CHAPTER-II

EXPERIMENTAL

2.1 Synthesis of electroluminescent phosphors:

i) Preparation of the basic material:

Cubic zinc sulphide was the basic material used in the synthesis of electroluminescent phosphors. It was prepared by using a precipitation method. The starting materials such as soluble zinc compounds, ammonium compounds, and ammonia were all of Analar grade purity. \( \text{H}_2\text{S} \) used for precipitation was prepared in a Kipp's apparatus using Analar grade chemicals. \( \text{H}_2\text{S} \) thus prepared, was further purified by passing through various absorbents (air, glass-wool, distilled water etc.). The gas was finally bubbled into the appropriate solution of the \( \text{Zn-salt} \), the pH of which was maintained between 8-10. The unreacted gas was passed through another flask connected in series with the first and containing a part of the same \( \text{Zn-solution} \). The solutions were continuously stirred during the course of the precipitation so that the reaction was quick.

The \( \text{ZnS} \) thus obtained was thoroughly washed with luke warm distilled water by vigorous stirring, and kept for a day for sedimentation. Washing by sedimentation and decantation were repeatedly carried out for about 8 days till the material was free from soluble impurities such as chlorides, sulphates, ammonia, \( \text{H}_2\text{S} \) etc. The residue (\( \text{ZnS} \)) after filtration was washed with luke warm distilled water and finally with absolute
alcohol. The sulphide was dried in an electric oven at 70°C. The dry material was crushed, finely ground and sieved. The powder was finally dried in a vacuum-desicator.

X-ray diffraction pattern of the sample (Fig. 1) gave only broad maxima at expected 2θ angles of the maximum intensity, thus indicating that the crystal size for the sample was very small and the substance was nearly amorphous or disordered.

ii) Synthesis of phosphors:

a) Host matrix mixture

It is well known that pure and stoichiometric ZnS is nonluminescent. It acquires luminescent property only after suitable activation. The activators and co-activators play an important role in the luminescence behaviour. The choice and quantity of these activators determine the spectral characteristics of the emitted light and the luminous efficiency. We have used the Mn²⁺ and Sm³⁺ as activator and co-activator and sodium chloride as flux in the synthesis.

The phosphors were prepared essentially in the same manner as described in literature². The ZnS prepared by the above method and CdS (99.999%) supplied by Koch-Light Laboratories Ltd., was used as host matrix materials in our system.

The ZnS with or without CdS was intimately mixed with appropriate amounts of impurities in the form of their carbonates and nitrates and sodium chloride as flux in ethanol and the resulting slurry was dried in an electric oven at 70°C.
The mixture 7 to 10 g was transferred to a silica-boat of suitable capacity. The boats containing these phosphor mixtures were heated to the required temperature in $\text{H}_2\text{S}$ atmosphere for different durations in a specially constructed silica tube furnace described below.

b) Fabrication of furnace:

The kanthal wire of 18 Swg was wound over the central part (12") of a long translucent silica tube of 2" internal diameter and 30" length, and covered by applying a special cement (9 parts kaolin and 1 part borax). The wound portion of the tube was enclosed in a wider silica tube of 4" internal diameter and 12" length so that it covered the wound portion of silica tube, and the whole assembly was enclosed within a box made of asbestos cement sheets, containing magnesia asbestos powder so that it will minimise the heat losses. The calibrated Chromel-Alumel thermocouple covered with a protective silica sheet was introduced in such a way that the measuring junction of the thermocouple was at the centre of the furnace where the phosphor mixture in silica boat was kept for heating.

