CHAPTER IV

FREQUENCY DEPENDENCE OF ELECTROLUMINESCENCE
4.1 INTRODUCTION

A study of the dependence of electroluminescence brightness on frequency affords insight into the mechanism of EL. It also helps to elucidate the kinetics involved in the recombination process and the energy distribution of the trap levels present in the phosphor matrix. A study of this dependence has therefore, been undertaken in the present investigation.

A frequency dependence of EL is known to be markedly affected by the use of dielectrics that are employed to prevent any glow discharge or electrical breakdown in an EL cell. It is of importance, therefore, to study the variation in permittivity of these dielectrics with and without the phosphors. In view of the above requirements, the variation of dielectric constant with frequency has also been investigated.

This chapter deals with the experimental details and the results of the above two studies. A brief review of the theories of frequency dependence of EL is also given.

4.2 BACKGROUND THEORY

Various formulae for the dependence of EL brightness (L) on frequency (F) have been proposed by several authors; but the exact form of this dependence has been found to be
different for different phosphors.

When $F$ increases, one generally observes an increase of $L$ more or less tending to saturation towards high frequencies. The interpretation proposed by Curie (1, 2) is based on the assumption that the recombination kinetics is bimolecular and that the same number of excited centres are produced per half cycle. Thus if $n(t)$ is the number of excited electrons remaining after time $t$, then

$$n(t) = \frac{n_0}{1 + n_0 \cdot t}$$

where $\times$ is a constant and $n_0$ the number of electrons initially excited. In a time $t = 1/2F$, ($F$ being the applied field frequency) the light sum ' $S$ ' is proportional to

$$\left\{ n_0 - \frac{n_0}{1 + \frac{n_0 \cdot \times}{2F}} \right\}$$

Or $n_0 - n(t)$, where $t = 1/2F$;

and brightness is given by

$$L = S \cdot 2F$$

so that

$$L = L_0 \frac{n_0}{1 + n_0 \cdot \times/2F} \quad (4.1)$$

This reduces to $L = L_0 \cdot 2n_0F$ for low enough $F$, indicating
thus the proportionality of $L$ in relation to $F$ at low frequencies (which is consistent with the impact ionization model). This Eqn. (4.1), although admittedly an oversimplification, also interprets the observed saturation at high frequencies.

Thornton (3) considered the recombination rate to be determined by field controlled thermal release of electrons from traps. In this case and again assuming a constant number of excited centres ($N_0$) for each half cycle of the voltage, the frequency dependence should be given by

$$L = N_0 F \left[ 1 - \exp \left( -A/F \right) \right]$$

(4.2)

where

$$A \sim \int_0^{2A} \exp \left( a V \sin X \right) dx ; \ x = wt.$$ 

The quantity $A$ increases as the voltage is increased. For very high frequency the output is given by $N_0 A$; with $N_0$ obviously a function of voltage. This result also correctly predicts the effect of voltage on the frequency dependence of output.

Zalm (4) has also made a calculation in which the rate determining factor for the recombination is not detrapping as assumed by Thornton or natural recombination as assumed by Curie, effectiveness of the voltage in driving electrons back to the empty luminescence centre. If the monomolecular kinetics is assumed, then the result is the same as equation (4.2) except
that \( A \) is directly proportional to \( V \).

Alfrey and Taylor (5) considered the number of electrons originating per second from the trap at the time \( t \) (after the start of the semiperiod) to be of the form

\[
\frac{n_0}{c} \exp \left( - \frac{t}{\tau} \right)
\]

where \( \tau \) is the life time of the trap at a given temperature. / Reckoning relation \( L = A \exp \left( - b / \sqrt{V} \right) \), and putting \( V = V_0 \sin \omega t \), the instantaneous luminescence will be given by

\[
L = \frac{n_0}{c} \exp \left( - \frac{t}{\tau} \right) \exp \left( - \frac{b}{\sqrt{V_0} \sin \omega t} \right)
\]

This gives the following relation for the integral luminescence (when we suppose \( V_0 < \beta \omega \tau \)):

\[
L = \frac{n_0}{c} \exp \left( - \frac{1}{4cF} \right) \exp \left( - \frac{b}{\sqrt{V_0}} \right)
\]  (4.3)

It is not possible with this expression (which is a function of \( \tau \)), however, to interpret the behaviour of EL which is a product of several groups of traps, unless, it is a matter of a limited range of frequency and temperature through which the influence of these groups is preponderant.

