CHAPTER - II

PHOSPHOR SYNTHESIS AND EXPERIMENTAL ASPECTS

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2-1 SYNTHESIS OF PHOSPHORS :

The phosphors are usually prepared by incorporating traces of impurities (1,2) in a pure semiconductor or insulating cystalline material. They can be prepared, as per requirement, in the form of single cystals, thin films or microcrystalline powders. Since, phosphors in the present study are prepared in the microcrystalline powder form, 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 predetermined period, in a suitable atmosphere.

i) 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 equal to or greater than

3 eV- the energy corresponding to the extreme violet. Combination of the elements of columns I, II, III B, IV A, V,VI A of the periodic table with those of the columns VI B and VII B fulfil this condition (3).

ii) <u>Activators</u> :

Impurities, which when incorporated provide localized energy levels in the forbidden energy gap of the insulator or semiconductor are called activators (4). The activators, depending upon the way of functioning, are classified as follows:

a) Originator : It gives rise to new emission lines or bands other than the interinsic luminescence of the host lattice.

b) Intensifier : It intensifies the intrinsic luminesence of the host lattice.

c) Dominant and auxiliary activators : Sometimes the efficiency of a singly activated phosphor is enhanced by adding a second activator, The first and the 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-activators : 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.

iii) Flux :

There are certain readily fuseble salts which when added to 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 -

a) enhances the rate of reaction at relatively lower temperature (9, 10);

b) affects the luminescence intensity (11); and

c) serves as charge compensating agent (5,6).

Generally, the effective fluxes are chlorides, Oxysalts and sulphates of sodium and potassium (12).

(B) Preparative parameters of phosphors :

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

i) Purity of ingredients :

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 ingredient to be used in 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.

ii) 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.

iii) 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); emperically 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).

iv) Atmosphere of firing :

The atmosphere in which phosphor ingreadients are fired has a pronounced effect on the character of the phosphor (15). 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 (16). Also some phosphors (17) which do not show electroluminescence responses when fired in H_2s, become electroluminescent after refiring in the presence of water vapour.

v) Grain size of ingredients :

The grain size of the basic ingredients required for phosphor preparation has a sriking 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~~n~~ are required (3, 18, 19).

vi) 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 flourescence (17).

Slow cooling rate helps in uniform distribution of imperfection throughout the phosphor (16). On the other hand, rapid cooling preserves the valence state prevalent at high temperature (21).

vii) Size of the charge :

Homogeneity of the final product is affected by the size of the charge (19). Preparation of phosphors 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 minimized by taking small quantity of mixture each time.

2-2 DETAILS OF THE METHOD FOLLOWED FOR PREPARATION OF C_aO:Bi.S_m Phosphors :

Generally, oxide phosphors are prepared from their carbonates. The method followed in the present investigation is the one developed by Willi Lehmann (22). J.D. Ranade et al (23). In principle, the method consists of heating of a calcium carbonate in air at about 1000 to 1100°c along with required amounts of activator and fluxes. The details of the method may be divided into two stages. The first stage involves preparation of charge containing basic ingradients while second one deals with firing of the charge at a suitable temperature. It should be mentioned that the adopted method is advantageous over others as activation and reaction processes take place simultaneously.

2-2-1. <u>First stage</u> :

(a) <u>Host materials</u> :

The starting material is $CaCO_3$ GR "Sarabhai M. Chemicals" with maximum limits of following impurities as labelled by manufacturer -

Calcium Carbonate Precipitated - $CaCO_3$ Ml. Wt.100.09

Assay .... Minimum 99.0 %

	Maximum		
Substances Soluble in Hydrochloric Acid	0.003 %	Aluminium (Al)	0.002 %
Soluble Alkali	0.25 mlN/1 %	Ammonium (NH_4)	0.05 %
Chloride (Cl)	0.001 %	Barium and strontium (Ba+Sr)	0.01 %
Nitrate (NO_3)	0.01 %	Iron (Fe)	0.002 %
Phosphate (PO_4)	0.001 %	Heavy Metals (Ph)	0.0005%
Silicate (SiO_2)	0.01 %	Magnesium (Mg)	0.01 %
Sulphate (SO_4)	0.005 %	Potassium (K)	0.005 %
		Sodium (Na)	0.02 %

b) Activator solution (Bi and Sm) :

The activators were added in the form of solutions of their salts. The weighed quantities of salts of Bi and Sm (both AR grade) were taken and their solutions were prepared by disolving them in double distilled water. These solutions were then diluted subsequently to suit various concentrations of the activators to be added.

c) Fluxes :

In the present study, sample Nos. S_{01} to S_{03} were prepared without fluxes and sample Nos. S_0 to S_{30} were prepared with fluxes. In fluxed sample the fluxes added were, Na_2SO_4 (0.3346 grams), $Na_2S_2O_3$ (0.836498 grams) and Na F (0.08348 grams) in 10 grams of $CaCO_3$. The said weight percent of fluxes were concluded by preparing number of trial samples and selecting the one which gives better emission. Moreover, to conclude about the percentage of fluxes in a phosphor, data reported by other workers (23) were also used as guide lines.

d) Preparation of charge for firing :

$CaCO_3$ (10 grams) was mixed intimately in double distilled water to give a slury. The activator solution in requisite amounts, along with few drops of absolute alcohol were then added and the charge was again thoroughly mixed. The addition of few drops of alcohol 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. For fluxed samples, charge was prepared by adding requisite amount of fluxes $Na_2S_2O_3$ (0.836498 grams), Na_2SO_4(0.3346 grams) and Na F (0.08348 grams).