The phosphor mixture was cooled under the $\text{H}_2\text{S}$ atmosphere to room temperature and was removed from the furnace. It was crushed to fine powders by mortar pestle grinding. The phosphors thus synthesized were tested for their electroluminescence performance in the EL cell. (Vide please Tables II.1, II.2 & II.3)
Table II.1

Activator concentrations of ZnS:Mn:Cl and ZnS:Sm:Cl phosphors with 1% NaCl flux.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Mg gm atom per mole of ZnS</th>
<th>Sample No.</th>
<th>Sm gm atom per mole of ZnS</th>
</tr>
</thead>
<tbody>
<tr>
<td>SA</td>
<td>SB</td>
<td>SC</td>
<td></td>
</tr>
<tr>
<td>A1</td>
<td>B1</td>
<td>C1</td>
<td>1 x 10^{-2}</td>
</tr>
<tr>
<td>A2</td>
<td>B2</td>
<td>C2</td>
<td>5 x 10^{-3}</td>
</tr>
<tr>
<td>A3</td>
<td>B3</td>
<td>C3</td>
<td>1 x 10^{-3}</td>
</tr>
<tr>
<td>A4</td>
<td>B4</td>
<td>C4</td>
<td>5 x 10^{-4}</td>
</tr>
<tr>
<td>A5</td>
<td>B5</td>
<td>C5</td>
<td>1 x 10^{-4}</td>
</tr>
<tr>
<td>A6</td>
<td>B6</td>
<td>C6</td>
<td>5 x 10^{-5}</td>
</tr>
<tr>
<td>A7</td>
<td>B7</td>
<td>C7</td>
<td>1 x 10^{-5}</td>
</tr>
<tr>
<td>A8</td>
<td>B8</td>
<td>C8</td>
<td></td>
</tr>
</tbody>
</table>

Phosphors A1 to A8 have been fired in Argon atmosphere, phosphors B1 to B8 and C1 to C8 have been fired in H₂S atmosphere. All the phosphors were fired at 900°C for two hours.
### Table II.2
Activator concentrations of (Zn:Cd)S:Mn:Cl and (Zn:Cd)S:Sm:Cl phosphors with 1% NaCl flux.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Mn gm atom per mole of (Zn:Cd)S</th>
<th>Sample No.</th>
<th>Sm gm atom per mole of (Zn:Cd)S</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1</td>
<td>$1 \times 10^{-3}$</td>
<td>E1</td>
<td>$1 \times 10^{-2}$</td>
</tr>
<tr>
<td>D2</td>
<td>$2 \times 10^{-3}$</td>
<td>E2</td>
<td>$5 \times 10^{-3}$</td>
</tr>
<tr>
<td>D3</td>
<td>$4 \times 10^{-3}$</td>
<td>E3</td>
<td>$1 \times 10^{-3}$</td>
</tr>
<tr>
<td>D4</td>
<td>$6 \times 10^{-3}$</td>
<td>E4</td>
<td>$5 \times 10^{-4}$</td>
</tr>
<tr>
<td>D5</td>
<td>$1 \times 10^{-3}$</td>
<td>E5</td>
<td>$1 \times 10^{-4}$</td>
</tr>
<tr>
<td>D6</td>
<td>$2 \times 10^{-3}$</td>
<td>E6</td>
<td>$5 \times 10^{-5}$</td>
</tr>
<tr>
<td>D7</td>
<td>$4 \times 10^{-3}$</td>
<td>E7</td>
<td>$1 \times 10^{-5}$</td>
</tr>
<tr>
<td>D8</td>
<td>$6 \times 10^{-3}$</td>
<td>E8</td>
<td>-</td>
</tr>
</tbody>
</table>

All the phosphors have been fired in H$_2$S. Sample No. D1 to D4 were fired at 950°C for one hour and others from D5 to D8 and E1 to E8 were fired at 900°C for two hours. The molar ratio of (Zn:Cd)S is 87.2.
**Table II.3**

Activator and co-activator concentrations of \((\text{Zn}:\text{Cd})\text{S}:\text{Mn}:\text{Sm}:\text{Cl}\) phosphors with 1% NaCl flux.*

