CHAPTER II

PREPERATION OF PHOSPHORS
INSTRUMENTATION AND
EXPERIMENTAL

C H A P T E R - II

PREPERATION OF PHOSPHORS, INSTRUMENTATION AND EXPERIMENTAL

2.1 PREPERATION OF PHOSPHORS :

Phosphors can be prepared as per the requirements

Single crystal,
Thin film,
and Microcyystalline powder.

It is observed that the phosphors of alkaline earth sulphide type decompose before they melt, and hence it is difficult to obtain such phosphors in crystalline form. However some succes in making thin film of such phosphors has been achieved.

1), also polycrystalline materials can be prepared.

In the present study, the phosphor is taken in microcrystalline form, There are several methods of preparation of CaS phosphor. The luminescent characteristics of prepared phossphor depend on the atmosphere of firing, firing temperature and rate of cooling.

2.1.1 General considerations for phosphor synthesis :

Since in the present study, the phosphors are prepared in micro-crystalline powder form, the preparation of the same is given in details :

A) Basic ingredients of phosphor :

To prepare the phosphor in the powder form following method is adopted. At start a pure host material is taken.

It is then mixed with a suitable flux along with the activator, element preferably in the form of solution. The ingradients are then thoroughly mixed to form a charge. The charge is then finally fired at a suitable temperature for a predetermined period in a suitable atmosphere.

a) The host material :

For luminescence in visible range the host material or the matrix crystal must have the band gap more than 1.5eV. Since there are the energies of photons corresponding to extreme red and voilet regions of the visible spectrum.

b) Activators :

The activator is one which provides localized energy levels in the forbidden energy gap of an insulator or semiconductor and that permits radiative transitions. According to the role performed, activators are classified as :

1) Originator : The activator which gives rise the new emission lines or bands other than the intrinsic luminescence of the host lattice.

2) Intensifier : It intensifies the intrinsic luminescence of the host lattice.

3) Dominant and auxillary activators : Some times the intensity of the singly activated phosphor is enhanced by adding a second activator. The first and the second activators are then referred as dominent and auxillary respectively.

4) Killer : It is one which inhibits the luminescence(2).

5) Coactivator : It provides the balance of charge in phosphors, activated by monovalent atoms. It is one which causes the luminescence and also enhances it which is produced by another activator. It may also affect the colour of emission, intensity and defect structure of the phosphor material.

6) Flux :

Flux material or fluxes are the salts which when added to the base material result in good phosphor. (3, 4). These fluxes play different roles in different phosphors. However it is generally observed that the fluxes,

1) enhance the rate of reaction of relatively lower temperature (5,6).

2) facilitate the incorporation of activator and its homogenous distribution in host lattice (5,6).

3) Promote the crystal growth at lower termperature.

4) Serve as charge compensator.

5) affect the luminescent intensity (7).

Generally the effective fluxes are oxysalts and sulphates of sodium and potassium (8)

B) Preparative parameters of phosphors :

The lumineascent properties of phosphor are found to depend on number of parameters during the synthesis process. Some of the important ones are as follows :

a) Purity of ingradients : Since the luminescence emission is very sensitive to the impurity atom a slight trace of any foreign element (10^{-6}gm) may cause either activation or poisoning. Hence purity of ingradients in preparing the phosphors is an important consideration. Therefore it is very essential to have clean laboratory and a special care is to be taken to maintain purity of ingredients throughout the process.

b) Reaction Vessels : The reaction vessels (crucibles) must possess properties such as chemical interteness, purity, high refractoriness and ability to withstand thermal and mechanical shocks.

c) Firing temperature and its duration : To get the optimum brightness, the phosphor is reduced to be fired for a suitable time at an appropriate temperature, empirically determined for each system of phosphor (3). Also the temperature within the heating chamber of the furnace is expected to be uniform and constant. Variation in the temperature of the furnace some times totally changes the crystal structure of the phosphor and thus effects the structural homogenity of the final product. (9, 10).

d) The atmosphere of firing : It is observed that the atmosphere in which phosphor ingradients are fired has a pronounced effect on the character of phosphor 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_2S atmosphere, also some phosphors which do not show electroluminescence responance when fired in H_2S atmosphere, Also some phosphors which do not show electroluminescence responance when fired in H_2S atmosphere, becomes electroluminescence when fixed in the presence of water vapour. (11).

e) Grain size of ingradients : The grain size of the basic ingredients required for phosphor preparation has a marked effect on the rate of solid state reaction and consequently the quality of the Phosphor. To have a good quality phosphor, the solid state reaction must be uniform and continuous. This is 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. (12, 13).

f) Rate of cooling : In general the rate of cooling affects the luminecent properties, such as absorption, spectral emission and the brightness of phosphor. It ...often affects phosphorescencent decay also (16). Sudden cooling some times changes the colour of fluorescence (17).Slow cooling rate helps in uniform distribution of imperfections throughout the phosphor. (18) . Also rapid cooling preserves the valence state prevalent at high temperature.

g) Size of charge : The size of the charge often affects the homogenity of the final product. (19). Preparation of phosphor in large quantities may involve different rates of heating due to poor conductivity of the charge. The mixture which is just in contact with the walls of its container will attain furnace temperature earlier than the central portion. This forms temperature gradient within it. This effect may be minimised by taking small quantity of mixture each time.

2.1.2 : Preperation of alkaline earth sulphate phosphors :

The most general method for preparing alkaline earth sulphate phosphors is suggested by wells (14). In this method a mixture of alkaline earth carbonates, oxides or hydroxides with suitable flux such as $Na_2 SO_4$, NaCl etc. together with a desired at a temperature above the melting point on the flux, is fired. In this process simultenous reduction and activation of phosphor takes place.

Several other methods are also available, in which first the different alkaline earth compounds are converted to the respective sulphides by heating them in the atmosphere like H_2, H_2S, NH_3, CS_2 etc. and then are activated with different impurities there by making reduction and activation by two different processes.

2.1.3 : Details of method followed to obtain $CaS:RE_1:RE_2$:

The sulphide phosphors in the microcrystalline powder form are generally prepared by method developed by Bhawalkar (15) . This method involves heating known mixture of pyrified calcium sulphate and carbon together with required amount of activators and fluxes. The reduction is carried out by heating the mixture at about 900°c for three hours. The impurity atom replaces the host substitutionally . There are various methods of express the percentage of impurity in the material. In the method developed by Bhawalkar the concentration of activators is expressed in weight percentage of host. How ever the atom percentage of impurity to the host cation will be a correct measure of effect of impurity in the luminescence process (19,20,21). Hence to express the concentration of activators atom percentage method is adopted and calculations are based on this method.

Above method is described briefly for CaS:Sm complex. Molecular weight of $CaSO_4 : 2H_2O$ is 172.17 therefore 172.17 gm. of $CaSO_4 \equiv N$ atom of of Ca, and N being Avogadro's number.

$\therefore$ 1 gm of $CaSO_4 : 2H_2O \equiv \frac{N}{117.17}$ atoms of Ca

Similarly molecular weight of $SmCl_3$ is 256.6

$\therefore$ 256.6 gm of $SmCl_3 \equiv$ N atoms of Sm

$\therefore$ 1 gm of $SmCl_3 \equiv N / 256.6$ atom of Sm

Now suppose one desires o.1 percentrage of Sm in Cas that means for every 1000 atoms of Ca there will be 1 atom of Sm.

$N/172.17$ atoms of $C \equiv$ 1 gm $CaSO_4 : 2H_2O$

$\therefore$ 1000 atom of Ca $\equiv \frac{172\ 70}{N}$ gm of $CaSO_4 : 2H_2O$

Similarly $\frac{N}{256.6}$ atom of Sm $\equiv$ 1 gm of $SmCl_3$

$\therefore$ 1 atom of Sm $\equiv \frac{256.6}{N}$ gm of $SmCl_3$.