2-2.2 Stage Second :

a) The firing of charge :

The mixed and dried charge was thoroughly grinded and powdered to a fine particle size and then filled in a prefired silica Crucible. A lid was put up over the crucible. The charged crucible was then fired at 1050°c ± 20°c in air for a duration of 5 hours. After firing, the charge was allowed to cool naturally to room temperature. The natural cooling favours the equilibrium distribution of crystal imperfections (23). The charge was then removed from furnance, crushed to a fine powder and was stored as a phosphors sample in a clean and air tight bottle. A special precaution was taken to keep the charge in a air tight bottle as CaO is chemically unstable in air, reacting with atmospheric moisture to non-luminescent $Ca(OH)_2$ (22).

The reduction of calcium carbonate into calcium oxide occurs according to the reaction

$$CaCO_3 : 5\,H_2O \xrightarrow{1050^{\circ}C} CaO + CO_2 + 5H_2O$$

2-2.3 Prepared Phosphors :

In all four series of fluxed CaO : Bi : Sm phosphors were prepared. The first and second series contained only Bi^{3+} and Sm^{3+} respectively. The concentrations were varied in amounts of 0.000025 gram to 0.05 gram i.e. 0.0005 to 1.0 wt % by weight of $CaCO_3$: 5 H_2O. The third series contained fixed concentration of Sm^{3+} (0.05 wt % by wt of $CaCO_3$: H_2O) and varying concentration of Bi^{3+} (from 0.001 to 1.0 wt % by wt of $CaCO_3$: 5 H_2O). While the last one contained fixed concentration of Bi^{3+} (0.05 wt % by wt of $CaCO_3$: 5 H_2O) and varying concentration of Sm^{3+} (from 0.001 to 1.0 wt % by wt of $CaCO_3$: 5 H_2O). The details of the samples prepared are given in tables 1 to 4. Some samples were also prepared without flux and their details are shown in table 5. All the prepared samples were more or less white in colour.

The homogeniety and uniformity of prepared samples was checked through photoluminescence. A uniform colour under UV excitation suggests the formation of the homogeneous compound structure. The XRD technique was also adopted to check the completion of the reaction. The XRD studies show that the prepared CaO : Bi : Sm phosphors has usual CaO cubic lattice with lattice constant 8.71 A°. The details of results are described elsewhere (Chapt. 4).

2-3 ABSORPTION MEASUREMENTS :

2-3.1 Experimental Set-up :

The absorption characteristics of the prepared samples have been studied in the visible and near visible region of the spectrum by making use of the reflectance technique. The basic principle involved is being, the reflection is high for wavelengths which are faintly absorbed and vice-versa. The study of spectral distribution of reflected radiation thus provides the information about the absorption bands. The measurements were carried out using Spekol Spectro - Colorimeter (Hergestestelit in BER - DDR, Carl Zeiss Jena) with slight modifications. A schematic view of the experimental set-up is shown in fig. 2.1 and it consists of a source of light, a sample holder, a dispersing unit and an intensity measuring unit.

i) Source of Light :

A tungsten fillament lamp operating at 230 volts a.c. and emitting a continuous spectra extending over and above the visible region of the spectrum was used as a source of light.

ii) Sample Holder :

A cassette, holding a black paper painted on it a phosphors layer using silicon grease, serves the purpose of a sample holder. The cassette is mounted on the reflecting side of the mirror and the reflection from the phosphors layer in directed towards the dispersing unit.

iii) Dispersing Unit :

A high quality reflection grating serves the purpose of dispersing unit. The motion of the calibrated wave length-drum selects the proper wavelength and the intensity corresponding to it can be measured at the exit slit using the intensity measuring unit.

iv) Intensity Measuring Unit :

The Photomultiplier tube (RCA 931 A . Toshiba, Japan) in conjunction with a d.c. microvoltmeter (Philips, PP 9004) was used as an intensity measuring unit.

2-3.2 Experimental Procedure :

A layer of freshly prepared MgO by burning a magnesium ribbon was painted over a fixed area of a black paper and illuminated with light from tungsten filament lamp. The intensity of reflected light was recorded as a function of wavelength in the wavelength range of 3400°A to 6500°A. The MgO layer was then replaced by coating a phosphors sample to be be studied. The reflectance spectra recorded for every sample was calibrated against MgO sample under the same physical conditions using the standard reflectance curve of MgO (see fig. 2.2). The measurements made can be symbolically represented in the following way.

Let $I_O(\lambda)$, a function of wavelength λ, be the intensity of exciting light which is reflected from the standard layer of MgO with known reflectance, say RMgO (λ). IMgO (λ) be the intensity of reflected light from MgO surface, $I_O(\lambda)$ for each wavelength can be calculated by the ratio

$$I_O(\lambda) = \frac{\mathrm{IMgO}(\lambda)}{\mathrm{RMgO}(\lambda)} \qquad \ldots (1)$$

Now, MgO surface is replaced by the sample to be studied and the intensity of reflected light coming from this very surface is, say, Is (λ). The reflectance $R_s(\lambda)$ for the surface, therefore, will be

$$R_s(\lambda) = \frac{I_s(\lambda)}{I_O(\lambda)} \qquad \ldots (2)$$

The absorption $A_s(\lambda)$ will then be -

$$A_s(\lambda) = 1 - R_s(\lambda) \qquad \ldots (3)$$

If the maximum reflectance is taken to be unity. The plot of $A_s(\lambda)$ against corresponding wavelength (λ) gives the absorption curve.

2-4 OPTICAL EMISSION MEASUREMENTS :

The experimental arrangement for optical emission measurements is schematically illustreted in fig. 2-3. The arrangement consists of :

i) Source of excitation
ii) Sample holder and
iii) Measuring unit (system)

i) Source of Excitation :

The excitation source used was an ultraviolet lamp (UV products, U.S.A. type UVS-12) emitting predoninently the 3650 A^{o} Hg doublet. A stabilizer was used in conjunction with the lamp to maintain exciting energy constant.

ii) Sample Holder :

A sample holder consists of a metal frame supporting cassette inclined at 45^{o}. A cassette carries a side painted with phosphors material. A beam of UV light projected on the inclined side excites the phosphors. The emission intensity, at right angles to the incident beam, is to be recorded by measuring unit.

2-4·1 Intensity Measuring Unit :

It consists of a photomultiplier tube, its power supply, D.C. microvoltmeter and interference filters. The photomultiplier tube used was "RCA 931 A". Its spectral response is shown in fig. 2.4. A well stabilized D.C. power supply giving an output 900 V was used to operate the photomultiplier tuble. To measure the output of PM tube a D.C. microvoltmeter (phillips, PP 9004) was used. The interference filters (Metall interferenz Filters) interposed between the phosphors sample and the PM tube analyse the emitted radiation. The filters spanned the interval between 4000 A° and 6000 A°, the region of better sensitivity of RCA 931 A. P.M. tube fig.(2.4).

2-4·2 Experimental Procedure :

The UV light (3650 A° Hg doublet) was allowed to fall on the phosphors layer mounted at the Cassette. The intensity of emitted radiation was measured with a PM tube in conjunction with a D.C. microvoltmeter by introducing filter in the path of emitted light. The measurements were carried out for different samples and were corrected for photomultiplier tube response.

2-5 X-RAY DIFFRECTION MEASUREMENTS :

X-ray diffraction technique was employed to check the formation of solid solution of the prepared phosphors. X-ray spectrograms giving directly the intensity of diffracted beam were taken at the Regional Sophisticated Instrumentation centre, IIT, Bombay. The X-ray diffractometer was operated at 31 kv, 20 mA using copper target and giving monochromatic X-rays of wavelengths 1.54 A°. The X-ray diffrectometer has a Geiger counter for measuring the intensity of the diffracted beams for different values of 2θ. The scanning rate was 2°/min.

2-6 ELECTRON PARAMAGNETIC RESONANCE (EPR) MEASUREMENTS :

Electron paramagnetic Resonance (EPR) spectra were recorded at the Regional Sophisticated Instrumentation Centre, IIT, Bombay. The EPR spectrometer used was an X-band varian E-109 operated at a microwave frequency of 9.4 91 GH_z and with 100 KH_z field modulation. TCNE was used as a standard field marker taking $g_{TCNE} = 2.002777$.

Details of the samples prepared

Series I to IV contains fluxes in combination ($Na_2S_2O_3$ + Na_2SO_4 + NaF in percentage of 29.86, 11.945 & 2.98 respectively) and series No. V is prepared without fluxes.

Table 1 : Fluxed Samples

Series No.	Sample No.	Concentration of Bi by wt.% of $CaCO_3:5H_2O$	Concentration of Sm by wt % of $CaCO_3:5H_2O$
I	S_0	0.0000	0.000
	S_1	0.0005	0.000
	S_2	0.001	0.000
	S_3	0.005	0.000
	S_4	0.01	0.000
	S_5	0.025	0.000
	S_6	0.05	0.000
	S_7	0.1	0.000
	S_8	0.25	0.000
	S_9	0.5	0.000
	S_{10}	1.0	0.000

Table 2 : Fluxed Samples

II	S_{11}	0.000	0.0005
	S_{12}	0.000	0.001
	S_{13}	0.000	0.005
	S_{14}	0.000	0.01
	S_{15}	0.000	0.025
	S_{16}	0.000	0.05
	S_{17}	0.000	0.1
	S_{18}	0.000	0.25
	S_{19}	0.000	0.5
	S_{20}	0.000	1.0

