions in the presence of charge compensator ion Na^{+}. The net effect of charge compensator is to increase the population of activator ions in the host lattice, increasing the number of luminescence centres which results into enhancement of fluorescence intensity of Na_2SO_4 added phosphors.

2.2.2 Prep~~e~~arative Parameters of Phosphors :

The luminescent properties of a phosphor depend upon number of parameters. They are as follows : -

a) Purity of ingredients

b) Grain size of ingradients

c) Reaction vessels

d) Firing temperature

e) Atmosphere of firing

f) Rate of cooling

g) Size of charge

a) Luminescent emission is very sensitive to the impurity atoms. Even a small trace of impurity elements may cause either activation or poisoning. Hence special care must be taken to mention the purity of ingradient and cleanliness through out the process.

b) Grain size of ingredients : The grain size will affect on the rate of solid state reaction and there by upon quality of the phosphor. To have good phosphor the solid state reaction must be uniform and continous. To have this, particles of very fine size with large surface to volume ratio are required (1, 11, 12).

c) Reaction Vessels :- The different reaction Vessels were tried i.e. Clay crucible and Combustion boats. But while using clay crucible the quality of phosphor found was not so good, and also some impurities were contributed by crucible material itself. and the colour of different phosphors prepared by using clay crucible was blackish. On the other hand the phosphors prepared by using combustion boats were good and having different colour shades for different conc. of activators. So that in the present work the use of clay crusible is avoided and combustion boates are used.

The combustion boats are chemically inert high refractiness and ability to with stand thermal and mechanical shocks.

d) Firing temperature:- The solid state reaction takes place only above certain desired temp. Hence charge must be fired for a suitable time at a suitable temp. (1) The temp. within the furnace must be uniform and constant. Variation in the temp, changes the crystal structure, which affects, the structural homogenity of the final product (1,12, 14). In the present work the firing temp. is kept 1000°c. for three hrs. This temp. was decided by referring study of earlier workers (Shahne G.S. and U.B.Kasture). They prepared phosphors at different temp. and found that samples prepared at 1000°c. were good.

e) Atmosphere of firing: Atmosphere of firing would affect on the character of phosphor (15). For example, hexagonal CdS when fired in neutral atmosphere, emits in the IR region, while it emits in green region after firing in H_2S atmosphere (16).

f) Rate of Cooling : - The rate of cooling would affect on luminescence brightness of phosphor, absorpiton and spectral emission. It also affects phosphorescence decay (17). Sudden cooling sometimes changes the colour of fluorescence (18). 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 temp. (19).

2.3 DETAILS OF METHOD FOLLOWED TO OBTAIN CaS:Mn:Dy ~~and~~ AND CaS:Bi:Tb ~~phosphors~~ : PHOSPHORS :

The sulphide phosphors are generally preparared in the micro-crystalline powder form by the method developed by Bhawalkar (20). This method involves heating an intimate mixture of the purified calcium ~~sulphide~~ sulphate and carbon together with required amount of activators and fluxes. The reduttion is carried out by heating the mixture at about 1000°C for three hours. The impurity atom replaces the host cation substitutionally. There are various methods to express the percentage of impurity in the material. In the method developed by Bhawalkar the concentration of activators is expressed in weight percentages of host, $CaSO_4:2H_2O$. However, the atom percent of impurity to the host cation will be a correct measure of effect of impurity in the luminescence process (21, 22, 23). Hence to express the concentration of activators, atom percentage method is adopted and calculations carried out are based on this method.

2.3.1 Method of calculation of the Bismuth percentage.

Molecular weight of $CaSO_4 : 2H_2O$ is 172.17 gms. Therefore, 172.17 gm of $CaSO_4 : 2H_2O \equiv$ N atoms of Ca, N being the Avagadros number.

$\therefore$ 1 gm of $CaSO_4 : 2H_2O \equiv \frac{N}{172.17}$ atoms of Ca.

Similarly, Molecular weight of $BiCl_3$ is 315. 33 gm.

$\therefore$ 1 gm of $BiCl_3 \equiv \frac{N}{315.33}$ atoms of Bi.

9 Now suppose one desires 0.1 percent of Bi in CaS. That means for every 1000 atoms of Ca the~~se~~re will be 1 atom of Bi.

$\frac{N}{172.17}$ atoms of Ca $\equiv$ 1 gm of $CaSO_4 : 2H_2O$

$\therefore$ 1000 atoms of Ca $= \frac{172170}{N}$ gm of $CaSO_4 : 2H_2O$, similarly N/315.33 atoms of Bi $\equiv$ 1 gm of $BiCl_3$

$\therefore$ 1 atom of Bi $\equiv \frac{315.33}{N}$ gm of $BiCl_3$

The proportion of $CaSO_4 : 2H_2O$ to $BiCl_3$ for 0.1% concentration of Bi in CaS is calculated as follows :

$\frac{172170}{N}$ gm of $CaSO_4 : 2H_2O \equiv \frac{315.33}{N}$ gm of $BiCl_3$

$$
\begin{aligned}
\therefore 1 \text{ gm of } CaSO_4 : 2H_2O &\equiv \frac{315.33}{N} \times \frac{N}{17270} \\
&\equiv \frac{315.33}{172170} \\
&\equiv 0.0018315 \text{ gm of } BiCl_3 \\
&\equiv 1.8315 \times 10^{-3} \text{ gm of } BiCl_3 \\
&\equiv 1.8315 \text{ mgm of } BiCl_3
\end{aligned}
$$

Thus 1 gm of $CaSO_4 : 2H_2O$ when added with 1.8315 mgm of $BiCl_3$, the percentage of Bi in CaS is 0.1% Depending upon the required conc. of Bi, corresponding ccs of prepared solution are added in the $CaSO_4 . 2H_2O$. Similar method is followed for other impurities.

2.3.2 Procedure followed in the preparation of phosphors

The method of preparation of sulphide can be divided into two stages.

A) First State : it involves the purification and preparation of basic ingredients.

B) Second Stage : It deals with preparation and firing of the charge at suitable temperature.

A) First Stage :

a) Purification of Calcium Sulphate - In this method calcium sulphate A.R. BDH is used as starting material. The maximum limit of impurities as labelled by manufacturer as,

Solubility in water	..	passes test
Free acid (as H_2SO_4)	..	0.01%
Free alkali (as $(Ca(OH)_2)$	..	0.01%
Chloride (Cl)	..	0.025 %
Iron (Fe)	..	0.002 %
Residue on ignition (700 °c)	..	79 - 80 %

b) Purification of carbon : A.R. grade E.Merck activated charcoal (Art 17505, B.N.G. 9 23861) was used as a reducing agent.

c) Activators : The activators Mn and Bi are used separately. They are added in the form of solutions of their salts ($MnSO_4.H_2O$) and Bi Cl_3. The weighed quantity of $MnSO_4.H_2O$ (L.R.grade) is dissolved in double distilled water. The required quantiy of solution was then added to give various concentrations of Mn and similarly the various conc. of Bi.

The second activators are Dy and Tb were also added in the form of solution of their chlorides. The weighed quantity of $DyCl_3$ (99.99%) pure) is dissolved in double distilled water. The required quality of solution was added to give various concentrations. Similarly $TbCl_3$ (99.90% pure), is also dissolved in distilled water and used for various concentration preparation.

d) Purification of Reaction Vessels : The combustion boats are used as reaction vessels. These boats were washed with double distilled water and dried. They were then fired at 1000°c. for three hours so as to remove any contaminating gases. It is also tested for their ability to withstand the thermal and mechanical shocks.

e) Flux : Phosphors were prepared with and without flux but phophors without flux shows very little luminescence and if we use the fluxes the luminescence increases. Hence samples were prepared with fluxes. The fluxes used are : -

1) Sodium sulphate anhydrous purified L.R.

Na_2SO_4 molecular weight 142.04 (B.N. 099/59/14091).

Minimum assay (99%).

Maximum limits of impurities

Loss on ignition	0.5%
Chloride (Cl)	0.01%
Nitrate (NO_3)	0.01%
Iron (Fe)	0.002 %
Potassium (K)	0.1 %

2) Sodium thiosulphate

$Na_2S_2O_3.5H_2O$ = 248.18 L R. LB. N. EL 0396 4908)

Minimum assay 99%

Maximum limits of impurities

Sulphate and sulphite (SO_4)	0.1%
Iron (Fe)	0.001 %
Potassium (K)	0.1 %

3) Sodium Fluoride

NaF M.H. 41.99 LiR.(9/49/28011)

Minimum assay (ion exchange) 97%

Maximum limits of impurities

Chloride (Cl)	0.02%
Sulphate (SO_4)	0.05%
Silica (SiO_2)	0.5%

Sodium thiosulphate was proved to be good flux(22).

B) Second Stage

a) Preparation of Charge

The charge was prepared by the following ways by taking the quantities as follows

i)	Calcium sulphate	5 gm.
ii)	Carbon	1.25 gm.
iii)	Sodium sulphate	0.25 gm.
iv)	Sodium thiosulphate	0.625 gm.
v)	Sodium fluorde	0.75 gm.

All these weighed qualities are mixed to form uniform mixture, The activator solutions were added in required amounts and then charge was again thoroughly mixed. It was then dried by using heating coil.

b) Firing of the Charge

The mixed and dried charge was packed in one of the purified combustion boat . A thin layer of purified carbon (in fixed quanity) was spread over the surface of the charge to keep the atmosphere reducing. The boat was then fired in an electric muffle furnace maintained at 1000°C. for three hours. After firing, the charge was removed from the furnace and immediately pulvarised while red hot. The reaction is -

$$CaSO_4 \cdot 2H_2O + 4C \xrightarrow{1000^\circ c} CaS + 4\,CO\uparrow + 2H_2O$$

since alkaline earth sulphides are hygroscopic; the prepared samples were immediately stored in sealed and numbered bottles.

2.3.3 Phosphor Preparation

In order to observe the effect of flux on the quality of phosphors trial samples were prepared without flux and with flux and their TL glow curves are recorded. From TL glow curves, it was observed that phosphors with flux give better luminescence than that without flux. Hence all phosphors were prepared with flux. Rare earths Dy, Tb, Sm, Nd are proved to be good activators in different lattices (21, 22, 23) . In order to find out suitable combination of Mn and rare earth, also Bi and rare earth, samples with different concentrations of activators are prepared. The TL glow curves were plotted and from this it was found that CaS:Mn:Dy (Rare-earth) gives better TL-glow and similarly CaS:Bi:Tb this combination is also giving good, better luminescance. In the present work, samples were prepared with optimum concentrations of activators (Mn and Bi) by changing the concentrations of rare earth (Dy and Tb), and their TL glow curves are plotted.

All the samples were prepared at 1000°C. and ~~all samples~~ were excited by uv source for equal amount of time and then again the luminescence was checked by visual inspection. It was found that with optimum concentration CaS:Mn:Dy and CaS:Bi:Tb gives maximum TL-glow. The details of the samples prepared are as shown in the table no.2.1 and 2.2

2.4 INSTRUMENTATION AND EXPERIMENTAL ASPECTS

Instruments required for preparation of phosphors and for study of phosphorescence decay, thermoluminescence and electroluminescence are listed below.

2.4.1 Instruments used for Preparation of Phosphors

a) Furnace

b) Heating Coil.

a) Furnace

Furnace used for preparation of present phosphor is Tempo Make, Model No. TL-58/58R/58HT.

The maximum temperature that can can be obtained is 1220°c. The furnace temperature is adjusted by an energy regulator, which controls the temperature by operating on a time cycle of 'ON' and 'OFF' thus varying the average energy input as desired. The electrical rating is 1.8 kw at 240 V. A.C. single phase. For measurements of temperature digital pannel is provided. Here the chromel Alumel thermocouple is used. Digital display helped in accurate adjustment of desired temperature.

b) Heating Coil

The electric coil is used to dry the prepared charge.

2.4.2 Phosphorescence Decay Measurement

A) Instruments used for PL Study :

Photoluminescence study was carried out at room temperature

The block diagram of experimental set up of PL is shown in fig. 2.1.

The experimental set up consists of -

1) Source of Excitation

2) Sample holder and

3) Intensity measuring unit.

a) Source of excitation

An Ultra-Violet Lamp (Germicidal Lamp, Model no. 415 T8) emitting ~~uv~~ UV rays of wavelength 253.6 nm. is used as excitation source. A stabilizer was used in conjuction with the lamp so as to maintain excitation energy constant.

b) Sample Holder

A Kanthal ~~S~~strip is used as sample holder, Kanthal is a mixture of (Fe 72%, Cr 23%, Al 3%, CO 2%) strip of 45 mm. length, 14 mm width and 0.025 mm. thick having central rectangular depression of about 0.5 mm. depth was used. The strip is fitted on two brass rods. The same strip was used to heat the samples in TL study. Below this strip a chromel Alumel thermocouple is spot welded to read the temp. This arrangement is fitted in ~~im~~ a wooden box. A window is opened in such a way that uv rays fall directly on the kanthal strip. The arrangement is shown in fig. 2.11

c) Intensity Measuring Unit

This unit consists of a photomultiplier tube, E.H.T. power supply and nanoammeter. The photomultiplier tube used was IP 21 made, by RCA. The arrangement of tube was such that its window directly faces the sample. The spectral response of tube is shown in fig. 2.9; The details of IP 21 photomultiplier tube as given below :-

Cathode area ..	1.9 cm^2
Spectral response ..	3000 - 6500A°
Cathode Sensitivity ..	20 - 40 uA/1 m.
Cathode darkcurrent ..	5×10^{-14}A.
Maximum overall voltage ..	1250 V.
Number of stages ..	9
Maximum voltage percentage	100 v.
Overall gain ..	2×10^6

Maximum current	..	0.1 mA
Anode dark current	..	0.1 μA
Length of tube	..	9.2 cm
Diameter of tube	..	3.3 cm.

The PM tube was operated at 925 volts D.C. obtained from E.H.T. supply. The specifications of model EHT-10 are given below :

Output	..	150v-1500v.contineously adjustable
current	..	2 mA maximum
Polarity	..	+ve or -ve as required.
Regulation	..	± 0.05% for 0 to 1 mA.
Stabilisation	..	0.02% for ± 10% change in mains voltage
Output meter	..	BPL panel meter 013 mm. scale with resolution of 15v/div.)
Connections	..	output through a Amphenol co-axial connectors on the front panel.
Protection	..	Procted fully against overload and short circuit by current limiting technique.
Power requirement	..	220V. A.C. ± 10%. single phase, 50Hz.

The out put of photomultiplier tube was recorded with the help of Nanoammeter (Model No. NM 21). The specification of nano-ammeter.

Applications	..	for low current measurement down to 10 pA,
Range	..	1nA, 10nA, 100nA, 1μA, 10 μA.
Polarity	..	Positive or negative through switch.
Meter	..	BPL moving coil meter with 100 mm. scale graduated in 100 divisions.
Accuracy	..	2%
Power	..	220 V. mains, ± 10% at 50 Hz.

