Luminescence is a general term which includes many phenomena involving absorption of energy by a substance and its re-emission as visible or near-visible radiation. Luminescent emission is distinguished from thermal radiation, in that, it does not obey Kirchhoff's law, and the energy density of luminescent emission per unit wavelength interval is always larger than that in the case of thermal radiation at the same temperature. It is also distinguished from Raman, Compton and Raleigh scatterings and Cerenkov radiation, in that the time delay in luminescence emission after excitation is larger than $10^{-9}$ second while Raman, Compton, Raleigh effects and Cerenkov radiation are completed in a time $10^{-14}$ second.

There are several types of luminescence, classified on the kinds of input energies which can excite the luminescent material.

i) When the excitation energy comes from particles produced in chemical reactions, as in the oxidation of phosphorus or certain organic compounds, the resulting luminescence is called chemiluminescence.

ii) When the excitation is by relatively low-energy photons, particularly in visible and near-visible radiation, the luminescence is called photoluminescence.

iii) Electroluminescence is a luminous emission from the luminescent material resulting from the applied electric field.
iv) In cathodoluminescence the luminescent material is excited by energetic electrons or cathode rays.

v) In triboluminescence, the mechanical energy of grinding of luminescent material is utilized to get light emission.

vi) Thermoluminescence, however, does not refer to thermal excitation but rather to the thermal stimulation of luminescent emission which is excited by other means.

vii) When the material is excited by the particles emitted from radioactive materials, the luminous emission is referred to as radioluminescence.

Luminescence:

The general phenomena of luminescence have been classified according to the duration of the emission following removal of excitation. There is invariably exponential afterglow, whose rate is independent of excitation intensity and of temperature. This is termed as fluorescence. There is an additional component of the afterglow, which decays more slowly and with more complex kinetics. This component is termed as phosphorescence.

i) Fluorescence:

A few authors choose to define fluorescence as emission during excitation. Fluorescence emission starts within $10^{-8}$ second from the instant of excitation and lasts to within $10^{-8}$ second after the excitation ceases. The fluorescence mechanism consists of the raising of an electron from its ground state to one of its excited state during absorption. The return of the electron from
the excited state to the ground state results into fluorescence emission.

ii) Phosphorescence:

Phosphorescence is delayed emission which persists after the excitation of the phosphor is ceased. Some luminescent substances may have short duration phosphorescence and some may have long duration phosphorescence.

iii) Impurity activated solid and the terms:

Luminescence is obtained by incorporating small but controlled amounts of foreign ions or impurities into the crystal lattice of a given base compound. The base compound is called the 'host lattice' or the 'matrix material'. The impurity or the foreign ion which causes luminescence is called the 'activator'. In some cases a second impurity introduced in addition to the first. In such cases the second impurity is called the 'co-activator' or 'sensitizer'. Due to the presence of some impurities (e.g. Fe, Co, Ni) the luminescence intensity decreases. These are termed as 'Killers' or 'Poisons'. The substance formed after incorporating the activator is called the 'phosphor'.

3. Electroluminescence:

Electroluminescence involves excitation by a voltage applied to the luminescent substance. In order to convert the electrical energy (from the applied voltage) into the visible or near-visible radiation, there are three sequential processes:
i) excitation by the applied field,
ii) energy transport, and
iii) radiative de-excitation.

The electroluminescent material is excited by the applied field to an electronic state of several electron volts above the ground state. The excited state may be at the bottom of the conduction band. The excitation may inject minority charge carriers within a band. The injection of minority charge carriers forms a "hot" carriers.

After the excitation it may be necessary to transport the excitation energy to a region where radiative de-excitation can occur. The electrostatic field in the region of the electroluminescent material where excitation occurs may be quite different from the field in the region where emission occurs. Excitation migration or resonance transfer is contributing to the energy transport.

The final step is radiative de-excitation. Radiative de-excitation may be intra or interdefect, defect band or intra-band transition.

Various combinations of these i) excitation, ii) energy transport, and iii) emission processes are expected from theoretical considerations, to occur in suitable luminescent materials with appropriate applied electric field.

3.2 Mechanism of electroluminescence:

Various models have been suggested to describe the electroluminescence mechanism. The different stages of EL mechanism...
are shown in Fig.1. The mechanism involved in each state can be described briefly in the following four stages:

3.2.1 State I.

**Excitation of charge carriers:**

There are three types of EL each with a different mechanism of excitation. They are:

i) Acceleration collision excitation EL

ii) Injection electroluminescence, and

iii) Direct field ionization EL.

1) **Acceleration collision excitation EL:**

(Field ionization of the impurity ions)

In this mechanism, the charge carriers are accelerated out of equilibrium with the lattice and to optical energies. The charge carriers have inelastic collisions with impurity or valence band electrons. They are excited to the state from which radiative de-excitation results.

A simplified form of this mechanism is shown in Fig.2(A). The carriers tunnel through the forbidden gap and are accelerated to high kinetic energies. The emission is a combination of inter- and intra-band transitions.

Curie¹ and Piper and Williams² deduced a mechanism for the Pestrian type of EL. This was based on the idea that charge carriers originate in a high-field cathode region and are accelerated by the applied field to sufficient kinetic energy for...
collision excitation of activators.

A Mott-Schottky exhaustion barrier at a metal n-type semiconductor contact satisfies the requirement of a high-field cathode region. For this barrier the work function of the metal, \( \phi_m \), and the electron affinity of the semiconductor, \( \chi_s \), are related as

\[
(\phi_m - \chi_s) > kT
\]  

...(1)

The thickness of the barrier, \( d \), is obtained by using Poisson's equation

\[
d = \left[ \frac{K (\phi_m - \chi_s)}{2 \varepsilon N} \right]^{1/2}
\]  

...(ii)

where \( N \) is the concentration of donors in excess of acceptors.

The local field \( F(x) \) with no applied voltage is

\[
F(x) = \frac{2 (\phi_m - \chi_s)}{\varepsilon d} (1 - \frac{\chi_s}{d})
\]  

...(iii)

With an applied voltage, the exhaustion barrier increases in thickness. The local field increases with increase of barrier. At a critical local field, \( F_c \), charge carriers will be created by field ionization of deep impurity states.

If we consider these states to be effective-mass-like, the probability of ionization per unit time \( P_i \), is given by a modification of the formula derived by Oppenheimer\(^3\) for field ionization of atomic hydrogen.
\[ P_1 = 17 \times 10^{12} \, \frac{\text{m}^2}{\text{m}} \left( \frac{E}{k_T} \right)^{1/4} \exp \left[ - \frac{7 \times 10^7 \, \frac{\text{m}^2}{\text{m}}}{E} P_n^{3/2} \right] \]  

where

\[ P_n = \frac{E^{3/2}}{2\hbar^2 k T} \]  

the given values.

The charge carriers released into the region with high field \( E \) have a probability \( P_E \) of attaining the energy \( E \) by having fewer than the average number of collisions with phonons. The probability \( P_E \) was derived by Seitz\(^4\) in connection with dielectric breakdown:

\[ P_E = \exp \left[ - \frac{(E/E_i)^{1/2}}{3E} E \right] \]  

Here \( E \) is the average frequency of collisions with phonons. If \( E \) is taken as the energy necessary for collision excitation of activators or of electron-hole pairs which excite activators, luminescence results.

ii) \textbf{Injection electroluminescence}:

(Injection of minority carriers)

The injection mechanism of EL refers to the injection of minority carriers into a semiconductor. The injection may occur from a surface, a defect, or an adjacent region of opposite type. The last constitutes a p-n junction, which we shall consider in detail.

Shockley\(^5\) analysed the injection characteristics of p-n junctions by using quasi-Fermi levels for two types of carrier, and Hall\(^6\) and Shockley and Read\(^7\) investigated the statistics of recombination of electrons and positive holes. The band theory
model of a p-n junction biased in the forward direction is shown in Fig. 2(B).

From continuity of steady-state current and Poisson's equation and from the assumption that the injected carrier density is small and diffusion-limited the equation is obtained for the minority carrier current with forward bias \( V_f \).

\[
I = n(D/\tau)^{1/2} \left[ \exp \left( \frac{eV}{kT} \right) - 1 \right] \quad \ldots \quad (vi)
\]

where \( n \) is the density of excess minority carriers, \( \tau \) is their lifetime, and \( D \) is their diffusion constant, which is related to the drift mobility \( \mu \).

\[
D = (kT/\phi)_\mu \quad \ldots \quad (vii)
\]

At higher applied voltages the carrier motion is determined by the electric field. Luminescent emission may occur in or near the p-n junction by either intrinsic or extrinsic radiative recombination. The donor acceptor pair in the junction region allows for alternate capture of injected electron and positive hole, followed by radiative recombination.

At very high injection densities the quasi-Fermi levels for the electrons and holes become sufficiently separated, as noted by Bernard and Duraffourg\(^3\), so that populations are inverted and lesser action is possible.

iii) **Field by direct field ionization:**

(Field ionization of valence electrons)

This mechanism could involve field ionization from the
valence band or from localized defect states. Franz calculated for large band gap materials the probability per unit time, $P_i$, for ionization from the valence band in the field $F$:

$$P_i = \frac{e a}{\hbar} F \exp \left[ -\frac{E_g (2m_e)^{1/2}}{\hbar e a} \frac{E}{F} \right]$$

(Eq. viii)

$E_g$ is the band gap and $a$ is the unit-cell dimension. The field ionization from the valence band or from localized defect states and field ionization of defect states requires fields in excess of those for dielectric breakdown.

3.2.2 State II

Acceleration of charge carriers in the crystal bands:

The carriers (electrons or holes) created in the crystal bands by any of the above processes are accelerated to high kinetic energies by the applied field. The conduction electrons (or holes) experience an acceleration force as a result of the field and a retarding force caused by the interaction with the phonons. At a field of the order of $10^5 - 10^6$ volts/cm, the electrons can be accelerated to energies required for the subsequent processes of the ionization of the impurity and valence electrons by collision process. This order of field can be achieved in experiments on EI, if there exists a narrow high field region, in series with an extensive low field region. Such configuration can exist if we have a Mott-Schottky exhaustion type barrier, a thin intervening intrinsic region or a p-n junction biased in the reverse direction.
3.2.3 State III:

Transport of the energy to the radiating site:

In the third state, the carriers accelerated as described above have to transport the energy to the site which would eventually lead to radiative transition. This is achieved by the motion of excited electron-hole pair known as exciton. Fano\textsuperscript{10} has suggested exciton diffusion as the mechanism of energy transport in the cathodoluminescence of ZnS. The accelerated particles create excitons which propagate through the crystal and transfer its energy at the appropriate radiating site.

i) Collision process:

An accelerated electron or a hole can, by simple collision process, promote another electron from the valence band to the conduction band or from one impurity level to another. The efficiency of the first process is given by

\[ \eta = \frac{A}{B^2} \exp \left(-\frac{E}{E_0}\right) \quad \ldots \quad (ix) \]

where \( E \) is the applied field and \( A, B \) are constants. There is a threshold value for the energy of an electron below which it cannot create an electron-hole pair. This is higher than the band gap and is approximately calculated to be \( 1.5 \ E_g \).

ii) Capture of charge carrier:

An impurity level may capture an electron or a hole from the valence or conduction band and gets excited. This gives EL, followed by radiative transition.
The excitation of radiating centre:

The excitation of radiating centre by direct interaction with an exciton is also probable but this does not involve any movement of charge carriers.

3.2.4 State IV:

Radiative de-excitation:

The transition can be classified as, band to band (interband), from one state to another in the same band (intraband), from band to impurity state and also from impurity state to impurity state.

4. Photoluminescence:

In this section we shall discuss luminescence in systems which absorb exciting energy in the host material or in the centre, and emit or dissipate the energy in a centre different from that responsible for absorption. We shall be concerned with the mechanisms involved in the transfer of excitation energy from the absorber to the emitting centre ('activator') or the quenching centre ('poison' or 'killer'). The PL mechanism can be understood by considering the three well-known mechanisms for luminescence as described below.

4.1 Schön-Klasens Model:

A model of this type of luminescent system was proposed by Schön and elaborated upon by Klasens and his co-workers. Fig.3(A) illustrates the Schön-Klasens model for the case of a single
luminescent centre. The luminescent centre is considered to possess an energy level close to the filled band. Normally this level contains an electron. If light is absorbed in the fundamental absorption band, free electrons and holes are produced. Next, a hole diffuses to the luminescent centre and captures the electron located there. This leaves the luminescent centre vacant so that a free electron may diffuse to the centre, and when captured gives off the excess energy as luminescent light. The cycle is now complete; a free electron and a free hole have recombined and the centre has an electron, as at the beginning of the process.

This model has been extended to include many phenomena such as doubly activated phosphors, traps, temperature quenching of luminescence; and the effects of “Poisons”.

4.2 Lange and Klick Model:

This model is illustrated in Fig. 3(b). It differs from Schön-Klasen model. In Schön-Klasen model, the trapping of the hole by the centre is considered to be a large energy transition and is assumed to give rise to luminescence. On an ionic picture of the centre, the substitution of a monovalent positive ion for a divalent one leaves the volume around the centre with a net-negative charge. This has two effects: 1) the cross section for trapping of a hole becomes large because of the Coulomb attraction, and 2) the energy released in the capture of a hole may be large.

The proposed cycle is then as follows:

1) