CHAPTER III
ELECTROLUMINESCENCE
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3.1 Voltage and frequency dependence of electroluminescent emission:

The electroluminescent emission of phosphors has been measured over a wide range of the sinusoidal voltage $V$, and the excitation frequency $F$. The measurements were made on conventional electroluminescent cells, as described in Chapter-II. The powdered phosphors were mixed with a little castor oil and the pasty suspension was placed in a cell consisting of an aluminum back electrode, and a front electrode of conducting glass with an electrode spacing of about 70-80 $\mu$. The details of the cell design and the intensity measuring unit have already been described in Chapter-II.

3.2 Voltage dependence of EL emission:

Destriau$^1$ made a generalized observation that the intensity of emitted radiation from a powder cell increases rather rapidly (exponentially), with increasing applied voltage. This has been confirmed in subsequent studies by other workers and found to be true for individual phosphor grains$^2$ and also for single crystals$^3$.

Destriau$^1$ had proposed the following relationship:

$$B = B_0 V^2 \exp \left(-\frac{C}{V}\right) \quad (i)$$

where $B$ is the intensity of EL emission, $V$ is the applied voltage,
and $B_0$ and $C$ are constants. Following Destriau, a number of equations for variation of EL brightness ($B$) as a function of applied voltage, have been proposed from time to time. Some of them have essentially forms $^4,5,6$, some differ only slightly $^7-8$ while others have a bearing on experimental data and are empirical in nature $^9,10,11$.

Thus, for a single phosphor particle, the variation was found to be linear by Waymouth and Bitter $^{12}$. They suggested a voltage threshold at which the effect commences. Similar observations regarding threshold voltage were made by others $^{13,14,15}$. For thin films, the average brightness of ZnS:Mn phosphor was found to vary approximately as the seventh power of the applied voltage $^{16}$.

On the basis of exhaustion barrier theory, Taylor $^{17}$ deduced the following relation:

$$B = B_0 \exp \left[ -\frac{(V_0/V)^{0.5}}{Y} \right]$$

(ii)

whereas on the basis of impact excitation mechanism Nagy $^{18}$ derived the following relation:

$$B = B_0 \exp \left[ -\frac{b}{(1 + CV)^2} \right]$$

(iii)

where $B_0$, $b$, and $C$ are constants.

Lehamann $^{19}$ and others $^{20}$ suggested various forms of the equation such as

$$B = B_0 V \exp \left[ -\frac{C}{(V + V_0)} \right]$$

(iv)
where $B_0$, $C$ and $V_0$ are very mostly linear with frequency. Over wider ranges of voltages, the equation was, however, modified as

$$B = B_0 \exp \left( -C/(V + V_0) \right)$$

(v)

At high voltages, where $B$ reaches a saturation ($\approx B_0$), the following relation was observed:

$$B = B_0 \exp (-C/V)$$

(vi)

Later in 1960 Lehmann reported that the basic excitation mechanism of EL follows the voltage dependence as

$$B = B_0 \exp (-\sqrt{V}/V)$$

(vii)

and the square root in the exponent of Taylor's equation is due mainly to the broad particle size distribution of regular phosphors. This view is supported by theoretical consideration.

Relations similar to those of Taylor were reported by several workers. There does not seem to be any noteworthy contribution to the study of voltage dependence of EL emission in the last few years and the relations deduced for brightness as a function of voltage are little different from those established earlier.

3.3 Frequency dependence of EL emission:

During each cyclic operation, the luminous condenser is charged and discharged resulting in a certain amount of light emission. It is expected that a more rapid cyclic operation would emit more light. This accounts for an approximately linear
Thus increase in brightness with increase in frequency was observed for single crystals (Piper and Williams\textsuperscript{3}) or thin films (Halsted and Koller\textsuperscript{26}) and powders (Zalm\textsuperscript{5}). However, deviations are observed at high frequencies where the intensity may saturate or even fall with increasing frequency\textsuperscript{27-29}. Zalm\textsuperscript{2} however, showed that the assumption of constant light being emitted in each half cycle was wrong. The light emitted from the EL cell can be expressed by equation

$$B = B_0 \exp \left(-\frac{C}{\sqrt{V}}\right)$$

where $B_0$ and $C$ are the constants. This means

$$B \propto \exp \left(-\frac{\text{const}}{\sqrt{V}}\right)$$

where voltage $V$ is function of $\omega t$, $\omega$ being the frequency and $t$ the time. So light emitted can be written as

$$B \propto \exp \left(-\frac{\text{const}}{\sqrt{f(\omega t)}}\right)$$

From equation (c) it is clear that the light emitted for a cycle is inversely proportional to $\omega$ and hence the total light emitted per unit time is independent of frequency which is contrary to the observation.