B) Experimental Procedure

A fix quantity of sample (20 mgm) was placed on the Kanthal strip (sample holder). The sample was then excited by ~~uv~~ UV rays to a saturation level(5 minutes). After excitation uv lamp was switched off and immediately phosphorescence intensity was measured with the help of nanoammeter. The readings were taken after regular interval of time.

2.4.3 Thermoluminescence measurement.

A) Instruments used for TL-study

The photograph of TL set up is shown in fig. 2.3 and a block diagram is shown on fig. 2.4. The experimental set up consists of a source of excitation, sample heating arrangement and intensity measuing unit.

a) Linear temperature programmer

The sample holder (kanthal strip) was heated linearly, with the help of linear temperature programmer. The programmer provides constant heating rates which can be adjusted for any suitable value. It has a facility of programmed heatings, isothermal heating and auto heat off and hold arrangement for recoding temperature meter is provided. A typical plot of temperature versus time is shown in fig. 2.5.

b) Intensity measuring unit.

This unit is same as used in phosphorescence decay study (section 2.4.2).

B) Experimental Procedure

A fixed quantity of sample (20 mgm) was spread on the kanthal strip. It was excited by excitation source for 5 minutes. After excitation sample was allowed to decay for five minutes. After five minutes sample was linearly heated with the help of linear temp.programmer and intensity was recorded with the help of nanoammeter.

2.4.4 Instruments used for EL measurements

The photograph of EL-set up is shown in fig. 2.6 and block diagram of experimental set up is shown in fig. 2.7 . The wide band amplifier designed in the laboratory fig. 2.8 shows the photograph of wide band amplifier. The maximum out put of the wide band amplifier is about 1000 volts r.m.s. in the frequency range of 100 Hz to 10 KHz. The high voltage is achieved by using good transformer with minimum losses.

The experimental set up consists of (a) EL-cell (b) Brightness measuring system (c) source of excitation.

a) Electroluminescence Cell

Fig. 2.7 shows the schematic diagram of EL-cell which is used for EL measurement in the present study. The design of EL cell depends upon the phosphor, nature of applied voltage (a.c. or d.c.) the order of applied voltage and frequency and type of binder.

The EL-cell consists of a backelite sheet of size 7 x 5.5 x 0.3 cm. with a window of size 1.5 x 0.7 cm so that light emission from phosphor is viewed by PM tube. A conducting glass (500 ohm/cm^2) and 80% transperancy) of appropriate size and thickness is fitted to the backelite sheet and acts as one electrode. An aluminium plate of appropriate size is fixed to another backelite sheet and acts as second electrode. Both these plates are rigidly screwed. A thin layer of phosphor embeded in binder alongwith thin and uniform mica sheet are sandwitched between two electrodes. A mica sheet having high dielectric constant and sufficient breakdown strength excluded the possibility of carrier injection at the electrical constacts. For an appropriate choice of binder various binders like castor oil, silicon gelly, resin of araldite, gleserol were tried. The EL out put using silicon gelly was found to be maximum. Therefore, in the EL-study of phosphors, silicon gelly was choosen as appropriate binder.

b) Brightness measurement system

The intensity measuring unit is used in phosphorescence decay measurement (section 2.4.2). Same is used for brightness measurement.

c) Source of excitation

To excite the sample a multifunction generator along with a wide band amplifier was used. The multifunction generator (Vasavi type VF 013) has a frequency range of 1Hz to 100 KHz and maximum output voltage of 10 volts. The output of wide band amplifier (900 volts rms) is given to the EL-Cell. This voltage is measured on dual trace CRO (Vasavi Electronics Model No. VCS 26). By using 10:1 probe the high voltage is reduced by ten times and then it is measured. Peak to peak voltage is measured on CRO which is then converted into corresponding rms. value. The EL cell current is measured with the help of digital multimeter.

B) Experimental Procedure

A thin layer of phosphor embeded in silicon gelly was applied to an alluminium plate. A constancy in layer thickness was ~~me~~maintained by taking a fixed quantity of phosphor spreading it over a fixed area. A mica sheet (thickness 70 ± 10 μ) was placed over the phosphor layer. The air gap is avoided by taking enough care. The conducting glass was mounted over mica sheet.

By adjusting the screws the distance and pressure between inter electrodes was adjusted.

The prepared cell was placed on a platform and PM tube is mounted in such a way that light emitted by phosphor falls on the PM tube.

By applying high voltage to EL cell the phosphor was excited, and with the help of nanoammeter the out-put of PM tube was measured, The observations were carried out by varing voltage and keeping frequency constant.

2.4.5 Conductivity (Electrical Resitivity) Measurement

A) Experimental Set Up

The resistivity of the samples in the form of pellet is measured with the help of four probe set up (Scientific Equipment & Servioes, Roorkee). The specification and discription of the apparatus is given below :

a) Oven : - It is a small oven for the variation of temperature of the crystal, from room temperature to about 250°c.

b) Probe Arrangement :- It has four spring loaded probes coated with Zn at the tips. The probes are colinear and equally spaced. The Zn coating and individual spring ~~I~~ensures good electrical contacts with the sample. The probes are mounted in a teflon bush which ~~I~~ensure a good electrical insulation betwen the probes. The whole arrangement is mounted on a suitable stand and can be placed in the Oven. The leads are provided for current source and voltage measurements.

c) Four Probe Set Up :- It consists of -

i) Constant current source (ii) Electronic millivoltmeter.
iii) Oven supply

i) <u>Constant Current Source</u> : - This constant current source generator is specially designed for four probe set up to provide 100% protection against crystal burnout due to excessive current. The supply is ripple free and highly regulated. The variation in the current is achieved by a potentiometer. The current will not exceed the present limit even if the out put is short circuited.

ii) <u>Electronic Millivoltmeter</u> : -It has three measuring ranges which enable the accurate measurements. Readings are directly obtained on a precision moving coil meter. An impedance balance control enables the millivoltmeter to be used with source having wide range of impedances.

Range	..	30 mV, 100 mV, 300 mV, 1V, 3V.
Input impedance	..	1 mΩ
source imepdance	..	0 - 10 kΩ
Accuracy	..	3%
Short term drift	..	± 2 mocrovolt refered to input.
Long term	..	± microvolt refered to input
Power	..	220V, 50Hz, 7 Watt.

iii) <u>Oven Supply</u> :- It is step down double wound transformer with provision of low, medium and high current. Temperature of oven is recorded by thermometer.

d) <u>Nano-ammeter</u> :- To measure a current a nanoammeter (Model No.121) was used. The specifications are described in(2.4.2).

2.4.6 X-ray diffraction studies :

The x-ray diffraction pattern for typical samples (MD 39, MD 40, MD 41) are shown in fig. 2.10. The diffraction pattern was obtained from a diffractometer (PW 1840) from National Institute of Oceanography, Goa, Dept. GOD. Section. Using copper target (λa-1.54060, , $\lambda a2$ - 1.54438). The diffraction pattern was obtained in the range of 10° to 70°. The interplaner distance 'd' obtained from Bragg's Law and those calculated the formula for cubic system, viz.

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

and the (h,k,l) values of different planes and interplaner distance 'd' are listed in table 2. 4. From the study of x-ray diffraction pattern it is found that the nature of diffraction pattern both for doped and undoped phosphors is not different as such but the relative peak intensities are slightly changed and the peak positions remain unaltered in both doped and undoped phosphors as shown in fig. 2.10. This feature of the XRD confirms that the method of preparation of phosphor is quite systematic without any other parameter affecting the structure. This supports that the method of preparation is standardised the basic structure of the host material is not changed with the addition of small amount impurity (activator).