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Mn gm atom per mole of ((\text{Zn}:\text{Cd})\text{S})</th>
<th>Sm gm atom per mole of ((\text{Zn}:\text{Cd})\text{S})</th>
<th>((\text{Zn}<em>x\text{Cd}</em>{1-x})\text{S}) Sample No.</th>
<th>((\text{Zn}<em>x\text{Cd}</em>{1-x})\text{S}) molar ratio*</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1</td>
<td>(4 \times 10^{-3})</td>
<td>(1 \times 10^{-2})</td>
<td>G1</td>
<td>(1/0)</td>
</tr>
<tr>
<td>F2</td>
<td>(4 \times 10^{-3})</td>
<td>(5 \times 10^{-3})</td>
<td>G2</td>
<td>(9/1)</td>
</tr>
<tr>
<td>F3</td>
<td>(4 \times 10^{-3})</td>
<td>(1 \times 10^{-3})</td>
<td>G3</td>
<td>(8/2)</td>
</tr>
<tr>
<td>F4</td>
<td>(4 \times 10^{-3})</td>
<td>(5 \times 10^{-4})</td>
<td>G4</td>
<td>(7/3)</td>
</tr>
<tr>
<td>F5</td>
<td>(4 \times 10^{-3})</td>
<td>(1 \times 10^{-4})</td>
<td>G5</td>
<td>(6/4)</td>
</tr>
<tr>
<td>F6</td>
<td>(4 \times 10^{-3})</td>
<td>(5 \times 10^{-5})</td>
<td>G6</td>
<td>(5/5)</td>
</tr>
<tr>
<td>F7</td>
<td>(4 \times 10^{-3})</td>
<td>(1 \times 10^{-5})</td>
<td>G7</td>
<td>(4/6)</td>
</tr>
</tbody>
</table>

All the phosphors from F1 to F7 were fired in \(\text{H}_2\text{S}\) at 900°C for two hours. Phosphors from G1 to G7 were prepared without flux.*

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* x*
2.2 Method of testing:

i) Electroluminescent cell:

An electroluminescent cell consists of a phosphor layer embedded in a dielectric and sandwiched between two plane parallel electrodes. One of the electrodes must necessarily be transparent so as to render observation of the light emitted in electroluminescence. The efficiency of an electroluminescent cell depends on the applied voltage and its frequency, the thickness of the phosphor and upon the quality of the phosphor used. Electroluminescent cell fabricated is described below.

The phosphor was sieved and its pasty suspension in castor oil was applied to a conducting glass, having resistance 100 to 200 ohms per square centimeter and optical transmission of 90% or more. It served as the first electrode. The paste on conducting glass was covered with a thin and uniform sheet of mica, having high dielectric constant and sufficient breakdown strength. Aluminum plate of desired size was used as the second electrode. The cell of this type behaves as a luminous condensor - the phosphor being sandwiched between two parallel electrodes. This condensor was enclosed in a backlite frame, provided with a small window in the middle of the top surface, and a screw arrangement to adjust the inter-electrode distance and pressure. The electroluminescent cell fabricated like this is shown in Fig. 2(a).
ii) **Voltage and frequency dependence of electroluminescence (EL) emission**

a) **Source of excitation**

The phosphors under the investigation were excited by applying sinusoidal voltage between the two electrodes of the EL cell. The sinusoidal voltage source was a Phillips audio frequency generator type GM 2308/90 having frequency range from 50 Hz to 16 kHz and output voltage with a minimum of 90 volts. As the voltage was not sufficient to excite the phosphor powder embedded in castor oil, the exciting source was coupled to a wide-band amplifier (Teletronics-SF-100) capable of giving voltage from 0 to 5 kV.

b) **Detector unit**

The electroluminescence emission from the cell was detected by IP21 photomultiplier tube operated with a stabilized DC power supply. The output of the IP21 photomultiplier tube was fed to a sensitive automatic plotter. Thus the voltage and frequency dependence of electroluminescence emission was recorded.

The schematic diagram of the EL measurements is shown in Fig. 2(b). For studies of the brightness waves, the output of the photomultiplier was fed to a double beam cathode-ray oscilloscope (Textronix, Type 422/R 422 with a.c. power supply SN 20,000 and up).

The spectral distribution of electroluminescence emission
was studied using a constant deviation spectrometer. The
electroluminescent cell was placed in front of the telescope of
contant deviation spectrometer as a source of light and
intensities of the spectral lines or bands were measured by
IP21 photomultiplier tube placed near the collimator.