Table : 3 : Fluxed Samples

Series No.	Sample No.	Concentration of Bi by wt.% of $CaCO_3{:}5H_2O$	Concentration of Sm by wt.% of $CaCO_3{:}5H_2O$
III	S_{21}	0.001	0.05
	S_{22}	0.01	0.05
	S_{23}	0.05	0.05
	S_{24}	0.25	0.05
	S_{25}	1.0	0.05

Table : 4 : Fluxed Samples

IV	S_{26}	0.05	0.001
	S_{27}	0.05	0.01
	S_{28}	0,05	0.05
	S_{29}	0.05	0.25
	S_{30}	0.05	1.0

Table : 5 : Samples Without flux

V	S_{01}	0.000	0.000
	S_{02}	0.000	1.00
	S_{03}	1.00	0.00

REFERENCES :

1 Vernailee, A., Compt. Rend, 103, 600 (1886), Ibid 104, 105 (1887).

2 Lenard and Klatt, Ann. Phy, 15, 225 (1904).

3 Leverenz, H.W., "An Introduction to Luminescence of Solids" (J.Wiley and Sons, New York, 1950).

4 Matossi, F and Nudelman, S., "Methods of experimental Physics" Solid State Physics, Vol. 6, Part B, 293 (1959).

5 Kroger, F.A., and Hellingman, J.E., J. Electrochem. Soc., 95, 68 (1948).

6 Kroger, F.A. and Dikhoft, J, Physica, 16, 297(1950).

7 Dubinin, V.G. and Trapezlikova, Z.A., Optics and spectrose (U.S.A.), 19, 245 (1960).

8 Kremheller, A and Faris, S., J. Electrochem., Soc., 107, 891 (1960).

9 Ward, R, "Cormell Symposium (John Kliley, New York, (1948).

10 Tunits kaya, V.F., Dokl. Akad, Naak, 3 SSR, 91, 507 (1952).

11 Smith, A.L., J. Electrochem. Soc. 96, 75 (1949).

12 Garlick, G.F.J., Rep. on progress in Physics, 12, 34 (1948-49).

13 Nagy, R. and Chungkwatilui, J. Opt. Soc. Physics, 37, 37 (1947).

14 Leverenz, H.W. and Seitz. F., J. Appl. Phys., 10, 479 (1939).

15 Kroger, F.A., Brit, J. Appl. Phys., 5, 11 (1955).

16 Kroger, F.A., "Some Aspects of luminescence of solids" (Elceveir, N.Y. 1940).

17 Froelich, H.C., J. Electrochem. Soc., 100, 496 (1953).

18 Levy, L.A. and West., D.W., Trans. Farad, Soc. 35, 128 (1939).

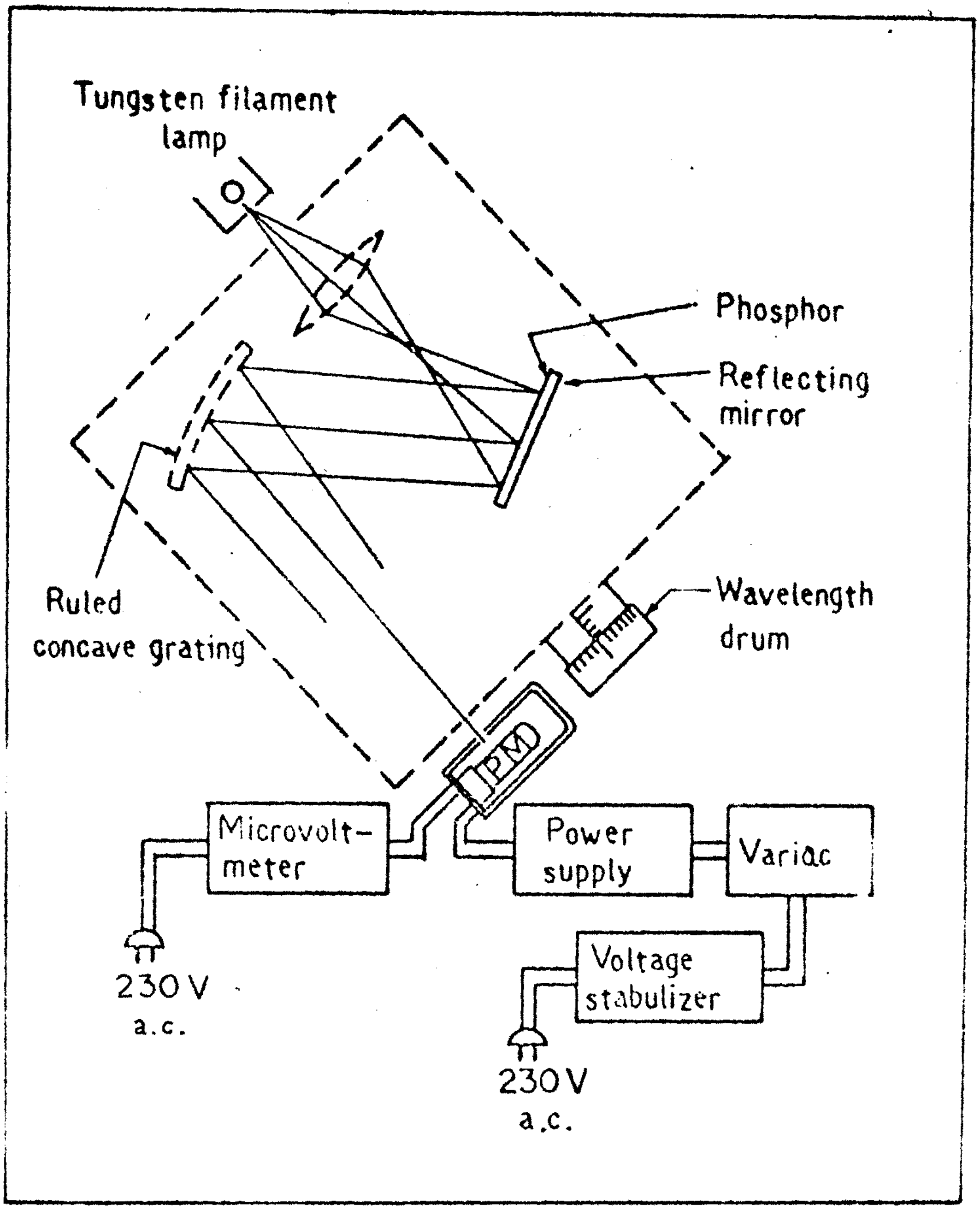
19 Froelich., H.C., "Cornell Symposium" (John Wiley and Sons, Inc., New York, 1948).