Several other authors (6-9) have proposed various expressions relating \( L \) to \( F \), some among them take into account
the time of transit of electrons from the high field region
down to the regions of low field. For example, the relation
proposed by Johnson et al (6) is

\[ L = 1 - a \left[ 1 - \exp \left( - \frac{1}{2F\tau_2} \right) \right] \exp \left( - \frac{1}{2F\tau_1} \right) \]  \quad (4.4)

in which, the constant \( \tau_1 \) is the time of relaxation of
excited electrons for returning into the empty centres and the
constant \( \tau_2 \) is the time of creation of primary electrons. This
relation is more complete but presents the same limit of validity
as the previous one (Eqn. 4.3).

4.3 EXPERIMENTAL PROCEDURE

4.3.1 Measurement of brightness variation with frequency

The experimental arrangement for studying the
frequency dependence of EL is the same as that utilized for
studying the voltage dependence (Sec. 3.3). The method
consists in exciting the EL cell by a sinusoidal electric
field and measuring the brightness output by photoelectric
means. For studying this dependence the phosphor (in an EL
cell) was kept at constant voltage and the field frequency was
varied from 30 Hz to 3 kHz. The resulting brightness was
recorded in terms of galvanometer deflection. The brightness
variation with frequency was recorded at different fixed voltages,
for each phosphor. The measurements were made up to 3 kHz only.
because above this frequency the observations are not very reliable due to perhaps the voltage losses in the transparent conducting electrode and also due to other experimental difficulties.

4.3.2 Measurement of dielectric variation with frequency

(a) Dielectric constant measuring bridge: We have employed a Universal Bridge (Type TF 2700, Associated Instruments Manufacturers Pvt. Ltd., India) for the measurement of dielectric constant. There is an arrangement in the instrument for the use of external a.c. and d.c. supplies. The initial energizing sources for the bridge are a 1kHz oscillator for d.c. measurements of capacitance, inductance and resistance, and a 9V power supply battery for d.c. resistance measurements. The detector has a usable response from 20 Hz to 20 KHz. This allows an external source to be used to energize the bridge for measurements over a wide range of frequencies. Capacitance values of 0.5 pf to 1100 pf may be measured at 1 kHz from the internal oscillator or at frequency of 20 Hz to 20 KHz from an external source where an alternative frequency is more appropriate.

Philips A.F. Generator (Type GM 2308/90, Philips India Ltd.) was used as external frequency source. This generator provides an a.c. voltage with which measurements can be carried out in the
audio-frequency range (30 Hz to 16 kHz). An insulating transformer (Type TM 7120, Marconi Instruments Ltd., England) was used as an optional accessory.

(b) Circuit arrangement and operating procedure: The circuit arrangement is shown in Fig. (4.1). Here the cell containing the dielectric material is connected across the two large terminals marked HI and DET + VE on the bridge. The leads connected to the upper terminal are sensitive specially to the external field stray and therefore shortest possible length of leads are taken. To avoid the stray capacitances and mains hum pick up further, ground and shielded leads are used for all the circuit connections. The body of the cell is also earthed. The external frequency source is connected to the Bridge via jack plug inserted into the EXT a.c. socket; the action of inserting the plug switches off the internal oscillator. The A.F. supply is connected via isolating transformer. The use of transformer eliminates the possibility of a false balance due to capacitative coupling when measuring low impedances at high frequencies. The earthy side of the A.F. oscillator output is connected to the input terminal of the transformer (TM 7120) adjacent to the screen terminal. These two terminals are then linked to the -ve (chassis) terminal of the bridge.