2.3 X-ray analysis of synthesized phosphors:

X-ray analysis of selected phosphors in relation to various
phases such as α and β ZnS and the disordered phase was done
using Cu Kα radiation (1.54 Å) of the Philips X-ray diffraction
generator (Type PW 1008). Nickel filter was used for the
elimination of Kβ radiation. The specimens were prepared by
coated fibre method. The phosphor powders were mixed with an
adhesive binder and then they were coated on the pyrex fibre.
The diameter of these fibers was of the order of 0.1 mm. The
Phillips Debije Scherrer powder camera (Type PW 1026/10) of
57.54 mm diameter was used with entry collimator and beam
exit tube for getting the X-ray diffraction patterns.

2.4 Fluorescence spectral measurements:

(a) Cryostat:

A metal cryostat was constructed by which the fluorescence
spectra of the sample was recorded at liquid nitrogen temperature.
The phosphor was cemented onto the sample holder with
nonfluorescent adhesive. After cooling with liquid nitrogen,
the equilibrium temperature of the sample was usually found
85° ± 1 K. The sample temperature could be measured to within
\(1 \text{K}\) with a copper-constant thermocouple (made of 30 gauge wire) with the junction cemented to the sample using the same adhesive.

(b) **Excitation source**:

The phosphors were excited by an ultraviolet source emitting predominantly the 3650 Å Hg doublet (UV products U.S.A. Type UVS-12) and low pressure mercury tube emitting predominantly 2537 Å (Mineralight, R51, UV products, Pennsylvania, U.S.A.). The phosphors were also excited by X-rays CuKa radiation (1.54 Å) (Phillips X-ray diffraction generator, Type PW-1008) using nickel filter. The X-ray machine was operated at 37 kV and 13 mA.

(c) **Detector unit**:

The fluorescence spectral measurements of the phosphors excited by 3650 Å and 2537 Å at room temperature and at liquid nitrogen temperature were carried out using the constant deviation spectrometer in front of the window B of the cryostat. The fluorescence spectral measurements of these phosphors excited by X-rays at room temperature were also carried out. The radiation of these excitation sources were focussed on the sample through window B, made of quartz. The intensities of lines or bands were detected by IP21 photomultiplier tube. The schematic diagram of fluorescence measurements is shown in Fig. 3.

2.5 **Luminescence efficiency**:

a) **Nitometer (Luxmeter)**:

The Nitometer has the first and immediate aim of measuring the shining of any object, which may concern the bodies which
radiate by themselves - sources of light such as sun, fire, metals at high temperature or objects which diffuse a light which they receive - moon, paper on which one writes, ceiling of a room, soil of road, etc.

The Nitometer can be similarly used as luxmeter for measuring the lighting and as photometer for measuring luminous intensities. The Nitometer thus finds its use in all the techniques which require the exact measurement of shining, the lighting or luminous intensities. The Nitometer enables correct determination of the time of pose, which depends in fact on the maximum and minimum shining of the objects viewed. Medical control and selection of observers, specially the night observers, where it is indispensable to know exactly the shining of the depth on which the activity tests are carried out. Industries of the luminescent products and industries using these products (watch making in particular) have Nitometer as good tool for measuring the efficiency.

b) Nitometer - General description :

The Nitometer has a sight glass with which we view the object of which we wish to measure the brilliance and in the field of which is found a small region whose brilliance, adjustable at will, by means of a neutral groove wedge, can be led to be the same as that of the object examined. Then we read on the operating organ of the wedge the required brilliance in candles/m^2.

The sight glass, with magnifying power 2 is formed of object C and of ocular A (Fig. 4). The object C gives the object viewed an image in the plane of a cube of Lummer C, transparent
through its surface except in a small region g, which acts as a mirror sending back towards the ocular A. The image of the opeline V is lighted by the lamp E.