Further, the voltage drop across the cell is governed by the extra capacitance and resistance present in the experimental EL cell. The actual voltage across the cell having the resistance $R$
for a series of capacitors all of value $C$, is given by

$$V = \omega R C V_0 \sqrt{1 + \omega^2 R^2 C^2}$$

where $V_0$ is the amplitude of the applied voltage. Thus it is evident that if $RC \gg 1/\omega$, the voltage across the cell and consequently the luminous emittance is independent of the frequency, while with $RC \ll 1/\omega$, the emittance increases more linearly with the frequency. It is thus possible to describe any observed frequency dependence with a suitable distribution in $RC$ values of the system.

Piper and Williams$^3$ have proposed a physical model which accounts for the linear frequency dependence in a different way. In addition to above, it is a common observation that at higher frequencies, saturation sets in and this occurs more quickly for the green than the blue emission bands. For instance, Waymouth and Bitter$^{12}$ observed that the green band in a ZnS:Cu:Pb phosphor was found to vary linearly with frequency up to several hundred cycles per second and to saturate above 1 kHz, whereas the blue band behaved linearly up to at least 2 kHz. Similar type of observations were also reported by other workers$^{30,31,32}$.

For Cu activated ZnS phosphors poisoned by Fe, Co or Ni, Lehmann$^6$ found that brightness increases with frequency. In some cases the brightness depends upon the impurity content and saturation was observed at higher frequencies. If there is only a single emission band, the frequency dependence of EL emission is found to be linear$^{33}$. Ballentyne and Ray$^{34}$ reported that the
brightness of conventional ZnS(Cu) EL phosphors varies sub-linearly with frequency and expressed as

\[ B \propto F^n \]

where \( n = 0.7 \) and 0.8. At higher frequency, in general a tendency to saturation was observed. The brightness variation of the blue band is expressed by the equation

\[ B = B_0 F^x \exp \left( \frac{-C}{\sqrt{V}} \right) \]

where \( x = 1 \) at high voltages but at lower voltages \( x \) is a function of voltage. Similarly the brightness variation of the red and green bands is expressed by the relation

\[ B = B_0 \sqrt{F} \exp \left( \frac{-C}{\sqrt{V}} \right) \]

where in equations (f) and (g) \( B_0 \) and \( C \) are constants independent of voltage and frequency.

3.4 Results and discussion:

a) Voltage dependence:

The voltage dependence of electroluminescent brightness at different frequencies is shown in Figs. 1, 2 and 3. Most of the phosphors examined show no noticeable colour change when the voltage is varied and qualitatively, all these phosphors have the same dependence of the emitted light intensity on the exciting voltage. Some special points of significance are:

a) The light intensity increases rapidly for low and slowly for high voltages.
b) Rate of increase is greater for higher frequencies and vice versa, and

c) The dependence of B on V cannot be expressed by a simple power law, otherwise the curves in Figs. 1 and 2 would be straight lines.

From Figs. 1, 2 and 3 we observe that the brightness follows the relation

\[ B = B_0 \exp \left(-\frac{C}{\sqrt{V}}\right) \]  

(A)

given by Alifrey and Taylor\(^4\) for a good range of frequencies, where \(B_0\) and C are constants and V is the applied potential. The values of \(B_0\) and C of some typical samples are listed in Table-1. The values of constant C were found to lie between 200 and 600. \(B_0\) is found to be more sensitive to frequency than C.

The variation of brightness according to the relation

\[ B = B_0 \exp \left(-\frac{C}{\sqrt{V}}\right) \]

indicates that barriers of Mott-Schottky type are formed in which the thickness of barrier increases as the square root of the applied voltage. The mechanism of excitation is, therefore, an acceleration collision type, according to which electrons from the donor levels liberated by the applied field or temperature, are accelerated and collides with an activator centre whereby the latter is ionized or excited. This mechanism was discussed already in Chapter-1.

b) Potential distribution inside EL ZnS particle:

It is of interest to see how the applied a.c. voltage is
### Table III.1

Values of the constants $B_0$ and $C$ at different frequencies.