Also, the first peak in the XRD pattern suggests that the structure of the crystal may be orthorhombic, but the other values of (h,k,l) planes of the sample match with cubic structure. As such the structure seems to be a composite. This is probably because of the temperature treatment given to samples during preparation (1000°C. for three hours). This may be the reason which is indicative of the composite nature of the host possessing cubic and orthorhombic system. Further, the phosphors prepared being polycrystalline in nature this possibility can not be ignored. The 'd' values calculated for CaS are given in table 2.4

Table No.2.1 : Showing details of samples prepared : concentration of activator Mn is constant 0.1% and Dy is varied.

Sample No.	Percentage Concentration of Dy
MD-26	1%
MD-27	0.5%
MD-28	0.3%
MD-29	0.1%
MD-30	0.05%
MD-31	0.01%
MD-32	0.005%
MD-33	0.001%
MD-36	2 %
MD-37	0.0005%

Table No. 2.2 : showing details of sample prepared with concentration of activator Bi is constant 0.1% and Tb is changed.

Sample no.	Tb concentration
MD-18	1%
MD-19	0.5%
MD-20	0.3%
MD-21	0.1%
MD-22	0.05%
MD-23	0.01%
MD-24	0.005%
MD-25	0.001%
MD-34	2%
MD-35	0.005%

Table No. 2.3 : showing samples prepared

Sample No.	Prepared samples
MD-39	CaS pure
MD-40	CaS:Mn: (0.1%)
MD-41	CaS:Bi (0.1%)
MD- 42	CaS with flux

Samples with Dy 0.05%

Sample No.	Mn	Dy
MD-1	0.5%	0.05%
MD-2	0.1%	0.05%
MD-3	0.05%	0.05%
MD-4	0.025%	0.05%

Samples with Tb 0.05%

Sample No.	Bi	Tb
MD-5	0.5 %	0.05 %
MD- 6	0.1 %	0.05%
MD- 7	0.05 %	0.05 %
MD- 8	0.025 %	0.05 %

Table No. 2.4 : X-ray diffraction data of CaS (undoped).

Sr.No.	Angle (deg) 2θ	Angle θ (deg)	Width (deg)	I/Imax	h,k,l	'd'calculated A°)
1.	25.560	12.78	0.160	100	111 (1,1,1)	3.0654
2.	31.520	15.76	0.220	36.97	(2 0 0) 2,0,0	2.6548
3.	38.785	19.392	0.260	25.40	3,3,1	1.2181
4.	40.930	20.460	0.220	27.88	4,4,0	0.9386
5.	48.875	24,437	0.280	26.21	6,2,0	2.6548
6.	55.915	27,957	0.360	21.53	3,3,1	1.6009
7	55.965	27,987	0.440	—	2,2,2	1.5327

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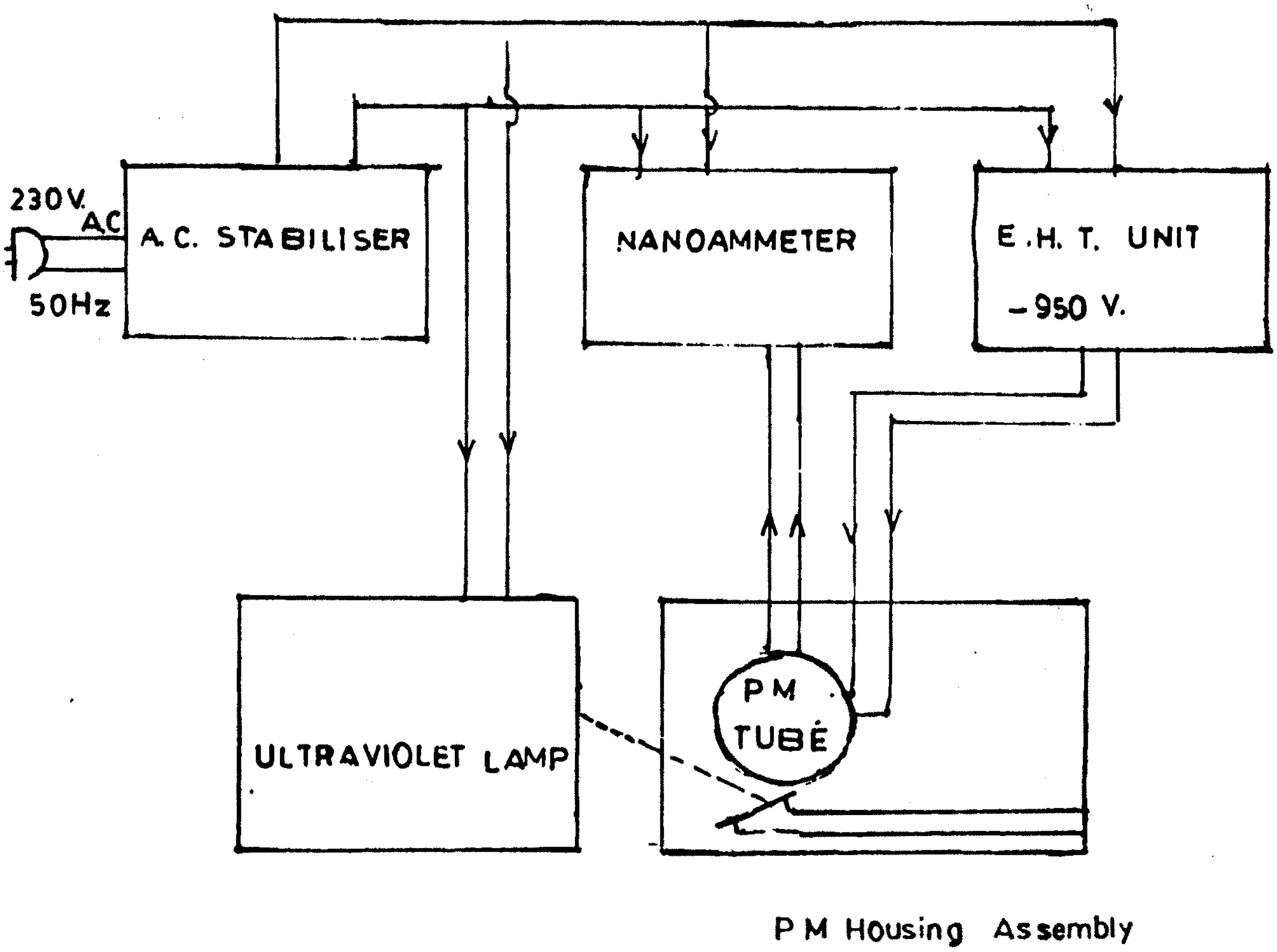
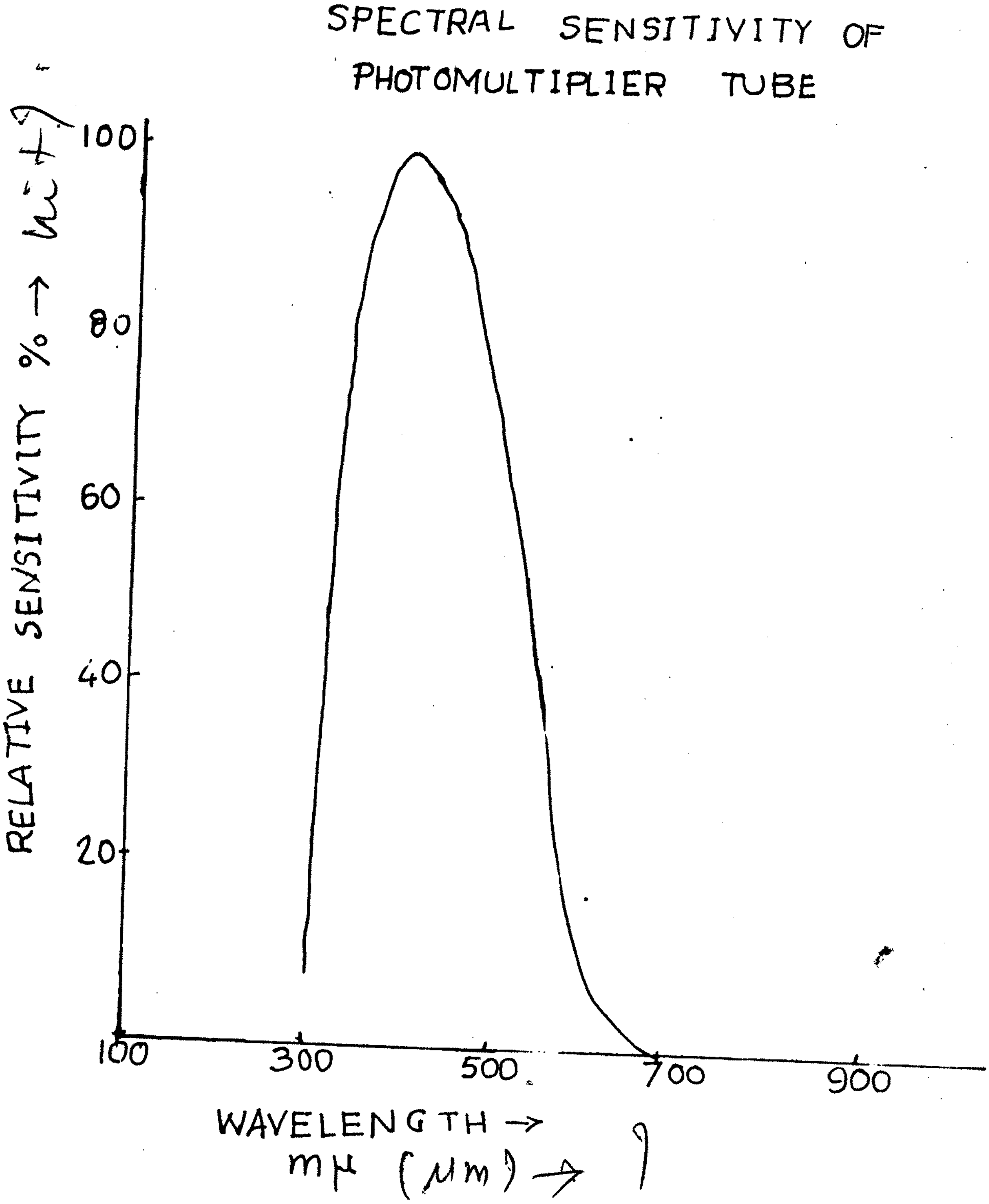


