CHAPTER VI

ELECTROLUMINESCENCE OF DOPED (Zn,Cd)S MIXED PHOSPHORS

6.1 INTRODUCTION

Electroluminescence (EL) is produced by the electric field (a.c or d.c) applied to the certain substances. A direct transformation (conversion) of electrical energy into light energy takes place in the phenomenon of EL. Electroluminescence is a limiting case of Electrophotoluminescence in which the effect of electric field alone is considered. The Electrolumiophor can be in the form of polycrystalline layer or a single crystal. In the case of polycrystalline layer one of the conducting electrodes is transparent and is separated by dielectric medium. The various effects known to date for crystalline solids can be divided into two main categories: (i) Pure or intrinsic Electroluminescence, which is the result of sole action of applied electric field, as in electroluminescent cells or panels and (ii) Electroluminescence due to charge carrier injection in which the emission is produced by injection of charge carrier through a rectifying contact on a crystal or a P-N junction. The luminescence intensity is approximately proportional to current passed. In contrast, for intrinsic electroluminescence the phosphor need not be in contact with the electrodes and no net current passes through the crystal fig (6.1).

D. Curie (1952), Piper and Williams (1955) described the electroluminescence mechanisms. It was concluded that the
Fig 6.1 (a) without applied field.
(b) field applied in forward direction:
  injection of minority carriers
  inferred from radiative recombination.
excitation process for the luminescence centres involves three parts: (a) The acceleration of the electron for rising to the conduction band.

(b) Acceleration of some of these electrons by the field (c) Collision of these electrons with the centres causing the excitation or ionization of the later and finally, the radiative or non-radiative recombination of electrons with centres will occur. There are several mechanisms by which EL can occur, Ivey (1963) explained the distinction between the two principal processes: (i) Minority carrier injection at a metal contact or P-N junction followed by recombination of free electron and hole with emission of photon of light, and (ii) Excitation of luminescence activator centres by energetic electrons accelerated in a very high electric field localized at some potential barrier followed by emission of light when the empty activator centre captures a free electron.

R. Goffaux (1954) suggested that the high intensity electric fields producing electroluminescence in phosphors result in an increase of conduction electron temperature over that of the lattice and lead to multiplication of carriers. The theory developed is applied to the dependence of emission on field frequency. Voltage dependence of electroluminescent brightness. I. of dielectric embedded phosphors were studied by Schwertz F.A. et al (1955). For seven different ZnS phosphors embedded in plastisized polyvinyl chloride and brightness voltage relation follows accurately the
theoretical equation of Alfrey and Taylor for single crystals. It is found that the brightness is proportional to frequency and is determined by the number of optically active luminescence centres.

Piper W.W. and Williams F.E (1955) reported the theory of Electroluminescence. The theoretical basis for exciting luminescence by the application of an electric potential to a crystalline dielectric or semiconductor was considered. Three mechanisms of excitation were shown to be theoretically feasible in appropriate solids and with suitable local field conditions: (i) the ionization of impurity systems directly by an electric field, (2) the acceleration of conduction electrons or positive holes in the valance band of kinetic energy sufficient to excite or ionize impurity system or valance electrons by inelastic collisions and (3) Injection of charge carriers. Radiative de-excitation is feasible by two mechanisms (a) direct recombination of conduction electrons and holes in the valance band and (b) optical transition characteristics of impurity systems known as activators. The characteristics of electroluminescence proceedings by these processes were examined theoretically.

Motassi F. and Nudelman S. (1955) reported the Electroluminescence excited by short field pulses. The decay of the light emitted from several electroluminescent phosphors excited by periodically repeated voltage pulses of the range from 40 to 2500 sec. duration has been determined.
The slopes of the decay curves after each individual pulse excitation becomes steeper as the pulse duration decreases. The heights of the luminescence peaks excited at the leading and trailing edges of the pulses also depend on the pulse time. The results are interpreted as confirming previous conclusions about the influence of polarization charges. Numerical evaluation yields the correct order of magnitude for the "critical time" needed for the accumulation of polarization charges.