The proportion of $CaSO_4 : 2H_2O$ to $SmCl_3$ for 0.1 % concentration of Sm in Cas is calculated as follows :

1,72,170 gm of $CaSO_4 : 2H_2O \equiv \frac{256.6}{N}$ gm. of $SmCl_3$.

$$\therefore \text{ 1 gm of } CaSO_4 : 2H_2O = \frac{256.6}{N} \cdot \frac{N}{172170}$$

$$= 1.490 \times 10^{-3} \text{ gm of } SmCl_3$$

$$= 1.\ 49 \text{ mgm of } SmCl_3.$$

Thus 1 gm. of $CaSO_4:2H_2O$ when added with 1.49 m gm. of $SmCl_3$, the percentage of Sm in CaS is 0.1 %. Depending upon the required concentration of Sm corresponding cc of prepared solution are added in the $CaSO_4:2H_2O$ similar methods are followed for other impurities.

A) Purification of Gypsum :

Calcium sulphate (dehydrated) of BDH grade was used to obtain host materials which is made by Thomos Bunkar, London, Molecular wt. is 172.17 gm. having purity 99%.

The maximum limit of impirities as labelled by manufacturer are calcium sulphide (Dihydrated) $CaSO_4: 2H_2O$ = 172.17. (Molecular wt.).

Minimum assy 99.0 %

Maximum limits of impurities.

Hydrochloric acid insoluble matter	---	0.01 %
Free acid (H_2SO_4)	-----	0.01 %
Carbonate (CO_3)	----	0.1 %
Chloride (Cl)	----	0.002%
Nitrate (NO_3)	----	0.002%
Arsenic (As)	----	0.0004%
Iron (Fe)	----	0.0005%
Lead (Pb)	----	0.001%
Magnesiom (Mg)	----	0.01%
Potensiom (K)	----	0.01%
Sodium (Na)	----	0.01%

B) Purification of the Carbon :

A.R. grade carbon was used as a reducing agent. To make the carobon free from other impurities, it was boiled with excess of double distilled water for about half an hour and then filtered. The resudue was then subsequently washed with hot double distilled water in repetition. Finally it was dried over a hot plate at 70° and stored in clean bottle.

C) Activator :

The activator Sm for the first series and Dy for another series of phosphors are used in the solution for m .

D) Co-activator :

The co-activator or second activator Nd used for first series and Tb used for second series by atom % method. Second activators are taken in the form of solution.

E) Purification of reaction vessels :

Clay crucible were used as reaction vessels. These were soaked in 13% nitric acid for two hours to ensure the complete convertion of contaminating impurities into water soluble nitrates. These were washed repeatedly with distilled water. The crucibles then fired at 900° c for one hour to remove any contamination of other gases. This also tested their ability to withstand the thermal and mechanical shocks.

F) **Fluxes Used :**

The samples were prepared both with and without fluxes. It was observed that the addition of the fluxes enhances the luminescence output. The fluxes used are -

1) Sodium sulphate (An-hydrous) Howard make.
2) Sodium thio-sulphate - Emark made.
3) Sodium fluoride - BDH variety.

Maximum limit of impurities as laballed by manufacturer are given below :

1) $Na_2S_2O_3 : 5H_2O$ sodium thio u ulphate L.R.

Minimum assay 99% (MW = 248.18)

Maximum limit of impurities

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

2) Sodium Fluoride

NaF MW 41.99

Minimum assay 97 %

Maximum limit of impurities

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

3) Sodium sulphate unhydrous pyrified (L.R.)

MW (42.04) minimum assay 99 %

Maximum limit of impurities

loss on ignision 0.5 %

Chloride (Cl) ----- 0.01 %

Nitrate (NO_3) ------0.01 %

Iron (Fe) ------0.01 %

Potassium (k) ----- 0.1 %

G) <u>Preperation of Charge</u> :

The charge was prepared by taking the following quantites with their respective weights.

1)	Calcium sulphate	.. 5 gms.
2)	Carbon	.. 1.25 gms.
3)	Sodium sulphate	.. .25 gms.
4)	Sodium fluoride	.. .75 gms.
5)	Sodium thiosulphate	.. .625 gms.

RE_1 and RE_2 were added by atum percentage method.

All these weighed quantities are thouroughly mixed to form uniform mixture. The activator solution is then added in requisite amount along with a few drops of alcohol. Again the charge was throughly mixed. The addition of few drops of alcohol facilited dispersion and diffusion of activator throughout the charge. It was then allowed to dry at 70^{o} over the hot plate.

H) <u>Firing of the charge</u> :

The mixed and dried charge was throughly grinded to a fine particle size and then packed in one of the prefired crucibles. A thin layer of the purified carbon (in fixed quantity) was spread over the surface of the filled charge to keep the atmosphere reducing. The 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 furnace maintained at 900^{o}c for three hours. After firing, the charge was removed from the furnance, and immediately pulvarised when it was red hot. The reduction of calcium sulphate into into calcium sulphide occur according to the reaction.

$$CaSO_4 : 2H_2O + 4C \longrightarrow Cas + 4\ Co + 2H_2O \quad \ldots(2.1)$$

Since alkaline earth sulphides are hydroscopic, the prepared samples were immediately stored in sealed and numbered bottles.

2.2 PREPARED PHOSPHORS :

The nature of activator RE (Nd, Sm, Tb, Dy) are decided by taking equal % of RE (.05%) in the host material. By visual inspection under uv excitation and TL glow curves fig.(4.2)above mentioned rare earth can act as an activator. Nature of Co-activator or second activator is decided by taking equal % of activator (RE_1) and equal % of co-activator (RE_2). These samples were excited under uv source. According to PL decay second activator was decided. It was found that activator , Second activator ($RE_1 : RE_2$) Sm : Nd and Dy : Tb is best combination in host material. By changing % of activator keeping % of second activator constant and vice-versa phosphor series was planned.

To observe the initial contribution in CaS undoped, CaS phosphor was prepared. Fig. 4.2 exibits that there are impurities in CaS phosphors as initial contribution.

Effect of flux in solid state reaction was also verified by preparing samples without flux, and with NaF , Na_2SO_4 and with NaF,$Na_2S_2O_3$ mixture.

It was observed that mixture of three fluxes Naf, Na_2SO_4 and $Na_2\ S_2\ O_3$ gives good quality of phosphor. The details of concentration of activator- Co-activator (Second activator) is given in table 2.1 and 2.2.

How ever KD (21) and KD (31) behaves as good phosphors in the prepared series. A simple chemical test was carried out to confirm formation of sulphide. Phosphor when treated with dilute HCl liberates H_2S gas, which was detected by lead acetate paper, which turns silvary black.

($Cas + 2\ HCl \longrightarrow CaCl_2 + H_2s$)

But calcium sulphate does not envolve H_2S gas

$CaSO_4 + 2HCl \longrightarrow CaCl_2 + H_2SO_4$

X- Ray diffraction analysis of synthasised phosphor :

The X-Ray diffraction pattern for a typical sample KD 21 is shown in fig.(2.1). The X-ray diffraction pattern was obtained from Philips X-ray diffractometer, cu target , $\lambda = 1.542$ A.U. Model no. (PW 1710) from USIc Shivaji University, Kolhapur. The diffraction patterns consist of 28 peaks in the range between 20°to 120° . By considering predominent plane for cubic structure, the value of lattice constant found is 9.4409 A.U. The imterplaner distance 'd' obtained from Braggs law and those calculated by using the formula $d = \frac{a}{h^2 + k^2 + l^2}$ are in good agreement. This suggest that phosphor has cubic structure, a, d and (h,k,l) values are listed in table (2.3).

2.3 INSTRUMENTATION AND EXPERIMENTAL :

The details of the Experimental techniques followed in phosphorescence decay, thermoluminescence electric conductivity and Electro-luminescence are as follows :

2.3.1 - Experimental-set up for preparation of phosphors :

Oven :

The charge prepared in the form of paste is dried in the oven. The oven used in Hot air oven, universal memmer type. It has a finishing like refrigarator bearing model no.MOD 102. the chember inside is made of Aluminium and the size of the Oven is 18" x 18" x 18".

Hot Plate :

Thermostatically controlled rectangular hot plate was used for drying A.R. grade charcoal. The rectangular plate has dimensions 10" x 12".

Muffle furnace :

Furnace used for preparation of phosphor is Tempo-make crucible furnace (Refractory type, Model No.TI 57 R). The maximum temperature that can be obtained is 1150°c. The electrical rating is 1.4 KW at 240 V.A.C. single phase and the temperature control is by energy regulator relay by adjusting its on and off duty cycle. The working chamber furnace is 10 cm. in diam. having depth 18 cm. The temperature measurements are done with pyrometer. Here a chromel-Alumel thermo couple is used.