BLOCK DIAGRAM OF PHOTOLUMINESCENCE

SET UP

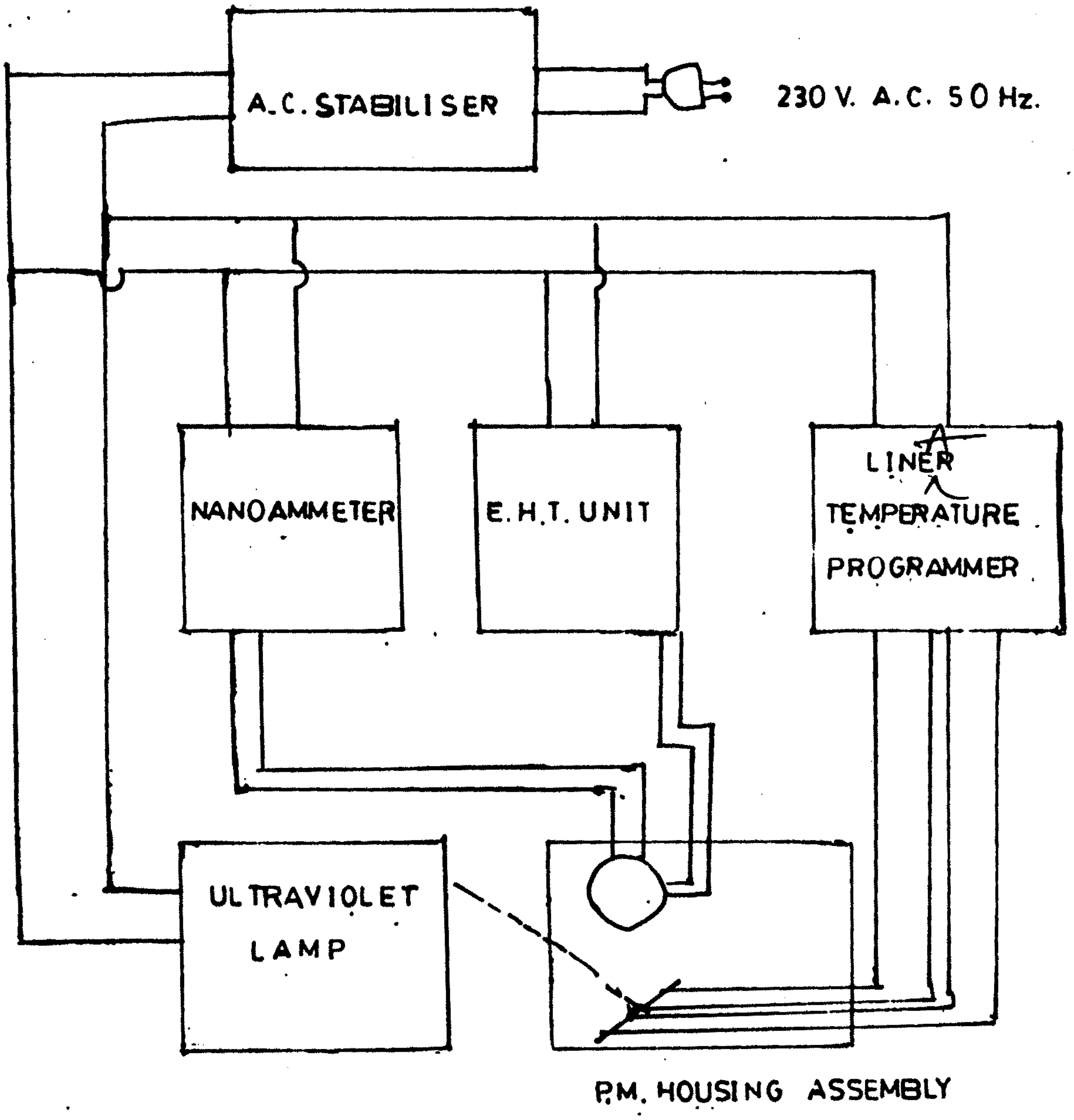
FIG. NO.: 2.1.