Normal balancing procedure entails adjusting the main BALANCE controls, in conjunction with the LOSS BALANCE control
FIG. 4.1: Experimental arrangement for the measurement of dielectric constant
for reactive components, in order to bring the meter to as near zero deflection as possible. The sensitivity control allows the detector sensitivity to be reduced for a clearer meter indications of approaching balance with components of unknown value.

The vacuum capacitance $C_0$ of the cell is calculated from its dimensions. The static dielectric constant is then simply obtained from the formula

$$ \varepsilon = \frac{C}{C_0} $$

4.4 RESULTS :

4.4.1 Frequency dependence of EL

The dependence of EL brightness on applied frequency is observed to be affected by several parameters; such as, applied voltage, activator concentration, type of activator and so on. The following are the results of this study for CaO : Cu and CaO : Mn phosphors.

(a) CaO : Cu : The brightness (L) versus frequency (F) plots vary from phosphor to phosphor. In the lower concentration range, brightness first decreases with frequency (from 30 to 80 Hz) then it increases linearly with $F$ up to $\sim 300$ Hz and beyond that tends towards saturation. The
representative curves of this type can be seen in Fig. (4.2). For the sample with Cu (2%), a dip is formed (between 30 and 100 Hz) in L vs F curves. As the voltage is increased, this dip gets shallower. Further, higher the applied voltage, higher is the frequency range over which linearity in the curves is observed. In the same Fig. (4.2), L - F curve at 420 volts shows a clear-cut saturation above 300 Hz, while at 440 volts, the curve slightly tends towards saturation, and at 460 volts, no saturation tendency is being observed.

As the concentration of copper is increased, the dip observed in these curves diminishes gradually and at 10% of Cu, no dip is observed, as can be seen in Figs. 4.3 and 4.4. Above 4% of Cu, that is, in the higher percentage range, the L - F curves are all linear between 60 Hz and 2 KHz.

(b) CaO : Mn: The frequency dependence of brightness of Mn-activated samples is almost similar to that observed in the case of Cu-activated phosphors.

In the concentration range 1 - 5% of Mn/Ca, the intensity first decreases with F up to 100 Hz and then increases linearly with the frequency. For the same phosphor, the dip formed at 100 Hz gets shallower as the applied potential is increased. As the Mn-concentration is increased, this dip vanishes gradually (compare Figs. 4.5 and 4.6) so that at sufficiently high concentration (10% Mn), the brightness
FIG. 4.5: Frequency dependence of EL
CaO: Mn (2%)
increases almost linearly beyond 60 Hz, without forming any dip (Fig. 4.7).

No saturation at any applied voltage is observed in these phosphors up to \( \sim 1 \text{ kHz} \), the limit of observation.

4.4.2 Brightness - Frequency Relationship

Of the several formulae discussed in Sec. 4.2, we tried to find out which one gives the best fit to our experimental data. These formulae are discussed, in the following lines, keeping in view the theoretical as well as experimental facts.

The two important relations (4.3 and 4.4), although more complete theoretically, do not seem to be applicable in these phosphors because there exist more than a single set of traps in these phosphors. The presence of several groups of traps is evident from the frequency dependence of the hypothetical term "brightness at infinite potential" (discussed in Chapter III) and also from the temperature dependence of EL (to be discussed in Chapter V). In fact, it is not possible with these relations (4.3 and 4.4) to interpret the behaviour of EL, which is a product of several groups of traps.

Considering equation (4.1), the brightness

\[ L \propto \frac{n_o^{2 \alpha}}{1 + n_o^{\alpha} / 2F} \]
so that \( \frac{1}{L} \propto \frac{1}{\eta^2} \left[ 1 + \frac{\eta \alpha}{2F} \right] \).

Thus \( 1/L \) should be a linear function of \( 1/F \). Accordingly, \( 1/L \) is plotted as a function of \( 1/F \) (Figs. 4.8 to 4.13). It is clear from these figures that systematic deviation from linearity occurs in \( 1/L \) vs \( 1/F \) curves, at low as well as high frequencies. In some cases, the deviations are larger at higher voltages, where they should be less, because it is at higher voltages that the brightness increases almost linearly with frequency. The fact is that Curie's relation (4.1) does not predict anything about the effect of voltage on the frequency dependence.