2.3.2- Experimental set-up for phosphorescence Decay measurements:

Experimental set up for measurement of phosphorescence decay is shown in photograph fig.2.2(a). The housing assembly of photomultiplier tube is fabricated in the laboratory. The phosphorescence decay measurements were carried out at room temperature. The block diagram of the set up is shown in fig.(2.3) The arrangement consists of :

a) Excitation source, (b) p.m. housing assembly (c) p.m.tube
d) E.H.T. supply unit (e) Nanometer, (f) Stabilised supply for all these units.

a) Excitation Source :

For photoluminescince study, the excitation source used was a germicidal lamp giving ultraviolet rays typically of the wave length 253.6 nm (15 watts) (model no.G 15 T 8). The tube is operated at 230 V.A.C. having wattage 15 w.a slit having dimension 4 cm x 1 cm, is made through which the samples are excited.

b) Photomultiplier tube housing assembly :

A systematic diagram of pm housing assembly is shown in fig(2.4). A black coloured wooden box having dimensions 22x15x16cm. is taken. A slit (width 5 cm.x1 cm.) is grooved to it making an angle of 45° so that the light is incident directly on the sample. A drawer with dimension 20 x 12.5 x 4 cm. has two conducting brass rods attached as shown in fig. 2.4(a). A kanthal strip is attached to one of these rods while other having ebonite terminals for the external connections. This arrangement forms the sample holder. pm tube with its slit fully open is mounted above this sample holder. This can be seen from fig.2.4.

Kanthal strip :

Sample holder consits of a Kanthal strip which is a mixture of (fe 72 % , Cr 23 %, Al 3 %, CO 2 %). The strip having length 74 mm and thickness 0.025 mm. The width of it is 45 mm and has a central rectangular depression of about ½ mm The Kanthal strip is used for holding the sample for PL studies TL study is also made with the same strip. A spot welded chromal Alumel thermo-couple is attached to read the temperature. The systematic diagram of kanthal strip is shown in fig. 2.4(b). It is worth mentioning that the pm tube housing assembly is fabricated in Research laboratory (Deptt. of Physics) Dayanand College, Solapur.

C) <u>Photomultiplier tube</u> :

The intensity of the luminescent light is measured with the help of photomultiplier tube IP 21 made by RCA. The Photomultiplier tube was operated at 900 v. dc supply obtained from EHT unit. The amlification of the tube was 10^6.

The out put from the photomultiplier tube is a linear function of incident light. The deviation from linearity are about 3% for the variation of the light between 10^{-6} and 10^{-3} lumen. The details of performanance of the above tube is given below :

Cathode area : 1.9 cm^2
Spectal responance : 3000 - 6500^{o} A
Cathoda sensitivity : 20-40 µA/lm.
Cathode dark current : 5 x 10^{-14} A.
Maximum over all volage: 1250 v
Number of stages : 9
Maximum voltage per stage : 100 v
Over all gain : 2 x 10^6
Maximum current : 0.1 MA.
Anode dark current : 0.1 µA.
length of the tube : 9.2 cm.
Diameter of the tube: 3.3. cm.

d) E.H.T.Supply unit for p.m. tube :

High d.c. voltage required to operate the photomultiplier tube was given from an E.H.T.power supply unit (Model EHT 10).

The power supply consists of a stable power oscillator whose out put is controlled by an input signal. A step up transformer is used to boost the out put of this oscillator out put is compared with a high stability temperature compensated reference and the error signal is used in the feed back path to control the out put of oscillator.

Specification of Model E.H.T. 10 :

Out put voltage	:	0 v+-1500 v. continuously adjustable.
Curent	:	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 .
Out put meter	:	BPL panel meter (113 mm scale) with a resolution of 15 V/div.
Connections	:	Output through a Amphenol Coaxial connectors on the front panel.
Protenction	:	Protected fully against over load and short circuit by current limiting technique.
Power requirement	:	220 V.A.C. ± 10 % (single phase 50 Hz.)

e) Nanoammeter :

The out put of the photomultiplier tube is recorded with the help of Nanoammeter. A nanoammeter (model Nm - 121) was used to record the out put. The unit has a facility to record a current deep down to 10 PA.

Specifications of Nanoammeter (Nm 121)

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

f) A.C.Stabiliser :

For all the instruments such as Nanoammeter, EHT unit, UV tube linear temperature programmer, a stabilised power supply is necessary. This is obtained from AC stabiliser. Details of the stabiliser are as follows :

Model No. CVL/250 : SER No. 1160/7558

1) Input Voltage : 180 V. to 250 V at 50 Hz.

2) Output Voltage : 230 V. with ± 1 %

A digital stop watch having least count 0.1 second was used for decay time measurement.

2.4 - EXPERIMENTAL SET UP FOR THERMOLUMINESCENCE STUDY :

Experimental sep up for Thermoluminescence study is shown in fig. 2.2 (b) - photograph. The assembly arrangement is shown in fig. (2.5) . Two different excitation sources were used. First being ultraviolet and second gamma source. Details of the first excitation source are discussed earlier.

2.4.1 Gamma Source :

Some phosphors were irradiated using gamma source. The source was made available by B.A.R.C. Bombay Unit.

Gamma irradiation of phosphors was carried out using gamma cell 220 of Atomic energy Canada Ltd. giving 4000 R/min

A 30 minute dose was given in 22 may 1990. However, actual TL study was done in 24 August 1990.

2.4.2 Linear temperature programmer :

A linear temperature programme Unit was built because of help of HealthPhysics Division of B.A.R.C. Bombay unit. The programmer provides a constant heating rate which can be adjusted to any suitable value. Automatic heat control facility is with it. All the samples were heated between range of room temperature to 390°c.

Linear temperature programmer has a facility of isothermal heating, A caliberated temp. meter is there on the front panel for temperature measurements.

Other units such as EHT, UV source, PM tube etc. were also used for TL measurement.

Experimental Procedure : Phosphorescence Decay Measurement :

Phosphorescence decay measurements were carried out at room temperature. A weighed quantity of phosphor (20 mg) was taken in Kanthal Strip was then excited for 200 second using ultravoilet source. During excitation, EHT unit was switched off. After excitation, the uv source was switched off and simultoneously the EHT unit swith was made on ; and decaying intensity was measured. Dark current present was 13 nA.

Experimental Procedure : Thermoluminescence Measurement :

The thermoluminescence measurements were carried out in the temperature range from 27^{o}c to 390^{o} c . The weighed samples were excited with ultraviolet source for 200 second. After complete PL decays these samples were then heated by linear temperature programmer with fast heating rate of 2^{o}c/sec.fig.(5.1). TL intensity was measured by nanoammeter.

2.5 Experimental set up for determination of conductivity at different temperatures by using four probe set up :

A Manufacturer " scientific equipment and Services " Roorkee fabricated four probe set-up to estimate resistivity and band gap energy for the case of doped semiconductors . The doped crystal CaS may be have as a semiconductor. Electrical behaviour of phosphor is studied by using four prob set up. The specification of the apparatus used in the experiment [a photograph shown in figure (2.2-c)], is described as follow :

a) Probes arrangement :

It has four individual spring loaded probs, coated with Zn at the tips. The probs are co-linear and equally spaced. The Zn coating and individual spring ensure good electrical contacts with the sample. The probes are mounted in telfon bush which insure a good electrical insulation between the probes. A telfon spacer near the tips is also provided to keep the probes at equal distance. 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.

b) The phosphor sample :

The phosphor crystal is prepared in the form of pallet with a pressure 5 tune/cm^2 . These pallets are prepared by the instrument available in the department of Physics, Shivaji University, Kolhapur.

c) Oven :

It is small oven for the variation of temperature of the crystal from room temperature to about 250°c . Electrical supply provided to electrical heater of the oven by provision of step down transformer having larger current capacity in three steps (Low, medium and high). Temperature of the oven was recorded by murcury thermometer.

d) Constant current source :

The constant current generator is specially desined for four proble set up to provided hundred percent protection against crystal burn out, due to excessive current. The basic scheme is due to feed back principle to limit the load current of the supply to preset maximum value . Variation of current are achived by potention meter included for that purpose. The supply is highly regulated and practically ripply free d.c. source. It uses an integrated circuit regulator type Ic 723. The current will not exceed the present limit even the out put is short circuited.

e) Electronic Millivolt meter :

Though specically designed for four probe methcd, It can also be used as a general purpose equipment for the measurement of low d.c. voltages down to full scale deflection of 30 mv.