SPECTRAL SENSITIVITY OF PHOTOMULTIPLIER TUBE

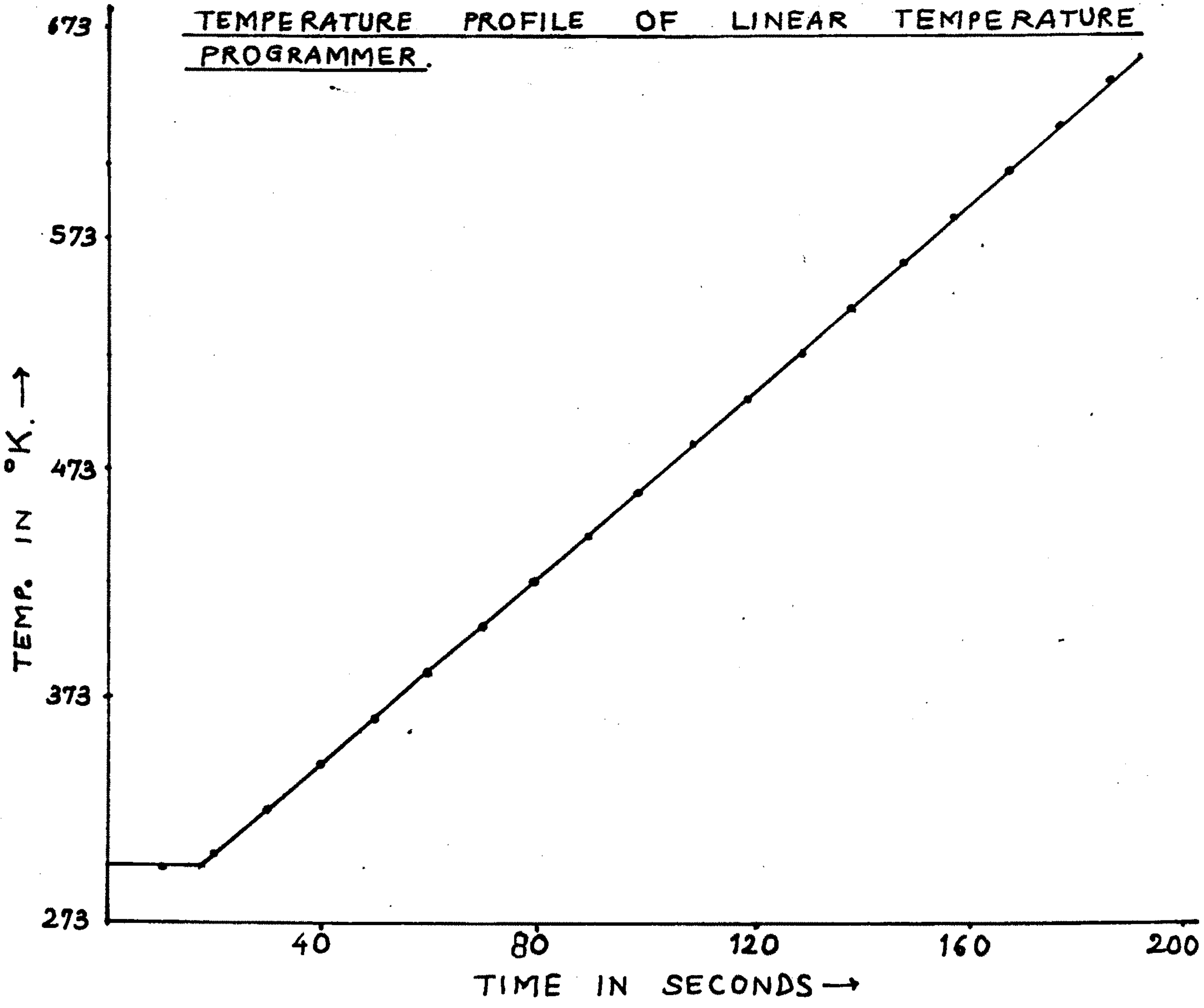
FIG. NO. : 2·2.

TL SET UP (Fig No 2·3)



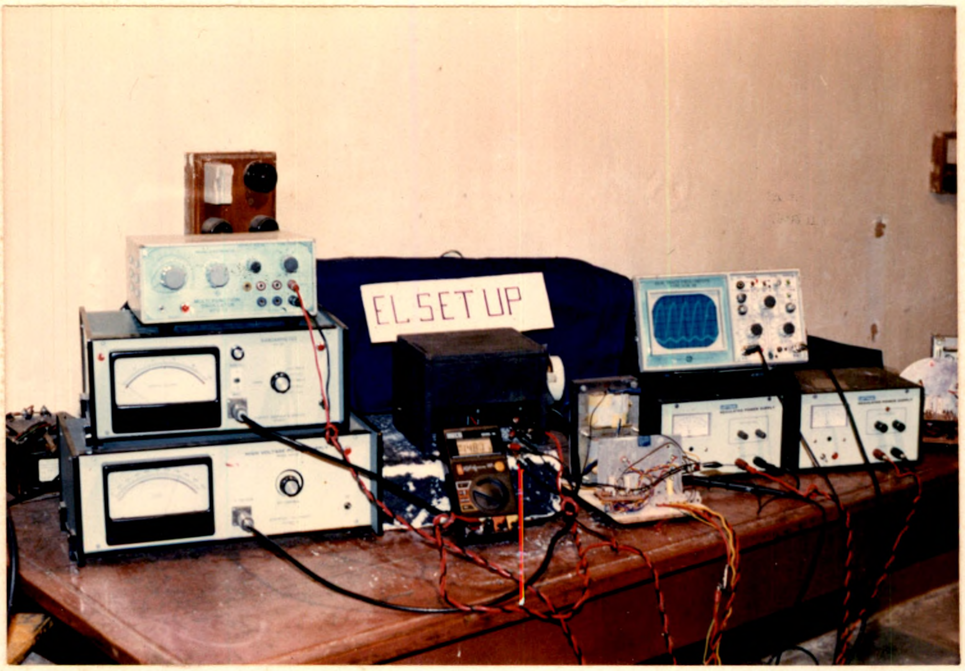
BLOCK DIAGRAM OF T. L. SET UP

FIG. NO.: 2·4.

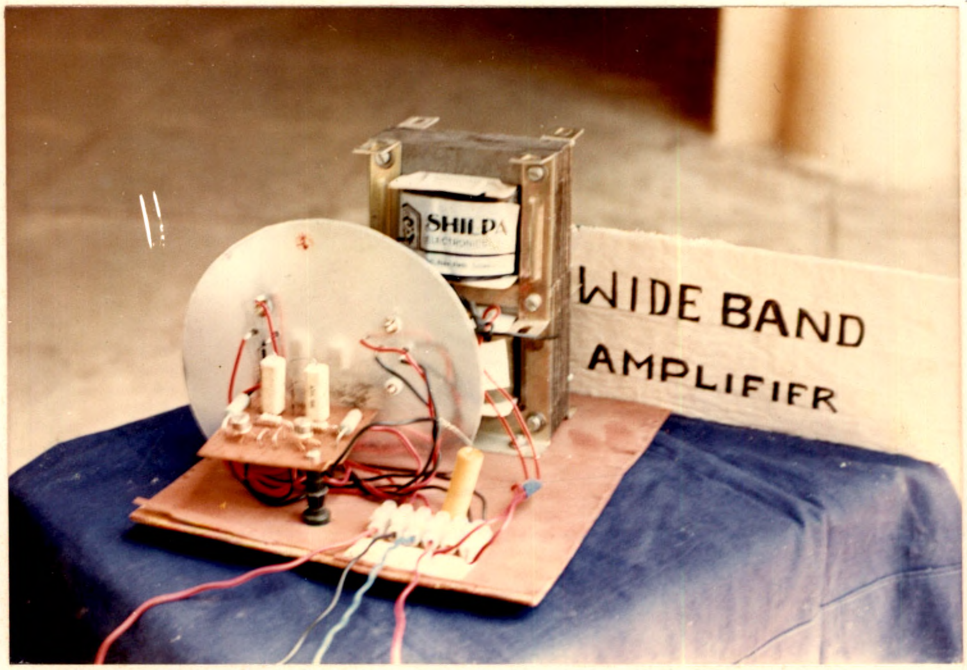


TEMPERATURE PROFILE OF LINEAR TEMPERATURE PROGRAMMER.