<table>
<thead>
<tr>
<th>Samples</th>
<th>500 C/S</th>
<th>2 k C/S</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$B_0$</td>
<td>$C$</td>
</tr>
<tr>
<td>ZnS:Sm:Cl</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C3</td>
<td>2512</td>
<td>71.4</td>
</tr>
<tr>
<td>C4</td>
<td>3631</td>
<td>69.0</td>
</tr>
<tr>
<td>C5</td>
<td>1318</td>
<td>178.6</td>
</tr>
<tr>
<td>C6</td>
<td>3090</td>
<td>80.0</td>
</tr>
<tr>
<td>C8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Zn,Cd)S:Mn:Cl</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>D2</td>
<td>676.1</td>
<td>222.2</td>
</tr>
<tr>
<td>D3</td>
<td>4266</td>
<td>144.0</td>
</tr>
<tr>
<td>D4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(Zn,Cd)S:Sm:Cl</td>
<td></td>
<td></td>
</tr>
<tr>
<td>E1</td>
<td>3548</td>
<td>141.2</td>
</tr>
<tr>
<td>E2</td>
<td>2239</td>
<td>120.0</td>
</tr>
<tr>
<td>E3</td>
<td>2692</td>
<td>70.0</td>
</tr>
<tr>
<td>E4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>E5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>E7</td>
<td>1070</td>
<td>61.6</td>
</tr>
<tr>
<td>(Zn,Cd)S:Mn: Sm:Cl</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F1</td>
<td>1995</td>
<td>153.8</td>
</tr>
<tr>
<td>F2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>F3</td>
<td>4571</td>
<td>126.3</td>
</tr>
<tr>
<td>F4</td>
<td>5370</td>
<td>100.0</td>
</tr>
<tr>
<td>F5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>F6</td>
<td>1820</td>
<td>200</td>
</tr>
<tr>
<td>F7</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
distributed in a phosphor system composed of microcrystallites. The result of a voltage saturation of EL brightness seems to be important, since it indicates that only a very limited number of carriers can be excited during each cycle of the applied alternating voltage even if this voltage becomes infinite. This also explains why for a given phosphor and for other given conditions, a brightness exceeding the saturation value cannot be obtained by an increase in voltage.

Voltage brightness relationships for EL powder phosphors of microcrystalite composition become complicated on account of non-uniformity of the emission through the phosphor volume and hence difficult for a consistent theoretical interpretation. Even the emission of a single phosphor particle normally is very non-uniform.

From microscopic studies, Zalm observed that the light is emitted by localized spots at the surface. The electrons are transported by the field to the right hand side of the grain, leaving behind a positive space charge. Due to this positive space charge, the field strength at the sensitive spot is enhanced and the rest released from surface donor levels and produce secondaries, enlarging the space charge and so on, thus starting an avalanche, until the voltage drop across such a spot reaches a maximum. Thus the theory supports the validity of equation

\[ B = B_0 \exp \left( \frac{-C}{\sqrt{V}} \right) \]

c) Frequency dependence:

Figs. 4, 5 and 6 show the frequency dependence of the phosphors.
It may be noted that the brightness may tend to saturate as the frequency is increased, and this tendency becomes less as applied voltage is increased. At higher applied voltage above 500 volts the emittance some times increases even more than linearly.

According to Thornton the rate of recombination is determined by field controlled release of electrons from traps and the brightness is given by

$$B = N_o f \left[ 1 - \exp \left( -\frac{A}{f} \right) \right]$$  \hspace{1cm} (i)

where $N_o$ is the constant number of excited centres for each half cycle of the voltage, and $A$ increases as the voltage is increased. With increase in frequency, the above equation tends to

$$B = N_o A \hspace{1cm} \cdots \hspace{1cm} (ii)$$

which accounts for the saturation effect.

At very low voltages, depletion of ionized activators does not occur during the cycle even at lower frequencies and $N_o$ is expected to be independent of frequency. At high voltages, however, depletion of ionized activators is strong and $N_o$ varies as $f^{1/2}$ and, therefore, the slope of the curves increases at higher voltages.

Piper and Williams have proposed a physical model which accounts for the linear frequency dependence of EL emittance. The primary electrons which start the excitation originate from the donor impurity levels inside the ZnS which are emptied by field ionization, a process which is strongly field dependent.
all available donor levels get almost immediately exhausted in a high field. For such a model, the following conditions are to be fulfilled for the emittance to be linearly dependent on frequency:

i) The time required for electrons to return to the excited region (donor levels) and to recombine there with the ionized centres should be shorter than the time between successive excitations.

ii) The rate of return of electrons to the excitation region increases with increasing voltage.