The electrical properties of electroluminescent phosphors in the form of powders and polycrystalline lumps have been measured by Ince, A.N. and Oatley, C.W. (1955). There appears to be two quite separate mechanisms giving rise to dispersion. One which is present in the dark and the other which is stimulated by irradiating the phosphor with UV light. The later is very similar to the dispersion found in ordinary non-electroluminescent powder and has not been studied further. The former, which seems to be characteristic of electroluminescent phosphors produce dispersion at very low frequencies and have been investigated in detail. Measurements have also been made of the variation of dielectric properties with voltage and with temperature. To explain the effects observed it is assumed that electronic barriers are formed in the specimen and that motion of some of the ions in the barrier region takes place. On the basis of this model it is found possible to account in a
semi-quantitative manner for the experimental results. Values are deduced for the height of the barrier and for the number and diffusion coefficient of the mobile ions.

Thornton W.A (1959) studied the A.C and D.C electroluminescence. The enhancement of electroluminescence, by the superposition of dF to aFc. Voltages, was observed in certain electroluminescent zinc sulphide powder phosphors. The addition of a d.c voltage to an a.c voltage exciting visible electroluminescence increase the emission as much as 250 times, under conditions where the d.c. electroluminescence alone is nearly equal to the initial a.c. electroluminescence wave-form. Transient and spectral measurements show that the increased emission is recombination at d.c ionized luminescence centres forced by the a.c. fields.

Thornton W.A (1960) described the maintenance of several electroluminescent phosphors, illustrating its dependence on phosphor properties, such as copper and chlorine additions and on lamp construction. Changes in properties other than light emission and recent maintenance improvements are also described. Thornton (1961) reported the electroluminescence in zinc sulphide as due to minority carrier injection. Under the proper experimental conditions which can be fulfilled in conventional electroluminescent ZnS powder dispersions in dielectric material or in luminescent films, the resistive component of the a.c. current follows the diode equation (for forward bias).
\[ I = I' \left( \exp \left( \frac{V'}{kT} \right) - 1 \right) \]

where \( V \) is the applied r.m.s. voltage. The parameter \( I' \) is proportional to \( \exp \left( - \frac{E_c}{kT} \right) \) and \( V' \) is proportional to temperature and phosphor layer thickness. Three independent determination give the number of active forward biased junction per micron of ZnS phosphor as about 15. The forward current was shown to be directly related to electroluminescence emission and were compared directly to a.c. current in Ge p-n junction. Irradiation effects on the conductance of a phosphor layer and a Ge photo junction were compared. D.C. electroluminescence in ZnS at 2.0 V was also cited against the acceleration-collision theory, and the major arguments in its favour were discounted.

Winkler H. and Roppisher H. (1960) observed a considerable intensification of luminescence under the influence of alternating electric field in zinc cadmium sulphide activated by manganese and excited by X-Rays. Intensification factors from 4 to 7 were measured in the yellow emission range. No field extinction was observed between the wave lengths of 430 and 700 nm. The intensification is voltage and frequency dependent and it was thus assumed that no radiation controlled luminescence has occurred.

Gol'dman O.G et al (1961) studied cells with an electroluminophor layer in air. The current through the cell was proportional to the frequency, so that the equivalent electric circuit for the cell was represented with sufficient
accuracy by a capacitor circuit. The frequency characteristic of the brightness $B$ of the cell with a constant value of the voltage was defined approximately, by the relationship $B = af^k$ where $K$ ranges in value between 0 and 1. On switching into the generator circuit, an electroluminescent cell with resistance, capacitance, inductance of their combinations, the frequency dependence of the brightness of the cell with a constant generator voltage is defined chiefly by a dependence on the frequency of the voltage exciting the cell. Therefore, the frequency dependence of the cell brightness may be given the desired form.

Enhancement by electric fields of the X-ray excited luminescence in ZnS: CdS:Mn phosphor was obtained showing an independence of X-ray wavelength and amplification by 6 to 10 times (Wendel G. 1960).