It has three measuring ranges(1,3,1 sequence).Which enable the accurate measurement through out the whole range. Readings are directly obtained on a (3.5") precious moving coil meter. conforming to the latest developments in instruments technology integrated circuits are used and almost all components are mounted on the printed circuits board. This ensures uniformity of performance, reduces maintanance and considerably extend the life of the instrument.

The main advantage achived over potentiometric system is that in present unit is direct reading requires minimum external adjustments. As impedence balance control enables the millivolt meter to be used with sources having wide range of impedences.

Specification :

Range : 30 mv, 100 mv, 300 mv,1v, 3v .
Input impedence : 1m.
Source impedence : 0 to 10 k.
Accurancy : 3 % .
Short term drift : ± 2 microvolt refered to input.
long term drift : ± 4 microvolt refered to in put
input power : 220 v , 50c / sec 7 W.

2.6 Experimental set up for Electroluminescence :

For easy and comfortable operations, the equipment employed in the EL set up were arranged in the photographs figure 2.2(d). Design and fabrication of EL set up in the laboratory was developed as part of desertation the EL set up consist of mainly of electroluminescent cell, electronic excitation source and brightness measuring system. This is schematically shown in fig. (2.6).

Electroluminescence cell :

The efficeency of EL cell depends upon its geometry and hence its design and construction are equally important factors in EL studies. The literature (22,23,24) describing the design aspect of EL cell gives many interesting modification in its construction. It is usually made in the form of a parallel plate condenser, of which at least one of the conducting plate is transferent. EL suitable in the present studies was fabricated in the laboratory and its main features are described below.

The sectional side view of EL cell and its top view are shown in fig. (2.7). The aluminium plate D was fixed in a bakelite frame (c) and was used as one electrode. A thin phosphor layer (E) was mounted on the aluminium plate. The phosphor layer was then covered with a uniform transferent mica sheet (F) of thickness 70 micron having high dielectric constant (25) and sufficient break down strength. A conducting glass plate (G) having resistance $200 \Omega / cm^2$ was used as a second electrode. It was fixed in a cavity grooved on lower surface of bakelite frame (H) which has a small window (I) of size(1.5 cm x 7 cm) in the middle of the top surface. The interelectrode distance and pressure can be adjusted with the help of screw (A) with spring (B) arrangement shown in fig (2.7).

Different dielectric media such as caster oil, silicon jelly, araldite resin etc. proposed in the literature have been tried. But with these media in present study, reproducibility of EL intensity was found satisfactory in silicon jelly.

The excitation source :

The excitation source includes wide band amplifier which is fabricated in the laboratory. Fig. (2.2 (e)) represents photograph of it. The wide band amplifier was fabricated by using electronic semiconductor devices. Audio frequency generator (Vasavi Electronics Secundrabad, Model VFO 13, frequency range 1 Hz to 100 KHz and out put voltage 0 to 5 v) is used as an input to the wide band amplifier. The frequency responçe is shown in fig. (2.8) . The 850 Vrms remain constant over a wide range of frequency however gain falls gradually beyond 7 KHz. Out put voltage was measured on calibrated C.R.O .(Vasavi Electronics, Secundrabad, 15 MHz model OS 15) With 1 : 10 x probe.

Brightness measurement :

Brightness measuing system includes photomultiplier tube and nanoammeter which are described in section (2.2) EL cell current is recorded by using digital multimeter.

TABLE 2.1 : DETAILS OF SAMPLE PREPARED. (host CaS)

BY ATOMIC % METHOD

Fluxes: 1) Naf (2) $Na_2S_2O_3$ (3) Na_2SO_3

Sample No.	% of Nd	% of Sm	% of Tb	% of Dy	Flux added
KD 1	-	-	-	-	1,2,3
KD 2	0.05	-	-	-	1,2,3
KD 3	-	0.05	-	-	1,2,3
KD 4	-	-	0.05	-	1,2,3
KD 5	-	-	-	0.05	1,2,3
KD 6	.1	-	0.05	-	1,2,3
KD 7	.1	-	-	.05	1,2,3
KD 8	-	0.05	.1	-	1,2,3
KD 9	-	-	.05	.1	1,2,3
KD 10	-	-	0.05	.1	-
KD 11	-	-	0.05	0.0075	1,3
KD 12	-	-	0.05	0.0075	1,2

TABLE 2.2 : DETAILS OF SAMPLE PREPARED (Host CaS) BY ATOMIC % METHOD

Sample No.	CaS : Sm : Nd Phosphors		CaS : Dy : Tb Phosphors		
	% of Sm.	% of Nd	Sample No.	% of Dy.	% of Tb
KD 13	.01	.1	KD 29	.0025	.05
KD 14	.02	.1	KD 30	.005	.05
KD 15	.03	.1	KD 31	.0075	.05
KD 16	.05	.1	KD 32	.01	.05
KD 17	.07	.1	KD 33	.02	.05
KD 18	.3	.1	KD 34	.03	.05
KD 19	.5	.1	KD 35	.05	.05
KD 20	.02	.01	KD 36	.07	.05
KD 21	.02	.02	KD 37	.1	.05
KD 22	.02	.03	KD 38	.2	.05
KD 23	.02	.05	KD 39	.3	.05
KD 24	.02	.07	KD 40	.5	.05
KD 25	.02	.09	KD 41	.0075	.005
KD 26	.02	.1	KD 42	.0075	.1
KD 27	.02	.3	KD 43	.0075	.2
KD 28	.02	.5	KD 44	.0075	.5

TABLE 2.3 :'d,VALUES AND (h,k,l) VALUES OF SAMPLE KD 21

Peak No.	2 θ	$h^2+k^2+k^2$	h,k,l	'Observed 'd, (AU) Braggre--lation	Calcu-lated (Dy(A.U)	$\frac{I}{I_{max}}$ · 100
1	2	3	4	5	6	7
1	26.620	7.9520	(2,2,0)	3.3459	3.3358	10.31
2	27.365	8.3948	(2,0,2)	3,2564	3,3358	4.18
3	28.295	8,9632	(3,0,0) (2,2,1)	3,1515	3.1450	8.31
4	31.420	11,0000	(3,1,1)	2.8448	2,8447	100.73
5	41.075	18.4657	(4,1,1) (3,3,0)	2.1957	2.1645	1.82
6	41.790	19.085	(3,3,1)	2.1597	2.1645	1.82
7	41.995	19.264	(3,1,3)	2,1497	2,1645	3.07
8	45.045	22.013	(3,2,2)	2.0109	2,0115	69.85
9	47.060	23,913	(4,2,2)	1,9294	1.9259	14.97
10	47.310	24.153	(4,2,2)	1,9198	1.9259	2.58
11	50.370	27.169	(5,1,1)	1,8101	1,8157	3.07
12	52.005	28.837	(5,2,0) (4,3,2)	1.7570	1.7570	2,13
13	55.925	32.987	(5,2,2)	1,6428	1.6424	26.11
14	56.925	34.078	(4,4,1) (5,3,0)	1.6163	1.6180	2.35
15	65.525	43.938	(6,2,2)	1.4234	1.4225	10.31
16	68.710	47.779	(4,4,4)	1.3650	1.3618	3.33
17	74.475	54.938	....	1.2729	1.2222	67.43
18	74.905	55.489	....	1.2667	1.2222	7.49

Contd... next page

TABLE 2.3 Contd....