Several other conditions have also been suggested, but those mentioned above would suffice to justify our observation on frequency dependence of EL emission.

d) Spectral composition:

i) ZnS:Mn:Cl phosphors:

The spectral distribution of the electroluminescent output for the ZnS:Mn:Cl electroluminophor is shown in Fig. 7(a). It may be noted that for ZnS:Mn:Cl electroluminophors have peak emission at about 580 nm. It is known that the yellow or orange emissions take place due to the transitions between the localised atomic levels for the manganese ions, whereas the green and blue emissions take place due to transitions between the perturbed crystal states and the levels in the crystal band. This view is supported by the fact that λ maximum remains unchanged over wide variation of Mn content and there is no colour shift observed spectroscopically.
The activator and co-activator ions, are necessary for the transfer of energy from an accelerated charge carrier to the Mn$^{2+}$ electron so that they get excited to a higher energy state. The excitation of Mn$^{2+}$ ions means a transition, $6S \rightarrow 4G$, which involves a spin reversal. It appears very unlikely that a mere collision with an accelerated charge carrier, having a large kinetic energy, would cause this transition. An intermediate state is necessary which appears to be furnished by Cl$^-$ ions. If Cl$^-$ and Mn$^{2+}$ occupy neighbouring sites, the electron localized around the Cl$^-$ ion can transfer its energy to the electron on the Mn$^{2+}$ ions, causing the transition $6S \rightarrow 4G$.

11) ZnS:Sm:Cl phosphor:

The spectral distribution of electroluminescent emission for ZnS:Sm:Cl powder electroluminophor is shown in Fig. 7(b). It may be noted that the EL spectrum shifts towards shorter wavelength side with increase in frequency. Here we may assume that different types of luminescent centres are formed due to Sm$^{3+}$. Now if we consider the Schön-Klasens model, an empty low-lying centre will be filled by an electron from a filled higher centre if sufficient time and activation energy for the transition are available (Zalm$^5$). At lower frequencies, sufficient time required to transfer the electron from the higher centre is available and hence the recombination takes place at a higher centre i.e. the longer wavelength emission will predominate. However, at higher frequencies, the case will be reversed and, therefore, there will
be no transfer of the electron from the higher centre. Consequently, shorter wavelength emission will be favoured.

iii) (Zn:Cd)S:Mn:Sm:Cl phosphors;

Electroluminescent zinc sulphide phosphors activated by copper and manganese have been studied extensively\(^\text{36-37}\) because they enable a wide range of colours to be achieved by variation in their compositions. Zinc and cadmium sulphide phosphors are found to be poorly electroluminescent. Several explanations have been given for this behaviour. One of the reasons for the poor electroluminescence of (Zn:Cd)S:Cu phosphors was explained by their tendency to crystallise only in the hexagonal modification. The particles of such hexagonal phosphors were much more perfect in structure than the particles of cubic or well EL ZnS phosphors. Thus they lack in having structural faults, stacking disorders, voids etc. which are believed to be essential for electroluminescence.

The spectral distribution of the electroluminescent output for the binary systems of (Zn:Cd)S:Mn:Cl and (Zn:Cd)S:Sm:Cl is shown in Figs. 7(c) and 7(d). It may be noted that these phosphors have peak emission at about 560 nm and 555 nm. The peak emission of (Zn:Cd)S:Mn:Cl electroluminophor also depends upon the duration of firing and atmosphere. Both Mn and Sm ions in (Zn:Cd)S show EL emission in nearly the same spectral region. The electron configurations of these ions relating to the EL emission belong to inner shell type. The luminescence transitions are different, that is, d-d transitions in Mn and f-f transitions in Sm ions respectively.
Fig. 7(e) shows the electroluminescent output of (Zn,Cd)S: Mn:Sm:Cl phosphors. It is seen that (Zn,Cd)S: Mn:Sm:Cl phosphors have peak emission at 580 nm. The colour of the emission of electroluminescent phosphors of this series does not change appreciably with frequency. The role of co-activator in (Zn,Cd)S: Mn:Sm:Cl phosphors is only to affect the intensity of electroluminescent emission. The possible EL mechanism of this system is an acceleration collision one and is discussed in Chapter I.

e) Studies of brightness waves:

The variation in the EL brightness with time, during the application of a.c. fields are called 'Brightness waves'. The shape of the brightness wave depends upon the field intensity, the frequency and the direction in which the light output is observed. It depends also on the nature of the activator and co-activator used in the system. For some phosphors, it is affected by the spectral region also.