In 1968 Bell scientists started work on thin film EL devices with vacuum deposited semiconductor layers proposing Lumocen (Luminescence from molecular centres) as a new concept in which direct electron impact excitation of inner shell transitions take place. They did detailed work and collected a lot of experimental facts about the processes in such structures using mainly rare earth doped ZnS as semiconductor layer in thickness scarcely exceeding 2000 Å. The work of Bell laboratory apparently stopped by claiming that light output from these devices could be inherently inefficient because of a "clamped" field inhibiting higher excitations. In this work two main errors made were; first
the work did not cover Mn as luminescence centre but mainly concentrated on rare earth elements. Secondly, too thin semiconductor films were used. At least 2000 Å are needed to overcome high disorder of the material condensed on to a cold glassy substrate.

Quantitative and qualitative observations were reported by Russian Scientists Stroganova.T.N. et al (1968), on the electroluminescence characteristics of the phosphor ZnS-Cu, BaS-Cu, ZnS-Cu, Mn, BaS-Cu, Mn, and ZnS-Cu, Al. Electroluminescence in II-VI compounds were reported by Aren.M. (1967). It was reported that luminescence in II-VI compounds resulting from the application of an electric field has been observed in a great variety of different junction structures. Most of those have hetero junction consisting of a luminescent and an electron or hole injecting component. Several homojunction systems received increased attention, which involved p-n junctions in simple and mixed crystal systems, as well as avalanche and photo p-n junction structures.

Research and development on the so called "The second Generation EL" started world wide after the presentation of two research papers at SID BY TOSHINO Inoguchi of sharp company, Japan. The title of those papers are "stable high brightness with thin film electroluminescent panels" presented in 1974 and inherent memory effects in ZnS:Mn thin film EL devices" Presented in 1975. The first paper
concluded that the thin film EL devices improved all the weak points of the first generation EL such as low brightness, short life and low contrast. Such success arise from the following points. First, the development of the process technology for the formation of II-VI compound semiconductor thin films with homogeneous constituent element towards growth direction. Second, the selection of device structure in which an EL active layer is sandwiched by two insulating layers with high voltage tolerance in order to be able to apply stable and sufficiently high voltage to the EL active layer. Third, the elimination of mobile ion such as copper ion which can move easily under high electric field. Recently the International conference on Electroluminescence held at Toffori Japan (1988) was mostly devoted to ac TFD where big optimistic views were expressed. Present activities in the field of just the Inoguchi type ac TFDs are known from sharp, IBM, bell, Tektronices, Rockwell, westing house (penal vision), siemens, Finlex (Lohja, Finland), sigmatron and from several japanese, French and US universities.

Although EL is an important developing field of electronic materials, we have limited interest in the study of EL in the present investigation. The reason of interest is that the electrical origin of ML in phosphors have been proposed by different workers (Meyer et al 1970, Curie and Prost 1946). For checking the fact that the ML in phosphors may be the deformation induced EL, the EL of doped \((\text{Zn, Cd})\)S
mixed phosphors is investigated. The present chapter reports the EL of (Zn, Cd)S:Mn, Cl and (Zn, Cd)S:Ag, Cl mixed phosphors, which are found to be highly mechanoluminescent as reported in chapter III.

Phosphors used in Electroluminescence:

Most often zinc sulphide activated by copper, silver or manganese is used. The respective emission bands are in the green and the blue regions for copper and in the blue for silver and the yellow orange region for manganese.

Addition of cadmium sulphide to zinc sulphide causes the emission bands to be displaced towards longer wavelengths. However, generally the electroluminescence of solid solutions of ZnS and CdS is not as good as that of ZnS (Zalm). The electroluminescence of cadmium sulphide has been observed, but under conditions which are nearly approach dielectric breakdown than in ZnS (K.W. Beer and Kummel, G. Die-mer). In other experiments, electroluminescence arises by the injection of charges followed by electron hole recombination (R.W. Smith).

It is likely that cadmium sulphide is too good a conductor for the internal field to be high, except in the neighbourhood of breakdown voltages.