The light coming from V crosses the neutral wedge D and a counter-wedge whose assembly forms the plane-parallel blade, optically and photometrically, in such a way as the pellet g appears of uniform brilliance. The counter-wedge I is fixed, the wedge D, on the contrary, can undergo a transfer by means of a system of gear and rack controlled by a drum B. This transfer can vary the thickness of the neutral glass interposed between V and g. It thus enables to adjust at will the brilliance of g. Besides, the surcharges of the neutral glass can be introduced either on the beam coming from V or on the beam coming from the object viewed.

The milling wheel controls the movement of the ocular A and enables its development on pellet G. It is the same for object C, which is moved by rotation of the polished disc, so as to form in the plane g the image of the object viewed, whatever may be their distance.

It is necessary that the lamp E communicates with the opeline V standard brilliance which is extremely constant. This result is obtained by lowering not the intensity of the electric current which crosses the lamp E but the internal resistance of E with a determined value. To that effect the lamp E is shown on one of the branches of Wheatstone's bridge in the diagonal of which is inserted a galvanoscope. The two extremities of the other
Thus the brilliances or luminescences of objects viewed with the Nitrometer are read directly on a drum in nits or candle per square meter.

2.6 **Electron paramagnetic resonance measurements**:

1) **The ESR spectrometer**:

The electron spin resonance studies were carried out in an X-band reflection cavity spectrometer. The apparatus consists of a Varian X-band microwave bridge (V-4500-40), the Varian Klystron power supply (V-4500-20), the Varian Klystron control unit (V-4500-10) and the microwave cavity (V-4500-30).

Provision was made, in this spectrometer for low frequency magnetic field modulation for derivative recording; this was provided by a 37 Sec⁻¹ oscillator and power amplifier. The output of a twin tee narrow band amplifier was detected with a phase sensitive detector and recorded on a Honeywell Brown strip chart recorder. There was, of course, the usual provision for oscilloscope display of the EPR signal by Crystal-Video detection.

The Varian V-4500-10 Klystron unit has provision for the stabilization of the frequency of the Klystron, with the sample cavity as reference. The Klystron is frequency modulated by impressing a 10 kHz modulation on its reflector voltage and 10 kHz...
component of the output of the microwave crystal diode (IN 23B) is
detected with a phase sensitive detector; the detected output fed
back to the reflector of the Klystron in the correct phase
stabilizes the Klystron frequency.

A Varian (V-4012-A), 12" diameter electromagnet together with
its V-1200-A power supply and V-2101-C voltage regulator provided
the magnetic field for the initial spin resonance studies. Later,
the Varian system was replaced by a 12" diameter electromagnet
(constructed locally from "Tata A grade steel") along with a
stabilized magnet power supply that was built in the T.I.F.R.
laboratories. The homogeneity of this magnet was found to be
3 parts in $10^5$ for a cylindrical sample of 1 cm length and 1 mm
in radius. This was obtained after shimming, using small strips
of nickel foil placed on the pole pieces.

ii) Measurements of magnetic field strength:

Magnetic fields were measured in terms of the proton
magnetic resonance frequency using a proton resonance apparatus
similar to that described by Knoebel and Hahn using mineral oil
as the proton sample. The proton resonance frequencies were
measured with the aid of a Hewlett-Packard Frequency counter.

A loosely coupled antenna placed inside the proton oscillator
box was coupled to a tunable radio frequency amplifier and output
of the amplifier was fed into a Hewlett-Packard frequency
converter (H.P. 525 A) and counter (H.P. 524 B) combination. The
error in the proton resonance frequency due to the dispersion
effect was measured by following, on the frequency counter, the
changes in the oscillator frequency when the magnetic field slowly passed through the resonance value. The error was found to be less than ± 40 Hz in 14 MHz (i.e., ≈ 3 parts in 10⁶). In order to minimise the errors due to dispersion, care was taken that the magnetic field did not drift during measurements of the proton resonance frequency.

The block diagram of the EPR spectrometer is shown in Fig. 5.
REFERENCES

1. Corey, A.S.

2. Wachtel, A.J.

NITOMETER

A - OCULAR
B - CONTROL KNOB
C - OBJECT
D - NEUTRAL GLASS
E - STANDARD LAMP
F - RHEOSTAT

FIG. 4
Fig. 5 Block diagram of simple spectrometer.