1	2	3	4	5	6	7
19	75.282	55.962	(6,4,2)	1.2612	1.2608	3.60
20	83.030	65.914	(8,1,1)	1.1621	1.1613	20.15
21	83.865	67.000	(7,3,3)	1.1527	1.1526	3.33
22	98.065	85.542	(9,2,1)	1.0201	1.0174	3.88
23	99.850	87.851	(6,6,4)	1.0066	1.0057	10.31
24	101.175	89.557	(9,3,0)	.9970	.9945	3.388
25	108.505	98.828	(7,7,1)	.9491	.9482	17.62
26	110.660	101.48	(10,1,0) (8,6,1)	.9366	.9382	7.49
27	113.145	104.50	(10,2,0) (8,6,2)	.9230	.9251	6.71
28	117.635	109.81	(9,5,2)	.9004	.8996	13.86

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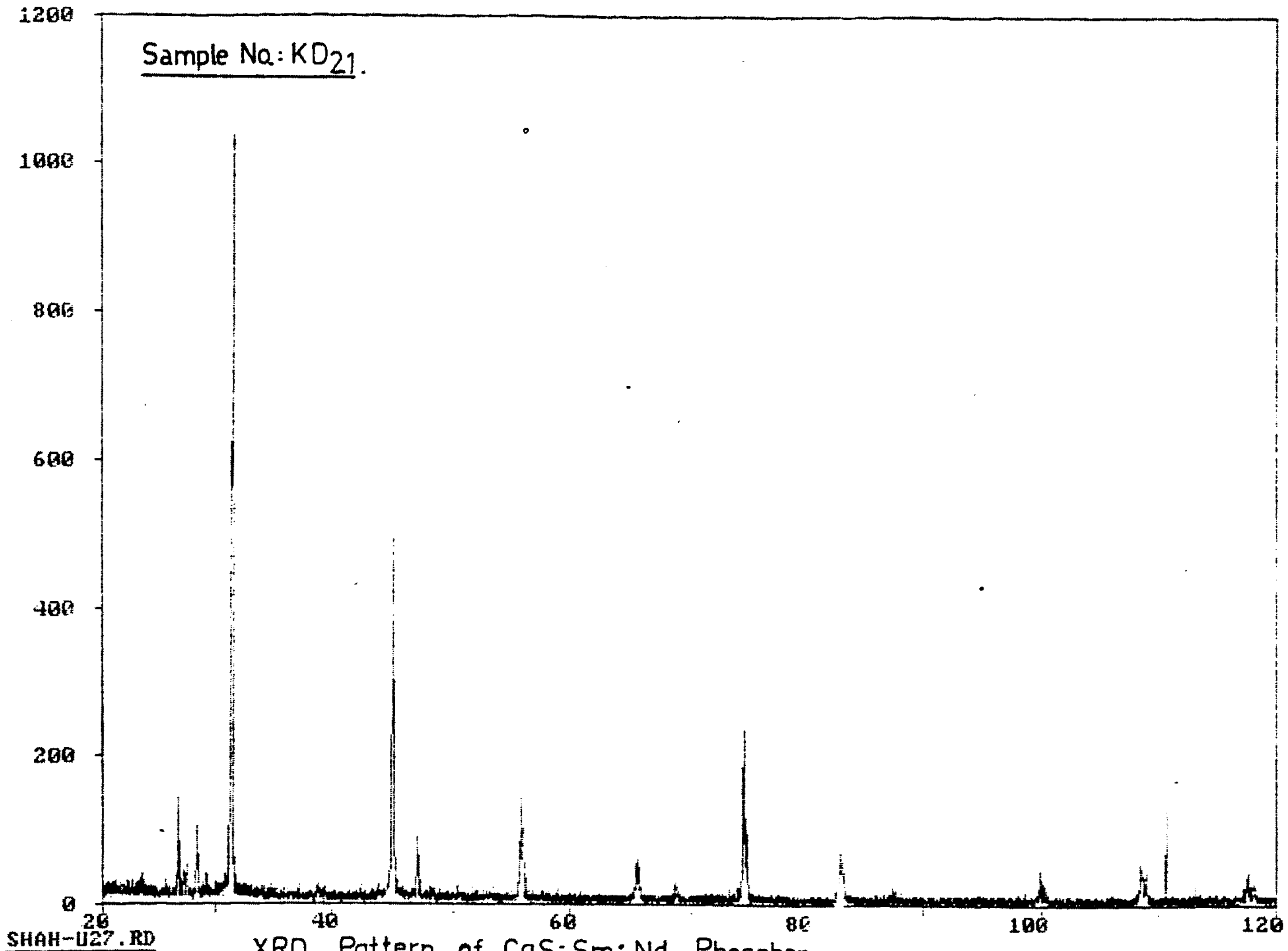
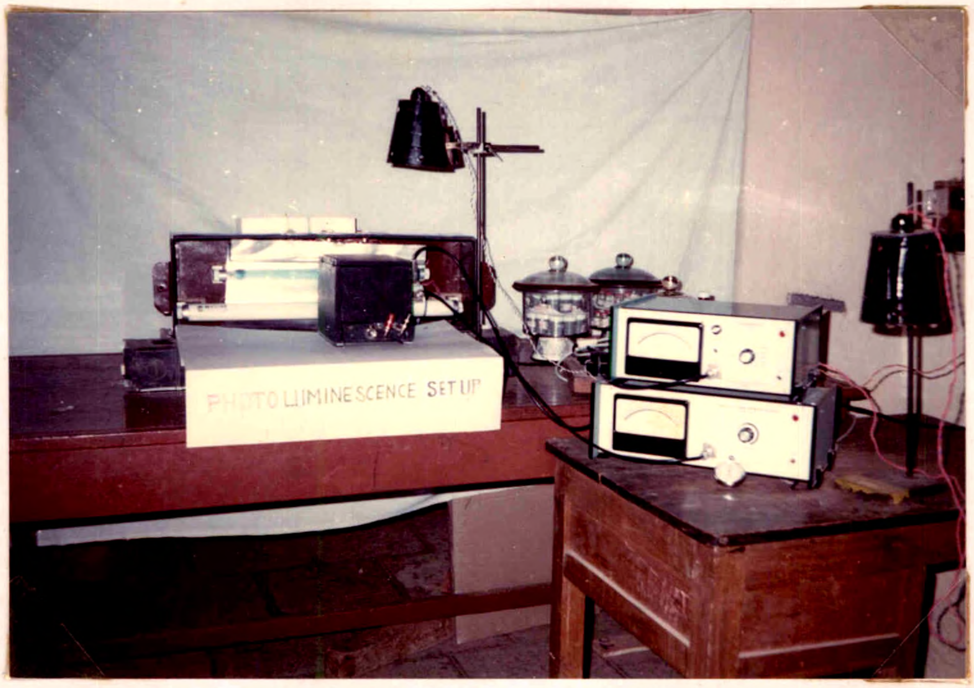


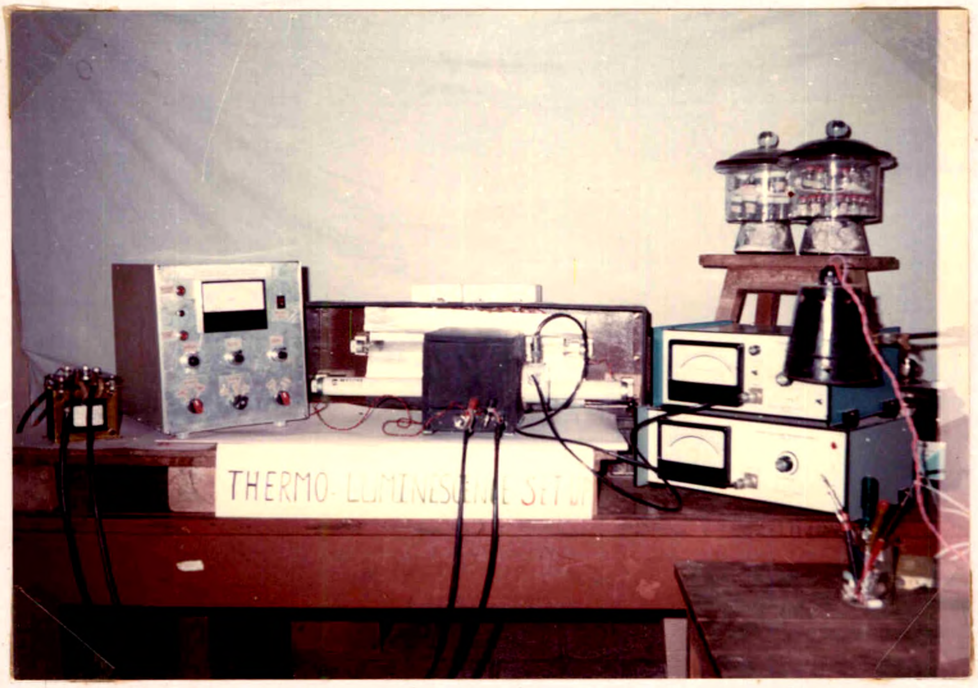
XRD Pattern of CaS: Sm: Nd Phosphor.