A wachtel (1960) has shown that for ZnS + HgS phosphor activated with copper a red electroluminescence can be obtained which completes the gamut of colours which can be obtained in electroluminescence.
6.2 EXPERIMENTAL

The electroluminescence brightness of a powdered phosphor is a function of many parameters such as, thickness of the phosphor layer, type of the phosphor, frequency and amplitude of the exciting voltage etc. Obviously, all of parameters are somewhat significant for interpreting the experimental results in a meaningful manner.

In order to study the voltage and frequency dependence of electroluminescence of the phosphor, electroluminescence cells were prepared. The cell was excited electrically and the emission was detected by a photomultiplier tube.

6.2A PREPARATION OF CONDUCTING GLASS PLATE:

A thin transparent film of tinoxide or titanium oxide on glass plate is generally used as one of the electrodes. In order to avoid undesirable voltage drop along the conducting electrode, conducting plate may be prepared by spraying solution of stannous chloride in acetone over heated glass or micaplate (Henish 1962). Some workers have used conducting mica sheet or conducting paste over mica as the second electrode (Prakash et al 1968).

For preparation of conducting glass plate, we have followed the method suggested by Gomer (1953). Thin glass plates of appropriate sizes were heated slowly upto 500°C to 600°C by placing them on a thick metallic plate. The vapours of stannous chloride were sprayed on this heated glass plate in the presence of air by using the spraying apparatus shown in Fig (6.2).
g.6.2 Experimental arrangement for the preparation of conducting mica sheets.
The device consists of a corning conical flask in which crystals of \( \text{Sn Cl}_2 \cdot 2\text{H}_2\text{O} \) were placed and heated to vapourize the stannous chloride. The vapours were blown towards the glass plate by giving the number of puffs to a rubber bladder connected to the flask. The vapour mixed with air gets deposited on the surface of the heated glass plate. The procedure was repeated by depositing the film until the desired results were obtained. Precaution was taken so that the transparency of glass plate should not be damaged. It was thus possible to prepare the transparent conducting glass plate.

6.2.B PREPARATION OF EL CELL

There exists a great deal of variation in the preparation of electroluminescent cells (Siddal 1959), Gaur and Bhawalkar (1969). The medium in which the phosphor powder is dispersed, should be reasonably translucent, chemically inert and should have a high dielectric constant so as to sustain only a small fraction of the applied voltage. In the present studies castor oil was used as the dielectric medium, since its dielectric constant does not change appreciably with temperature. If the thickness of the dielectric is as small as compared to the total thickness of the cell (Andre 1952).

The powder of electroluminophor was mixed with a small amount of castor oil and was spread on an aluminium plate. A thin sheet of mica was pressed on the phosphor powder and fixed by adhesive tape over the non conducting side of glass plate and an aluminium foil was inserted which worked as one
Figure 6.3 Two electrode configuration of an electroluminescence cell (1 - mica sheet, 2 - conducting surface of mica sheet, 3 - sample grains in araldite, or Kester oil, 4 - steel plate)
of the electrodes. The aluminium plate itself was the second electrode. The electrode configuration is shown in fig (6.3).

6.2.C SOURCE OF EXCITATION

A high alternating or pulsating voltage is needed to excite the electroluminescence. In the present studies, the cell was excited by an A.C. voltage.

(i) Oscillator:

Aplab 2002 sine/square oscillator was used to generate audio frequency oscillations. The frequency range is from few hertz to 20 kilo hertz. The voltage available is from a fraction of milivolts to 10 volts.

(ii) Wide band High Voltage Amplifier:

Wide band high voltage amplifier (Model M-EHT-100 F-G) supplied by M/S Mishra Raidos, Gwalior was used for obtaining high voltage at high frequencies.

The device in optimum gain position amplify the input about 300 times. The output voltage could be increased upto 1000 volts (rms).

(iii) Coupling Transformer.

A step up transformer connected to the output of the wide band amplifier further increases the voltage which is to be applied to the cell. It is used mainly for impedance matching.

6.2.D DETECTION AND MEASUREMENTS

The EL detection and measurements were carried out by the technique described below.