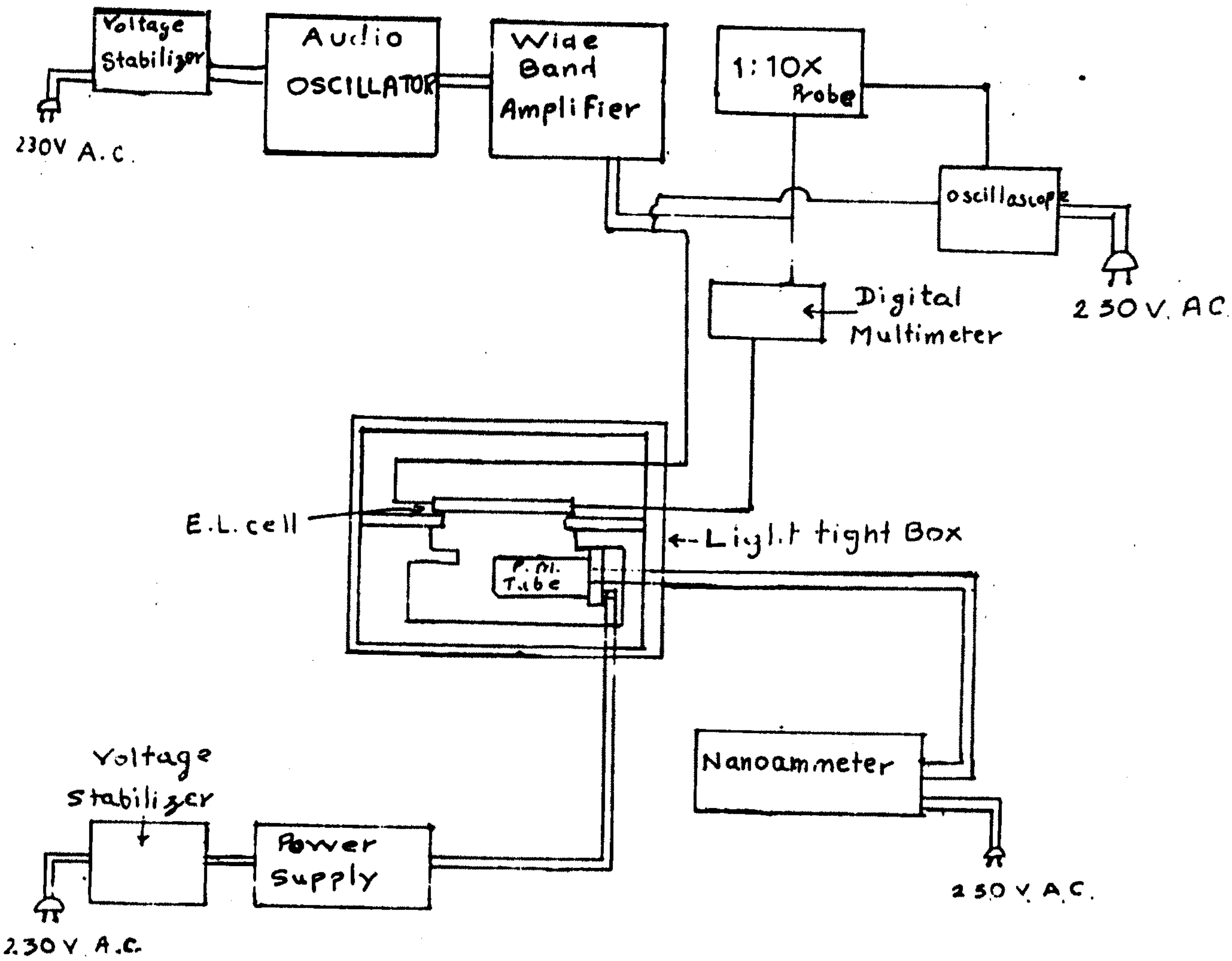
FIG. NO.: 2·5.



EL SET UP (Fig No. 2·6)

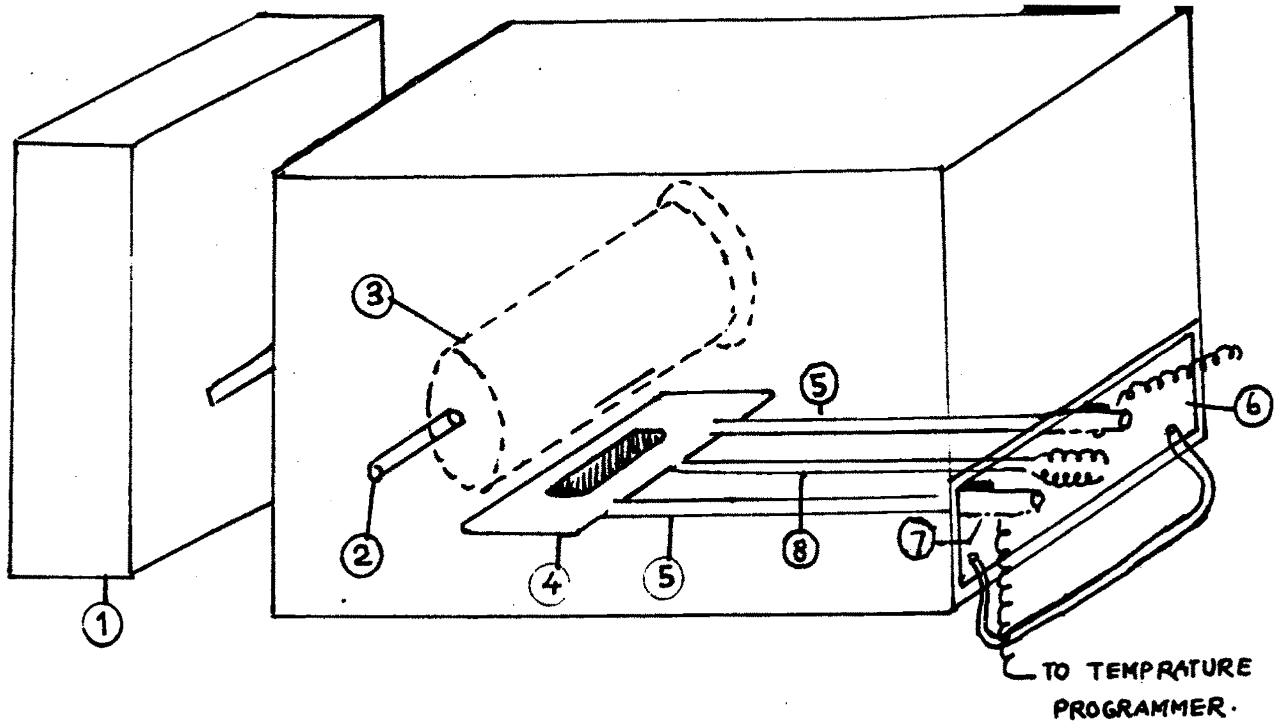


WIDE BAND AMPLIFIER (Fig No. 2·8)



BLOCK DIAGRAM OF EL SET UP

FIG. NO.: 2.7.