20 Ishler, W.F. Apple., F.E. and Froelich, H.C. Acta. Phys. Huuger, 14, 295 (1962).

21 Vij, D.R., and Mathur, V.K., Proc. Halt, Symp. on Thermolurninescence and its applications Kalpkkam, Madras, P. 545 (1975).

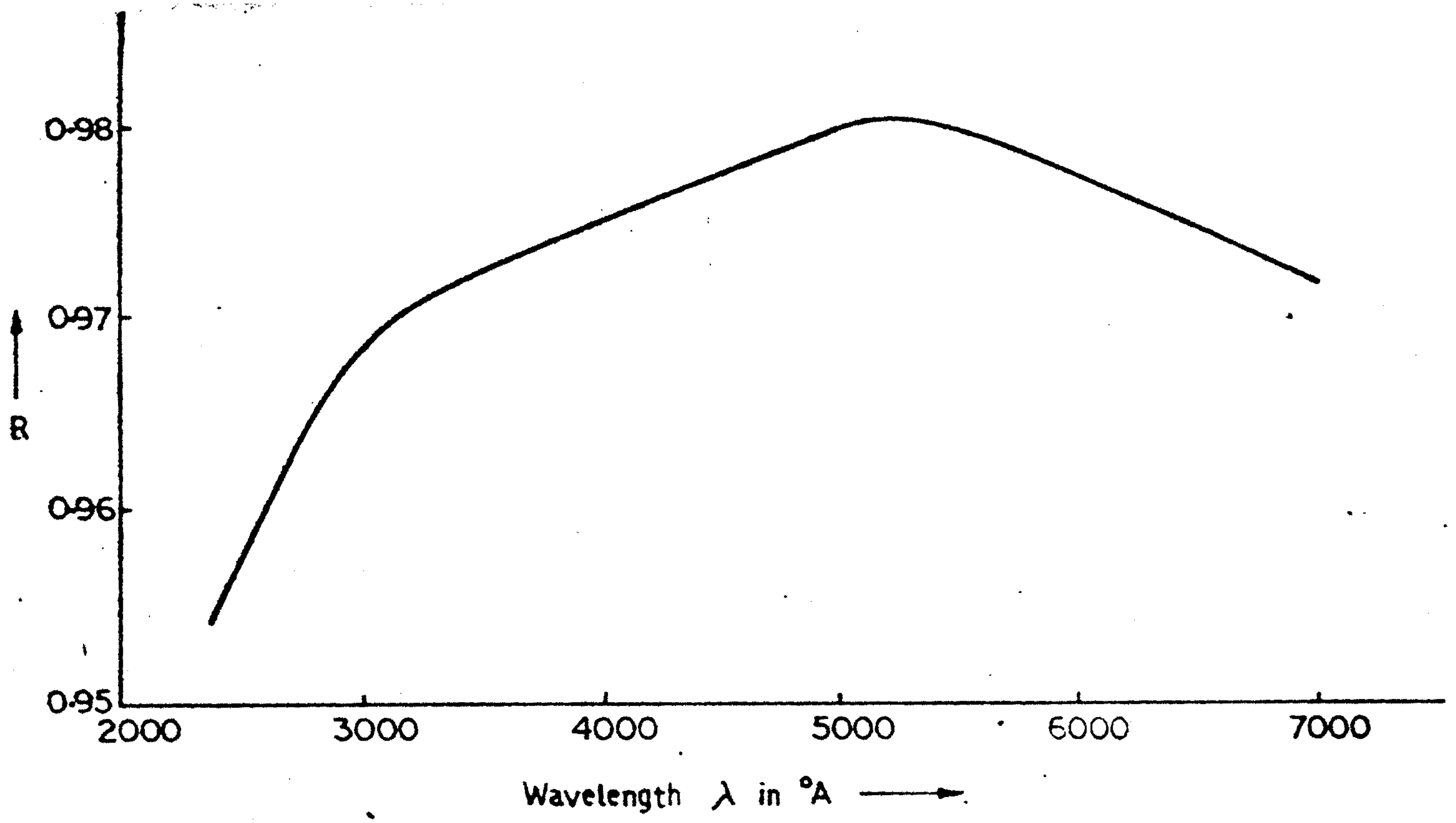
22 Willi Lehmann, J. of Luminescence 6 (1973) 455-470 @ North-Holland Publishing Company.