(i) Photomultiplier Tube

RCA - 931 A photomultiplier tube is used for detecting
the light emitted by EL cell. The details of the tube have already been described in chapter II.

(ii) High Voltage Supply

High Voltage power supply mode EHT-10 was used for supplying necessary voltage to the photomultiplier tube. It can supply voltage upto 1500 volts D.C.

(iii) Nanoammeter

Model NM-122 nanoammeter is suitable to measure the output of PMT. It can measure current from one tenth of a nanoampere to hundred microampere. The dark current is minimized by the zero adjustment before starting the measurements in each range.

(iv) Digital Multimeter

A digital multimeter was used for measuring the instantaneous voltage applied at the EL cell.

6.2E. PROCEDURE

The output of the audio oscillator was fed to the input of the wide band amplifier fig (6.4) whose output was connected to the primary of the step up transformer. The transformer secondary was connected to the electrodes of the EL cell and also to a digital multimeter in parallel. The photomultiplier was supplied 750 volts by the power supply and the EL output was measured in terms of the deflection in the nanoammeter. The oscillator was set to a fixed frequency and its voltage was varied. The multimeter voltage reading at which luminescence started were recorded along with the nanoammeter readings. Next, a set of reading of EL
Fig. 6.4 Experimental arrangement used for the measurement of voltage and frequency dependence of EL brightness.
brightness for different voltages was taken. This procedure was repeated at other frequency settings of the oscillator changed in discrete steps. In the present investigation the different frequencies studied were 500 Hz, 1KHz, 3KHz and 5KHz and with voltage variation from 350 to 800 Volts. All the observations has been taken in the Department of physics, Rani Durgavati University (Jabalpur) under the supervision of Dr.B.P.Chandra.

6.3 RESULTS:

The voltage dependence of EL brightness of hexagonal (Zn, Cd)S:Mn, Cl phosphor (having activator concentration $4 \times 10^{-3}$ by the weight of 1 gm. of matrix for different frequencies of the applied electric field is shown in fig. (6.5). It is seen that the brightness increases with the applied voltage at a given frequency. Fig (6.6) shows that the plot of logarithm of brightness versus $\frac{100}{\sqrt{V}}$ is a straight line with a negative slope which suggests the relation $B = B_0 \exp \left( -\frac{b}{\sqrt{V}} \right)$, where $B_0$ and $b$ are constants. Similar results has been found for (Zn, Cd)S:Ag, Cl. Fig (6.7) and fig (6.8)

The frequency dependence of brightness of (Zn, Cd)S:Mn, Cl is shown in fig (6.9) and of (Zn, Cd)S:Ag, Cl in fig (6.10) for different voltages. It is seen that the EL brightness increases with increasing frequency of the applied electric field. The measurements of EL brightness are made without using any filter or monochromator between the EL cell and the photomultiplier tube. Similar frequency and voltage
dependence was found for all other hexagonal phosphors with different concentration of the activator and different amounts of CdS. Fig (6.11) shows that the brightness is maximum for a particular concentration of activator. For hexagonal mixed phosphors, the EL brightness is maximum for activator concentration $4 \times 10^{-3}$ by weight in 1 gm of matrix. Critical activator concentration for which the EL brightness is maximum, slightly decreases with the CdS content in the doped $(Zn, Cd)S$ mixed phosphors.

Fig (6.12) shows the effect of CdS content on the EL brightness of $(Zn, Cd)S$:Mn, Cl phosphors. It is seen that the EL brightness of hexagonal Mn doped $(Zn, Cd)S$ mixed phosphor decreases with increasing contents of CdS. Similar result is found for $(Zn, Cd)S$:Ag, Cl. This result is in contrast with the ML results, where ML is maximum for particular CdS content in the phosphor. Fig (6.13) and fig (6.14) shows the EL spectra of hexagonal $(Zn, Cd)S$:Mn, Cl and $(Zn, Cd)S$:Ag, Cl phosphors. It is seen from the figure (6.14) that the peak of the EL spectra shifts towards higher wavelength values with increasing CdS contents in the $(Zn, Cd)S$:Ag, Cl phosphor while for Mn doped $(Zn, Cd)S$ mixed phosphor the peak of the EL spectra does not shift towards higher wavelength values with increasing CdS contents, fig (6.13). From the spectroscopic point of view the ML spectra are similar to the EL spectra.
Fig. 6.5 Voltage dependence of EL brightness at difference frequency of \((\text{Zn,Cd})\text{S} : \text{Mn,Cl}\) phosphor. (10\% Cd S).
Fig. 6.6. Plot of logarithm of EL brightness versus 100/TV in ZnCdS:MnCl.