FIG. NO: 2·1.



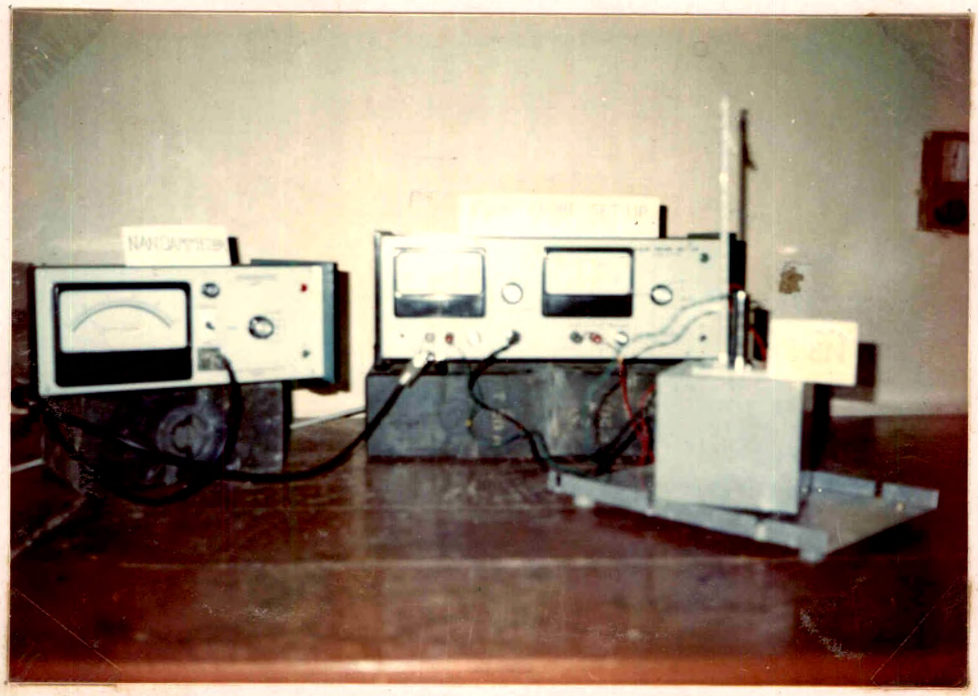
PL SET UP

Fig. No.: 2·2(a)



TL SET UP

Fig. No.: 2·2(b)

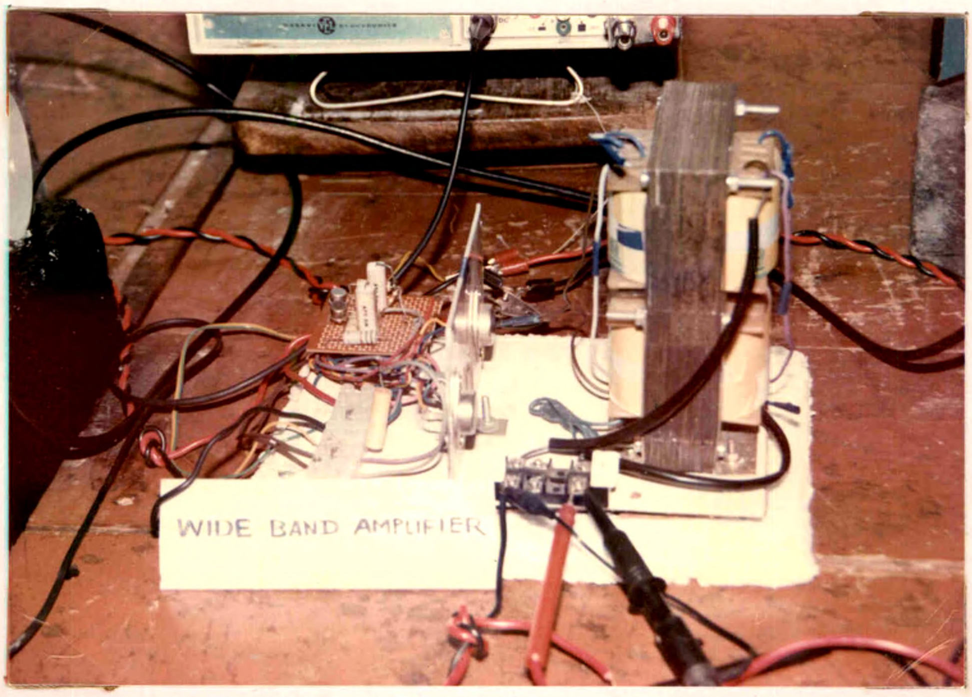


FOUR PROBE SET UP

Fig. No.: 2·2(c)

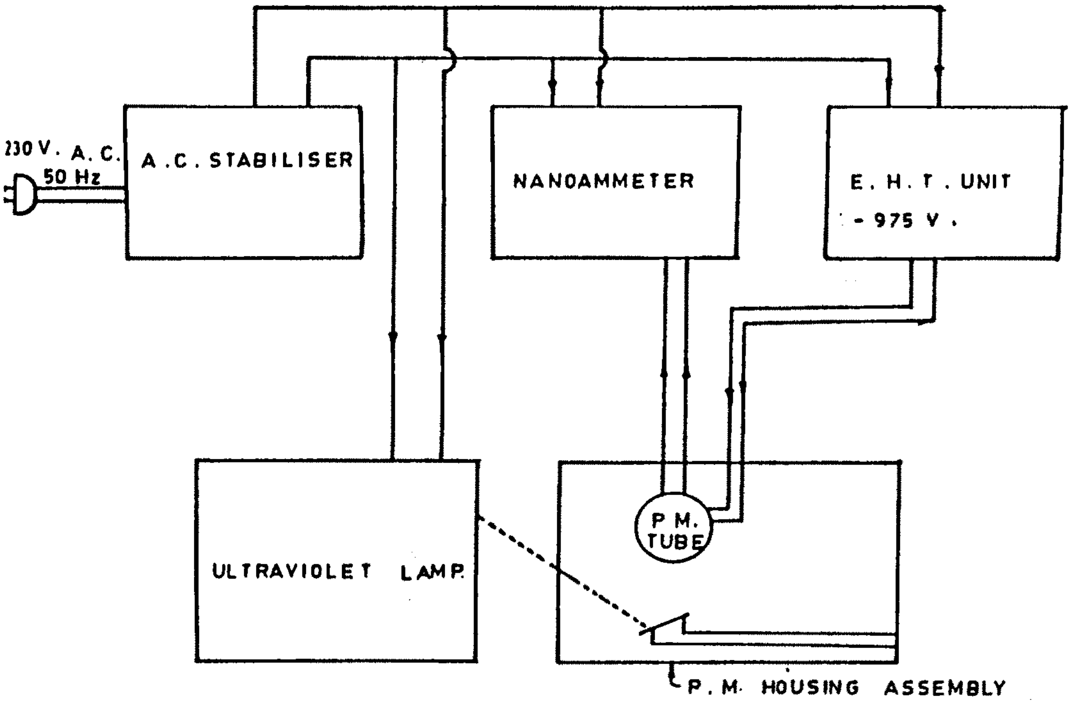
EL SET UP

Fig. No.: 2·2(d)