23. J.D. Ranade, R.P. Khare, Ind. J. Pure and Appl. Phys. Vol. 15, Jan. (1977), PP 14-16.



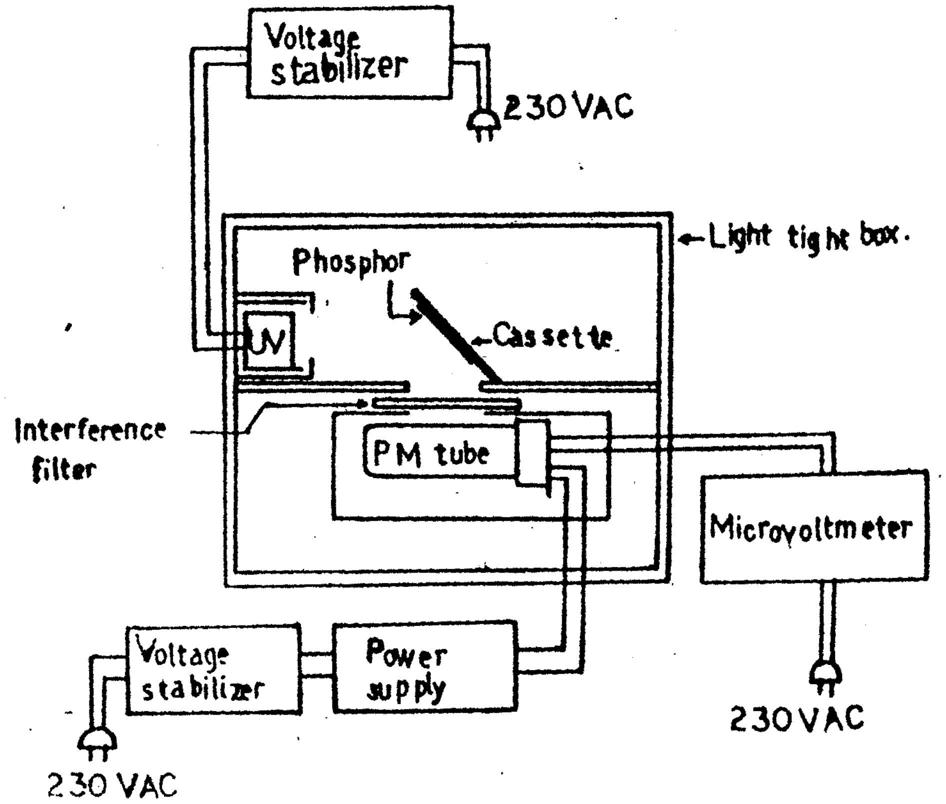
Experimental set up for absorption studies.