- O 500 Cls
- @ 1KClS
- x 3KClS
- □ 5KClS
Fig. 6.7 Voltage dependance of EL brightness of (Zn, Cd)S: Ag, CI (10% CdS) at different frequencies.
Fig. 6.6 Plot of logarithm of EL brightness versus $100/\sqrt{V}$ in (Zn,Cd)S:AgCl.
Fig 6.9 Dependence of frequency on EL brightness in (Zn,Cd)S:MnCl Phosphor.
Fig. 6.10 Frequency dependence of EL brightness of \((\text{Zn}_x\text{Cd})\text{S}:\text{Ag}_3\text{Cl}\) Phosphor at different applied voltages.
Fig. 6.11 - Effect of activator concentration on EL brightness in hexagonal (Zn,Cd)S:Mn,Cr phosphor.
Fig. 6.12 - Effect of CdS concentration on EL brightness in (Zn,Cd)S: Mn,Cl and (Zn,Cd)S: Ag,Cl.
FIG. 6.13 EL SPECTRA OF (Zn,Cd)S: Mn,Cl PHOSPHORS.
FIG. 6.14 EL SPECTRA OF (Zn,Cd)S: Ag,Cl PHOSPHORS.
6.4 DISCUSSION:

6.4 (A) VOLTAGE DEPENDENCE OF ELECTROLUMINESCENCE BRIGHTNESS.

In powder dielectric cells, the brightness is found to be an increasing function of voltage. The current voltage characteristics of electroluminescent powders and films obey the normal relation for forward biased diode rectifier, which establish the existence of a rectifying barrier, Thornton (1961). The width of schottky potential barrier varies with the square root of applied voltage across the phosphor crystals and follows the relation.

\[
d = \frac{(KV)^{1/2}}{2N_0} \quad \text{(6.1)}
\]

Where \( K \) is the dielectric constant of the embadding medium and \( N_0 \) is the charge carrier density.

Thornton (1956) suggested that for higher values of voltage, the width extension should depend upon the particle size or other geometrical factors. In this case the field should be proportional to the applied voltage rather than to \( V^{1/2} \). Thornton has also found that the size of the excitation region increases with the increase in the applied voltage as expected in case of schottky barrier. Similar conclusions has been drawn from the experiments on ZnS phosphors (Alfery and Taylor 1957, Alfery et al 1960).

A number of empirical and theoretical relations have been proposed (Destriaau and Ivey 1955, Piper and Williams
1955), the most suited relation for powder phosphors, over a wide range is

\[ B = B_0 \exp \left( \frac{-b}{\sqrt{V}} \right) \] -------- (6.2)

Where \( B_0 \) and \( b \) are constants which depend on temperature and frequency of the applied voltage and on the size of the EL cell, (Alfery and Taylor 1955, Zalm et al 1955). The voltage dependence is found to be greater at higher frequencies and low temperature. The square root of the voltage is explained on the basis of electron acceleration mechanism. At very low voltages the brightness may vary as the nineth or the tenth power of the voltage. At voltages approaching breakdown of the layer, the dependence usually approximates to \( V^2 \) or even a lower power of \( V \). Morehead (1958) derived a theoretical expression which reduces to relation (6.2), at low frequency, high voltage and and high temperature. While for high frequency, low voltage low temperature the following relation holds good

\[ B = B_0 V \exp \left[ - \left( \frac{V_0}{V} \right)^{\frac{1}{2}} \right] \] -------- (6.3)

Fritzsche (1960) explained that equation (6.2) stands for lower activator concentration, while for higher activator concentration equation (6.3) holds good. Goldberg (1966) proposed another relation for phosphors poisoned by Co or Ni, which is as follows.

\[ B = A \exp \left( \frac{-b}{V} \right) + \frac{V_1}{V} \] -------- (6.4)
where the constant \( V_1 \) depends on the statistical variations of the properties of individual particles.