Generally, phosphors exhibit two main or the so-called 'primary' peaks during each cycle of the applied voltage. Some phosphors, however, show additional much smaller or minor peaks referred to as 'secondary' peaks. The existence of 'secondary' peaks is related to the electrons, which recombine with luminescence centres after a delay resulting from trapping.  

The electroluminescent brightness patterns at room temperature obtained by varying either the voltage or the frequency are shown in Fig. 8(a,b,c,d). It may be noted that only one peak per half
cycle of the applied voltage is observed, since luminescent centres are directly excited by accelerated electrons which are supplied by tunnelling from electrode.\(^{40-41}\).

The observed peaks are not of equal amplitude. According to Destriau this is on account of the fact that the exciting voltage is not perfectly sinusoidal but contains certain harmonics. Ince\(^{42}\) showed that a 6\% harmonic content in the applied waveform leads to a difference in the peak height of 40\%, whereas this difference is negligible for a harmonic content of only 0.3\%. The same asymmetry is also observed by Zalm\(^{5}\) and they have concluded that this lack of symmetry is due to the emission of light at the side facing the cathode. This asymmetry may also be due to the self-absorption of light or due to the scattering of light by interadjacent layers of powder or by the individual particles.\(^{43}\)

The brightness waves do not show the secondary peaks. The secondary peaks occur in brightness waves due to release of electrons trapped at a considerable distance away from the ionized luminescence centres.\(^{43}\) Absence of secondary peaks in the present study leads to the conclusion that the electron traps located close to the luminescence centres.

3.5 **Summary:**

It was confirmed experimentally that the (Zn:Cd)S:Mn:Sm:Cl electroluminescent phosphor has the voltage dependence of brightness expressed by the equation

\[ B = B_0 \exp \left( -\frac{c}{\sqrt{v}} \right). \]
The electroluminescent brightness shows saturation at higher frequencies.

Both Mn and Sm ions in (Zn: Cd)S show electroluminescent emission in nearly the same spectral region, and the electron configuration of these ions relating to luminescence belongs to the inner shell type. The luminescence transitions are different, that is, d-d transition in Mn ions and f-f transition in Sm ions, respectively. The role of co-activator in (Zn: Cd): Mn: Sm: Cl phosphor is only to affect the intensity of electroluminescent emission.

The brightness waves do not show the secondary peaks but shows two primary peaks per cycle of applied voltage. The electron traps, therefore, are located close to the luminescence centres.

The mechanism of excitation is an acceleration collision one, according to which electrons from the donor levels liberated by the applied field or temperature, are accelerated and collide with an activator centre whereby the latter is ionized or excited.
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ZnS: Sm: Cl

500 C/S

FIG 1 A
(Zn: Cd)S : Mn: Cl

500 C/S
(Zn:Cd)S:Sm:Cl

FIG 1 C

500 C/S

V

B

V

FIG 1 C

1

2

3

7
(Zn:Cd)S:Mn:Sm:Cl

500 C/S

FIG 1 D
ZnS:Sm:Cl

500 C/S

FIG 2A
(Zn:Cd)S:Mn:Cl

FIG 2 B
(Zn:Cd)S:Sm:Cl

FIG 2c
(Zn: Cd)S:Mn:Sm:Cl

FIG 2D
$(Zn: Cd)S: Mn: Cl$
(Zn: Cd) S: Sm: Cl

FIG 3c

\[ \log B \] vs. \( \frac{1}{\sqrt{V}} \)
F SERIES

FIG 6

LOG F

0.8  1.2  1.6  2.0  2.4  2.6

1 KV  500 V  700 V  300 V  200 V

3.0  3.2  3.4  3.6
ZnS: Mn: Cl.
AT 500 C/S

FIG 7a

Intensity (A.U.)

Voltage:
- 3000 V
- 2500 V
- 2000 V

Wavelength (nm):
- From 500 to 660 nm
FIG 8 A
FIG 8 B

V = 1 kV
F = 60 Hz

V = 1 kV
F = 300 Hz

V = 1.2 kV
F = 1 kHz

D3  D6  D7
$V = 400$
$F = 60\,\text{Hz}$

$V = 1\,\text{kV}$
$F = 300\,\text{Hz}$

$V = 1\,\text{kV}$
$F = 1\,\text{kHz}$
FIG 8 D

V = 375
F = 60 Hz

V = 1 KV
F = 300 Hz

V = 1.5 KV
F = 1 kHz

F₁   F₄   F₆   F₇