FIG. 2·1



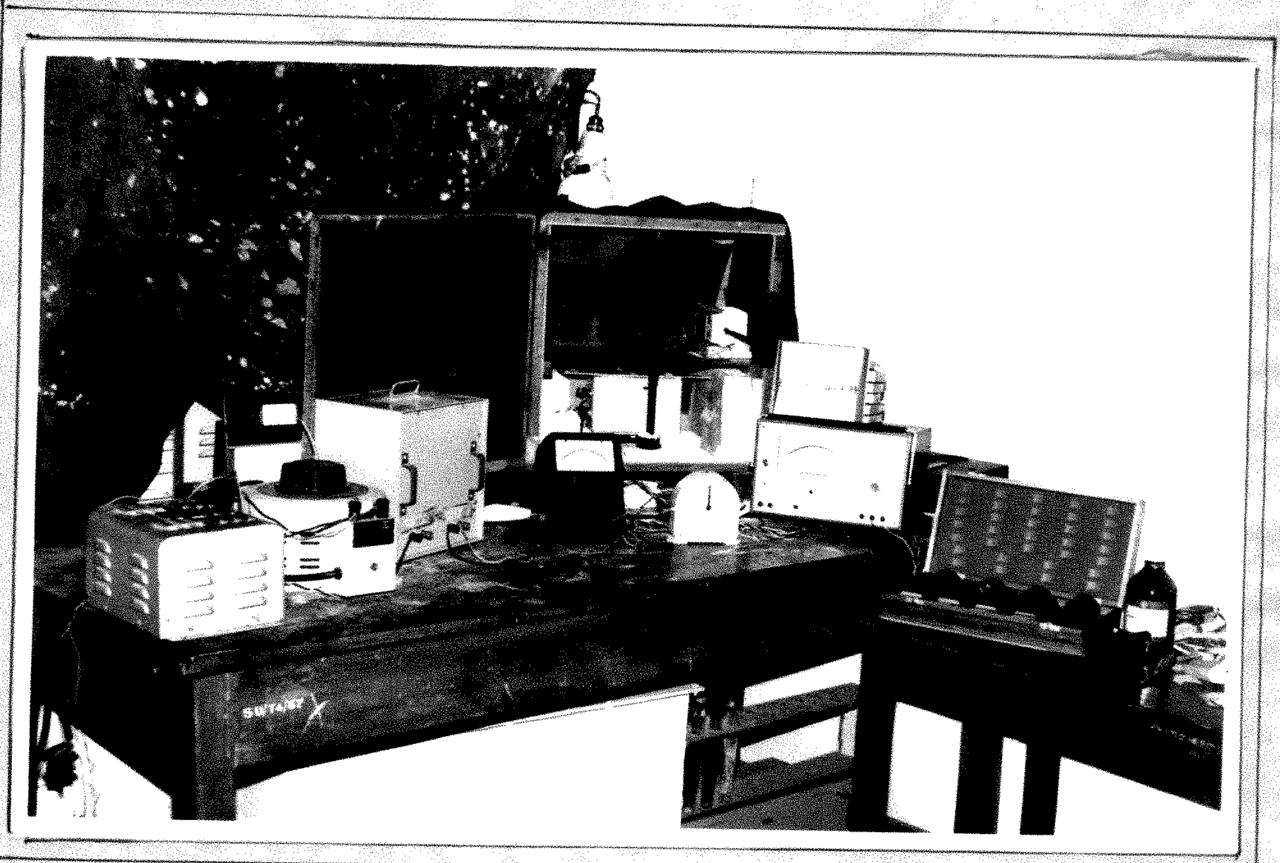
Standard reflectance of MgO.

FIG. 2·2



- Experimental set up for spectral emission studies.

FIG. 2.3



Photograph of
Experimental Set-up for Spectral Emission Studies.