Lehman (1958, 1960) and Goldberg (1959) studied the effect of particle size on the voltage dependence of EL output. It is found that the values of parameters and \( V_0 \) in equation (6.2) increases with decrease in the particle size. It is explained on the basis of the statistics of a random dispersion of the particles in a dielectric of different dielectric constant. Lehman (1956) found that the addition of Ni effects the value of \( B_0 \) only.

Many workers have claimed that equation (6.2) holds good at low voltages, while at higher voltages the following relation is obeyed

\[
B = a \exp \left( \frac{-b}{v} \right) \tag{6.5}
\]

Zalm et al (1954) found that the emission from a single particle of the phosphor follows the above relation, while the integrated output of many particles of a phosphor obeys equation (6.2). Similar results has also been found by Lehman (1956, 1960); thus he considered equation (6.3) to be the basic one for electroluminescence while equation (6.2) results only from a statistical effect in powder.

The EL output for ZnS: Cu, Cl films may be increased if a thin insulating layer is interposed between the phosphor film and the metal electrodes, Harper (1962). Zalm (1956) concluded that the emission may also be obtained with D.C.
excitation, if electroluminescent powder are placed in a conducting medium. The voltage dependence of the EL output for D.C. is more rapid than that of the same material for A.C. excitation (Piper and Williams 1952, Favorin and Kozina 1961). Thornton has shown that for D.C. excitation the brightness obeys the relation

\[ B = A \exp \left( \frac{V}{B} - 1 \right) \] ---- (6.6)

Where A and B are constants.

The voltage dependence of EL brightness of doped (Zn, Cd)S mixed phosphors follows the relation

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

which is the characteristics of acceleration -collision mechanism and thus suggests the existence of a potential barrier of Mott-Schottky type. Therefore, it may be concluded that the electroluminescence mechanism in doped (Zn, Cd)S mixed phosphors requires the existence of a high field region (Mott-Schottky type barrier), where charge carriers are accelerated to sufficient energies so as to ionize the luminescent centres by impact and causing emission.

6.4 (B) FREQUENCY DEPENDENCE OF ELECTROLUMINESCENCE BRIGHTNESS

The dependence of EL brightness on the frequency of applied field for doped (Zn, Cd)S mixed phosphors shows that at low frequencies the brightness increases linearly with the applied frequency. At each instance the luminous condenser
is charged or discharged, hence certain amount of light is expected to be emitted. As such, more rapidly this cyclic operation is repeated, more light is emitted from the system.

Bramely and Rosenthal (1952), Jerome (1953) found that the dependence of EL brightness on frequency is different for different phosphor. At low Voltages, with increasing frequency, the brightness tends towards saturation, but at high voltages it increases almost linearly.

The increase in brightness with frequency can be understood on the basis of rapidity of emptying and refilling of the luminescent centres, (Ivey 1957). But when the time period of applied alternating field becomes nearly equal to the life time of excited electrons, the electrons do not have enough time to emerge out from the trap and hence, saturation can be expected at high frequencies. This has been observed for alkaline earth sulphide and oxide phosphors by Hassorkar and Ranade (1973); Ranade et al (1977).

The saturation in output for sulphide phosphors at higher frequencies can be understood in a qualitative way, since the characteristic decay time of these phosphors is of the order of $10^{-4}$ second. Curie (1952, 53, 57) assumed a biomolecular recombination kinetics, according to which the free electrons are removed to some distance from the centres during excitation i.e. a hyperbolic recombination process occurs and thus we have

$$N_t = \frac{N}{1 + N_0 t} \quad (6.8)$$
where \( N_0 \) is the number of excited electrons at the time \( t = 0 \); 
\( N_t \) is number of electrons (excited) remaining after \( t \) seconds 
and \( N \) is a constant.