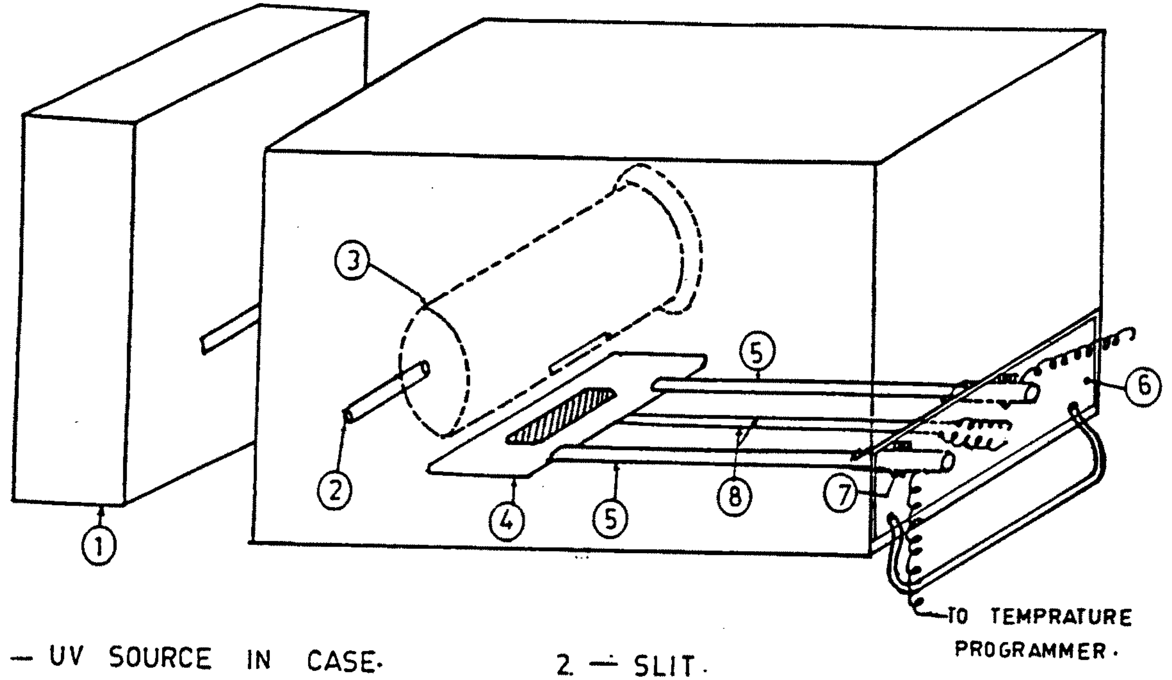
WIDE BAND AMPLIFIER

Fig. No.: 2·2(e)



BLOCK DIAGRAM OF PHOTOLUMINESCENCE SET UP

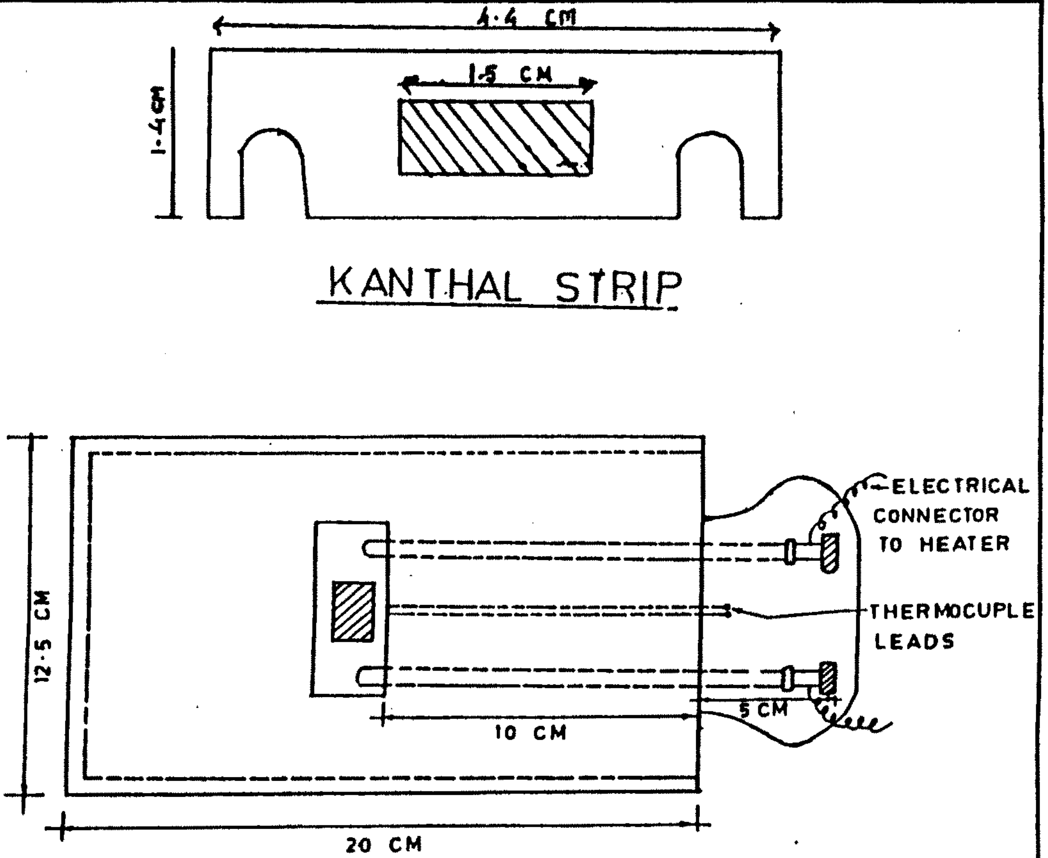
FIG. NO.: 2·3



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

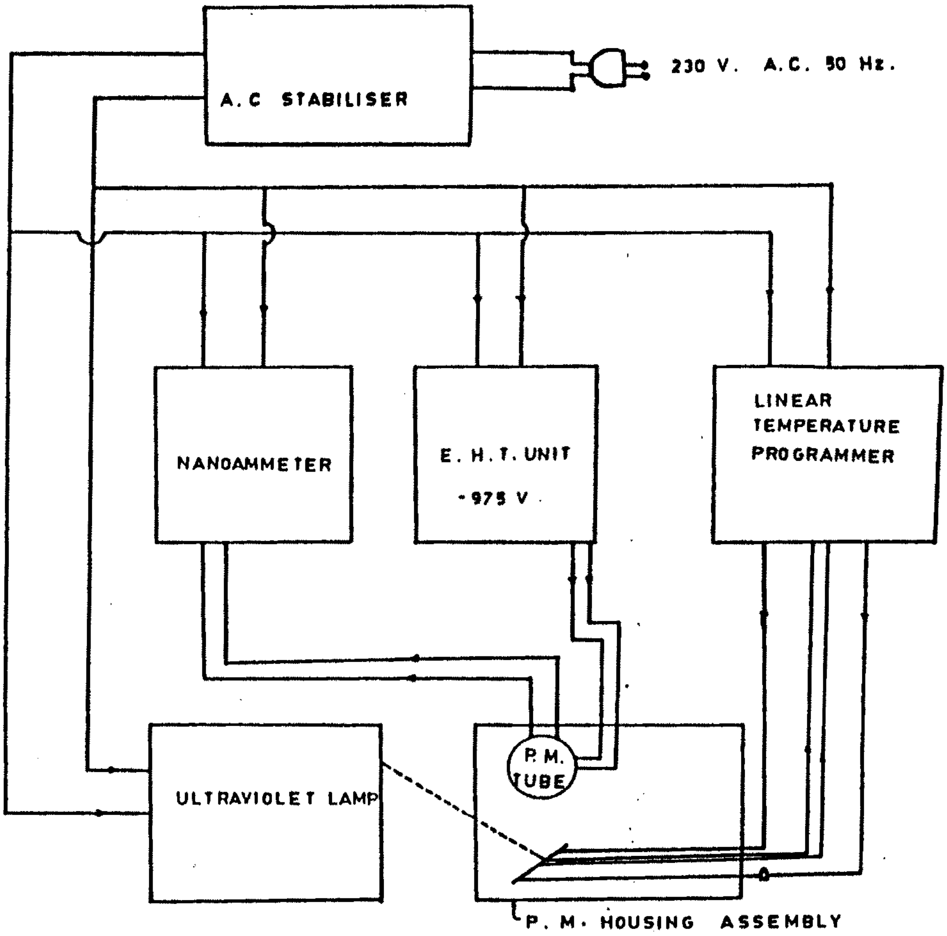
FIG. NO.: 2·4.