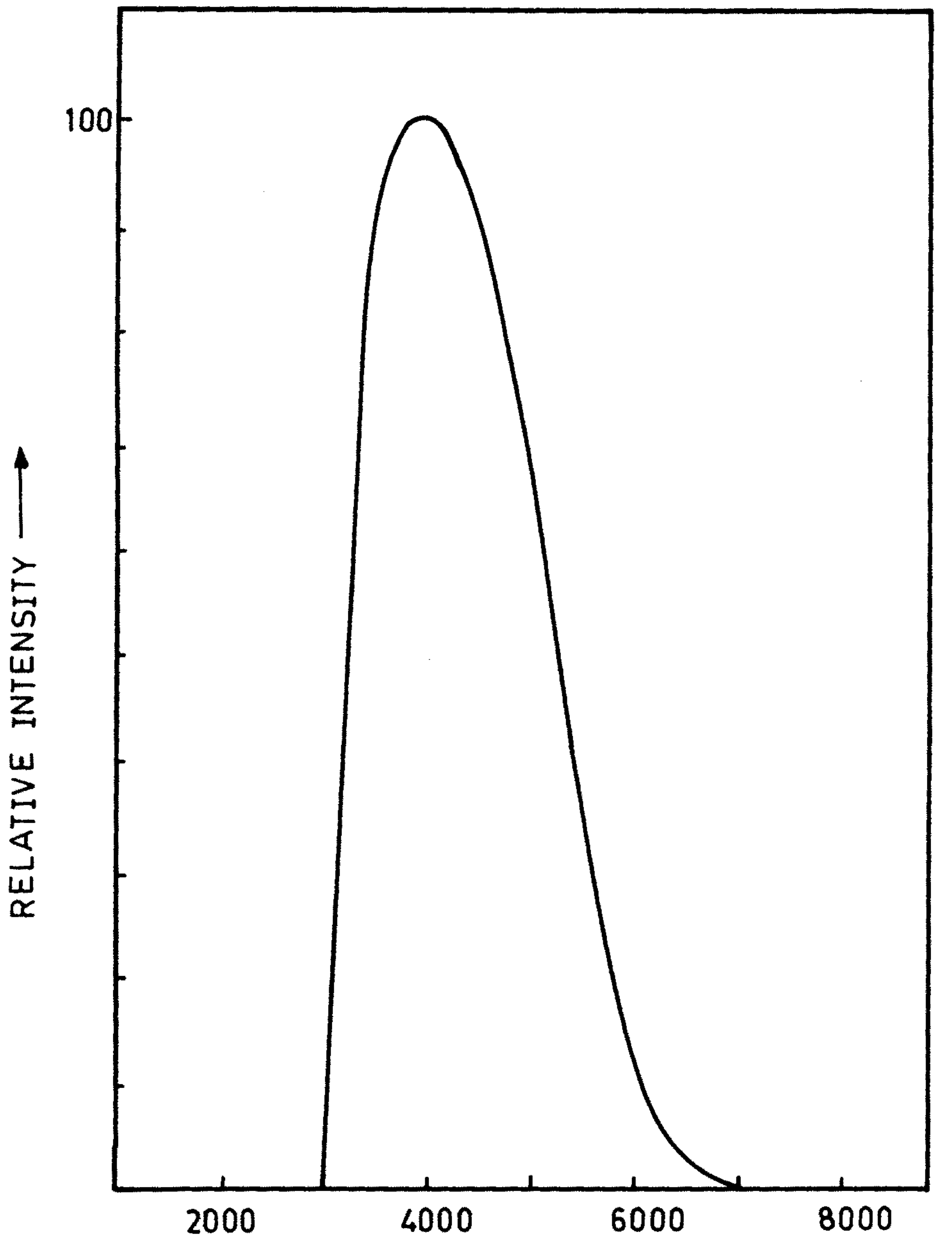
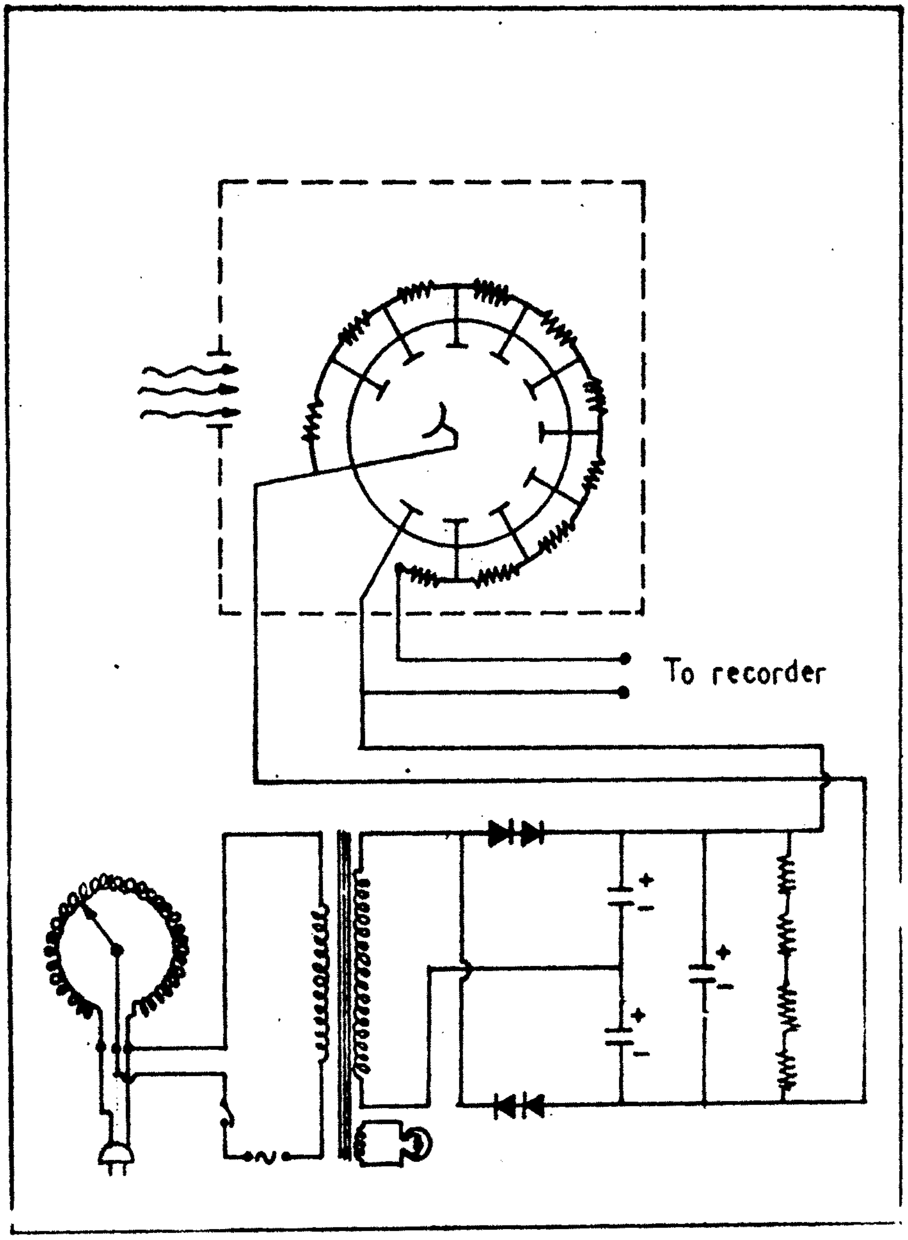


FIG. 2·4 : SPECTRAL RESPONSE CURRE FOR RCA 931A PM TUBE.



Circuit diagram of D.C. power supply and PM tube.