If 'f' is the frequency of the applied Voltage, then

\[
t = \frac{1}{2f} \quad (6.9)
\]

while the integrated output brightness can be expressed as

\[
B \sim (N_0)^2 \left/ \left( 1 + \frac{N_0}{2f} \right) \right. \quad (6.10)
\]

or

\[
B = K(N_0)^2 \left/ \left( 1 + \frac{N_0}{2f} \right) \right. \quad (6.11)
\]

where \( K \) is a constant.

It is clear from the above relation that at low frequency of the applied field the life time of the excited electrons will be less as compared to the time period of the applied field. Hence, if \( N_0 \) is large and \( f \) is low i.e \( N_0/2f \gg 1 \), then relation (6.11) reduces to

\[
B = K \left( \frac{N_0}{2f} \right) \quad (6.12)
\]

or

\[
B \propto \frac{N_0}{2f} \quad (6.13)
\]

Thus at low frequency, the brightness is proportional to the frequency of applied electric field.

At high frequency, the life time of the excited electrons will be large as compared to the time period of the applied field, thus

\[
N_0/2f \ll 1
\]

Hence, relation (6.11) reduces to

\[
B = K(N_0)^2 \quad (6.15)
\]

This expression shows that at higher frequency the
brightness should attain saturation. This is due to the fact that the electrons, which are liberated in the first half cycle, do not fully recombine before the next half cycle.

At higher frequencies the output can also be expressed in the following form

\[ B = \frac{S}{1 + K (rs)^{1/2}/f} \]  \hspace{1cm} (6.16)

Where \( S \) is the saturation output for high frequency, \( r \) is the recombination constant (inversely related to decay time) and \( K \) is a constant. It is clear from the above relation that for higher values of the applied frequency \( f \), the brightness should attain a saturation value.

The recombination rate has been determined by field controlled release of the electrons from traps Thorton (1956). In this case, by assuming a constant number of excited centres (\( N_0 \)) for each half cycle of the applied voltage, the frequency dependence should be given by the relation

\[ B = N_0 f [1 - \exp (-A/f)] \]  \hspace{1cm} (6.17)

The value of \( A \) is expressed as

\[ A = \exp \{ a v \sin (\omega t) \} \, d(\omega t) \]

The above relation shows that the value of \( A \) increases with increase in voltage. For very high frequency, the output can be given by \( N_0 A \), which shows that the output saturates.

The effect of voltage on frequency dependence can also be predicted by the above relation. A linear response followed by saturation has been reported for different electroluminophor systems e.g SrS:Cu (Hassorkar and Ranade 1973), (Zn, Cd)S:Mn:Sm, Cl. (Awate and Jombagi 1975), ZnS:Mn,
Cl (Chen 1974) and CaS:Bi:Pd (Lawangar et al 1977).

A physical model have been proposed by Piper and Williams (1952, 1958) for linear frequency dependent EL output. According to which the primary electrons, which start the excitation, originate from the donor impurity levels inside the phosphor crystal, emptied by field ionization. Thus the process is strongly field dependent. For the emission to be linearly dependent on frequency, the model must fulfill the following conditions.

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

(ii) The rate of return of electrons to be excitation region should increase with increasing voltage.

Hakke (1957) explained the fall of EL output after a particular frequency by considering that above that frequency the available time for exhaustion of trapped electron is decreased, requiring higher energy to empty the traps. Similar results for decrease in EL output at high frequencies have also been reported by other workers (Piper 1958, Prakash 1973). The saturation frequency for EL output depends upon the impurity contents Hanisch (1962).

Similarity of ML and EL spectra and the occurrence of optimum ML and EL brightness for a given concentration of the activator suggest the electrical origin of ML whether the ML is deformation induced EL or it is some other type of emission will be discussed in chapter VII in details.
6.5 REFERENCES


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