KANTHAL STRIP

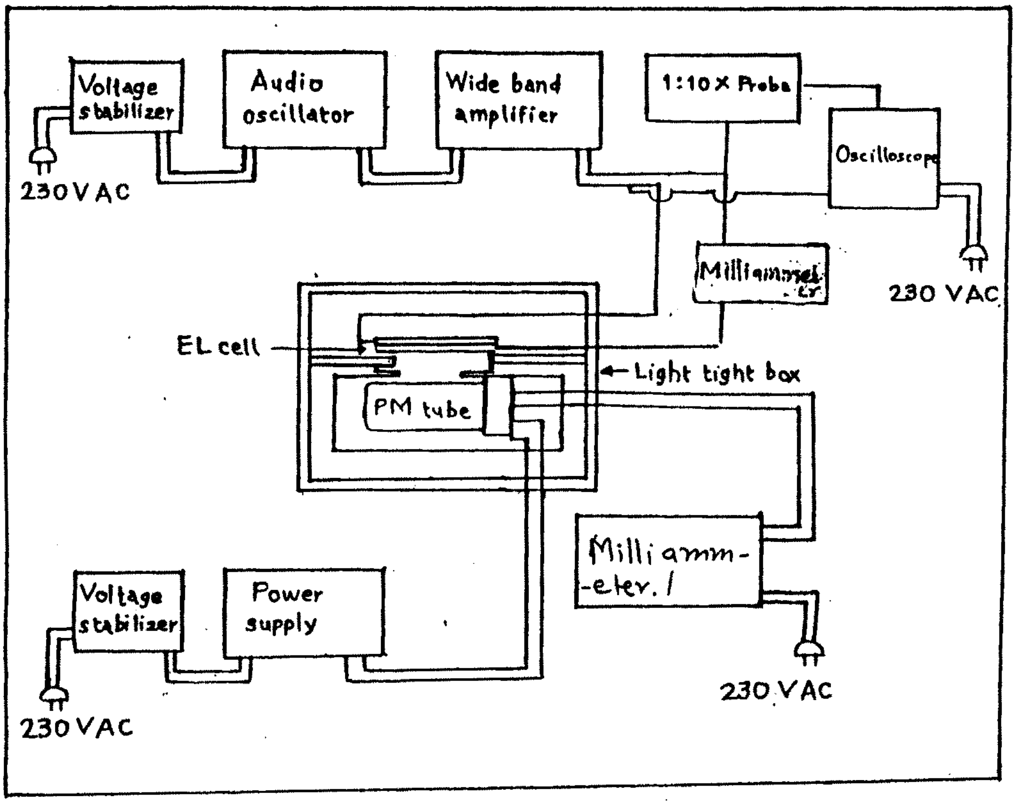
DRAWER ASSEMBLY

FIG. NO: 2·4 a



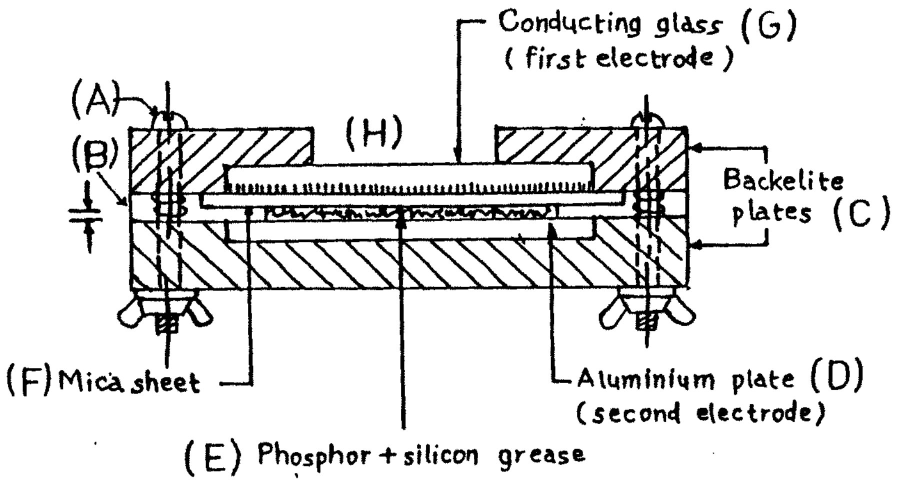
BLOCK DIAGRAM OF T.L SET UP

FIG. NO. - 2·5.



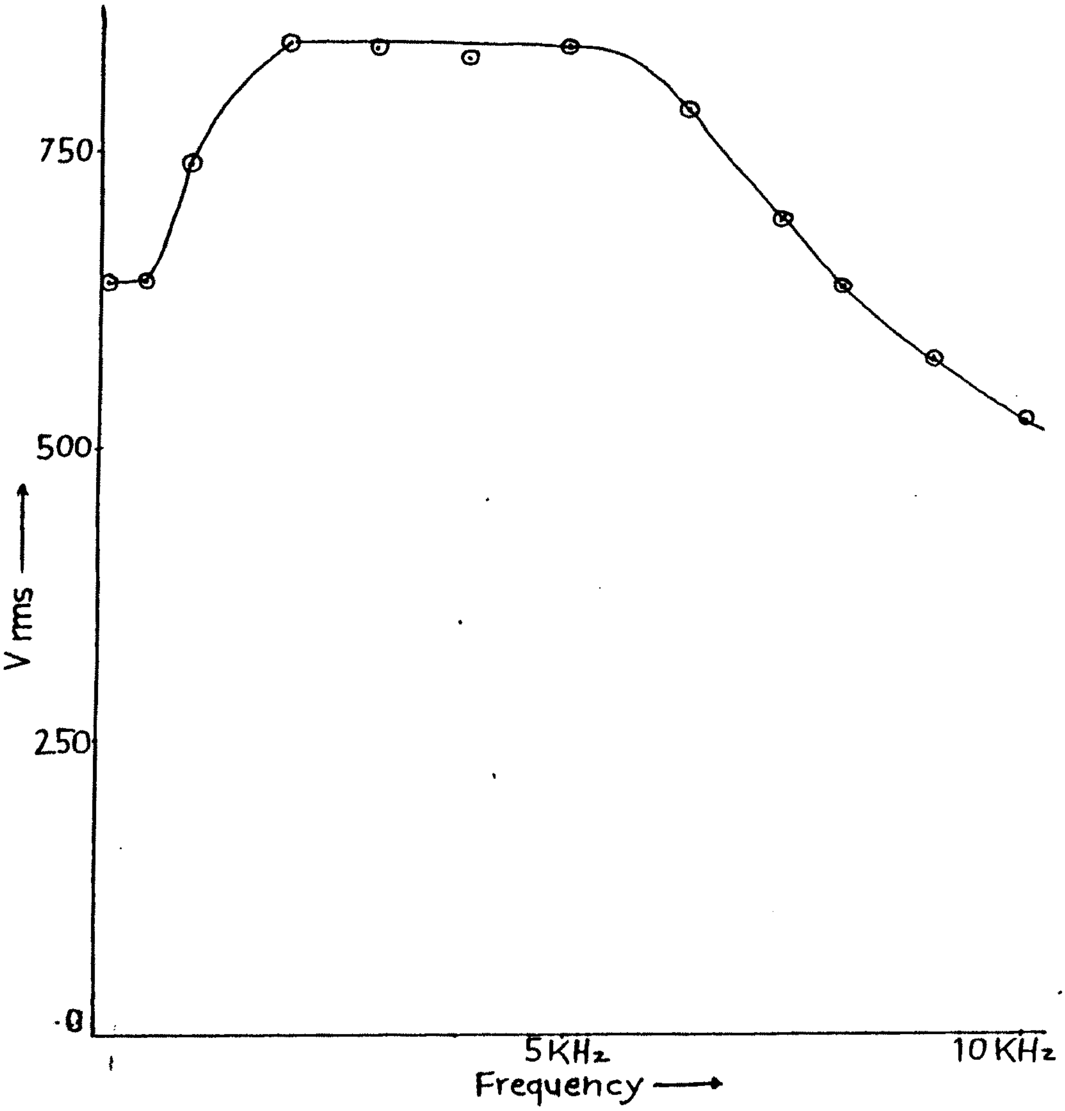
Experimental Set up for Electroluminescence.

FIG. NO.: 2·6.



Electroluminescence (EL) cell.

FIG. NO.: 2·7.



Plot of Vrms Vs Frequency of Wide Band Amplifier

FIG. NO.: 2·8.