Now considering Thornton's relation (Eqn. 4.2) for frequency dependence, which gives

\[
L = N_0 F \left[ 1 - \exp \left( -\frac{A}{F} \right) \right],
\]

we have \( \frac{L}{F} = N_0 \left[ 1 - \exp \left( -\frac{A}{F} \right) \right] \)

i.e., \( \log \left( \frac{L}{F} \right) \propto -\frac{A}{F} \),

so that, if we plot logarithm of \( (L/F) \) against \( (1/F) \), the curve should be a straight line, with a negative slope. These curves are shown in Figs. 4.14 to 4.19 for the representative samples. It is evident from these figures that the logarithm of brightness per cycle \( (L/F) \) varies almost linearly with \( (1/F) \).
Fig. 4.8: $1/L$ vs $1/F$ curves for CaO:Cu (2%)  

Fig. 4.9: $1/L$ vs $1/F$ curves for CaO:Cu (5%)  

Fig. 4.10: $1/L$ vs $1/F$ curves for CaO:Cu (10%)
FIG. 4.11: 1/L vs 1/F curves for CaO:Mn (2%) (CaO:Mn:CaO:Mn (2%))

FIG. 4.12: 1/L vs 1/F curves for CaO:Mn (5%)

FIG. 4.13: 1/L vs 1/F curves for CaO:Mn (10%)
FIG. 4.17: Log(L/F) as a function of 1/F
CaO: Mn (2%)  

FIG. 4.18: Log(L/F) as a function of 1/F
CaO: Mn (5%)  

FIG. 4.19: Log(L/F) as a function of 1/F
CaO: Mn (10%)
in most cases. In some cases, deviation from linearity occurs below 100 Hz. This deviation is smaller at higher voltages. Further, according to Eqn. (4.2), the factor (L/F) should decrease at higher frequencies (where the saturation occurs). This is experimentally observed in our investigation also (See, Fig. 4.14). Regarding the effect of applied voltage on the frequency dependence of output, the results seem to be in accordance with Thornton's prediction.

Thus, in conclusion, it appears that Thornton's relation (Eqn. 4.2) gives a better fit to our experimental data as compared to other relations.

4.4.3 Frequency dependence of Dielectric constant

The dielectric behaviour of the same pellets as used in recording the frequency dependence of EL was studied in relation to frequency. This study is performed to know the variation of electric field across the EL capacitor when the frequency of excitation varies. The pellet, sandwiched between the electrodes, forms a condenser with three dielectrics having different capacities (say C₁, C₂ and C₃); as shown in Fig. 4.20.

![Diagram of dielectric behaviour]

Fig. 4.20
FIG. 4.21: Variation of capacity & dielectric constant with frequency

(a) mica & araldite; ($\varepsilon = 0.200 \times$ capacity)
(b) mica, araldite & CaO: Mn (3%); ($\varepsilon = 0.185 \times$ capacity)
(c) mica, araldite & CaO: Cu (3%); ($\varepsilon = 0.192 \times$ capacity)
In the first instance, dielectric variation of mica and araldite (i.e., $C_1 + C_2$) only was studied and later the same variation was recorded for a combination of $(C_1 + C_2) + C_3$ using different phosphors in place of $C_3$. It is found that the dielectric constant ($\varepsilon$), of the combination $(C_1 + C_2)$ decreases with frequency up to $\sim 100$ Hz and then becomes almost constant.

Qualitatively, similar behaviour is observed for the pellets containing phosphors (Cu/Mn) also (Fig. 4.21). That is to say that $\varepsilon$ of the phosphor embedded pellets also decreases with $F$ up to $\sim 100$ Hz and then becomes almost constant; the only difference being that the values of $\varepsilon$ here are higher than those for $(C_1 + C_2)$. 
REFERENCES


(3) W.A. Thornton: Phys. Rev. 102, 38 (1956); 103, 1585 (1956).