1 — UV SOURCE IN CASE.
2 — SLIT.
3 – P.M. TUBE.
4. — KANTHAL STRIP.
5 — BRASS ROD.
6 – DRAWER.
7 – EBONYTE TERMINAL.
8 – THERMOCUPLE.

PHOTOMULTIPLIER HOUSING ASSEMBLY

FIG. NO.: 2·9

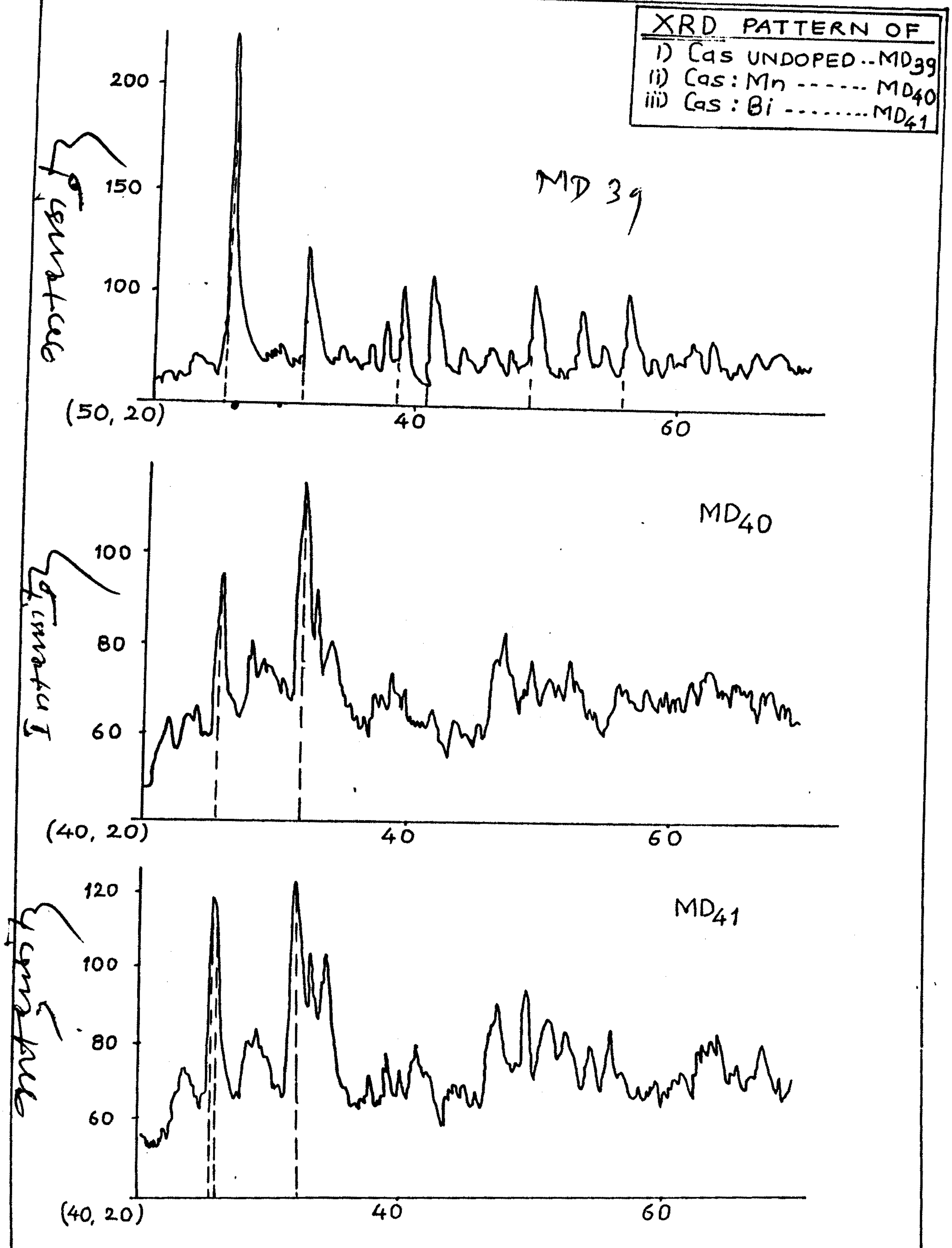
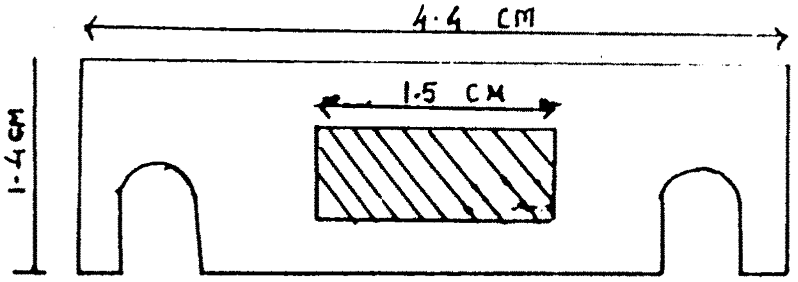
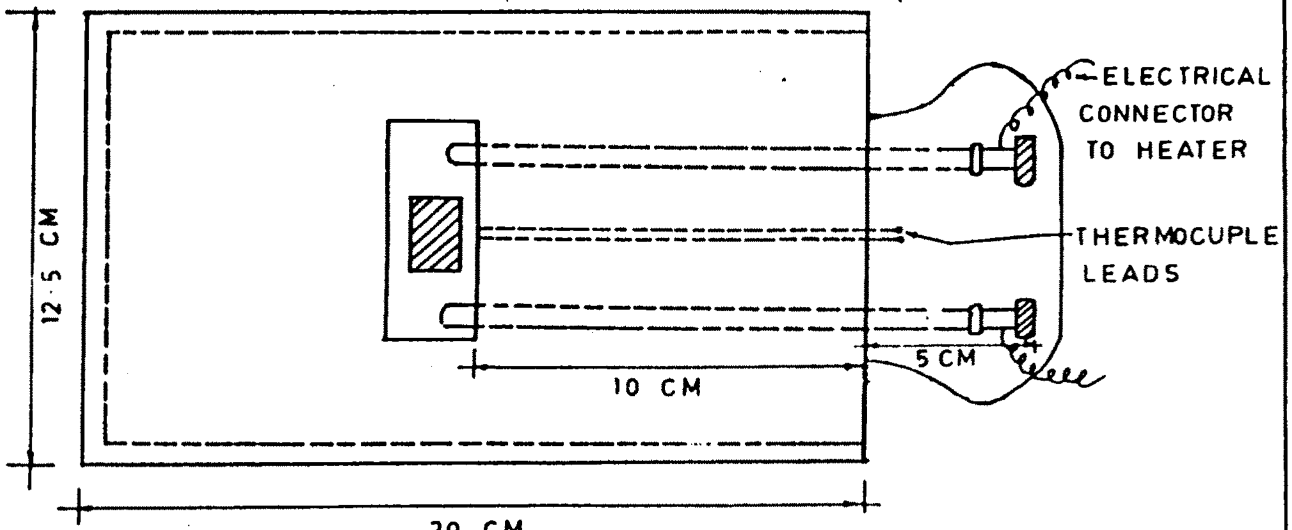

XRD PATTERN OF
i) CaS UNDOPED .. MD_{39}
ii) CaS : Mn ------ MD_{40}
iii) CaS : Bi .... MD_{41}
MD 39
200
150
100
(50, 20)
40
60
MD_{40}
100
80
60
(40, 20)
40
60
MD_{41}
120
100
80
60
(40, 20)
40
60

FIG. NO.: 2·1[illegible]



KANTHAL STRIP



DRAWER ASSEMBLY

FIG.NO:2·11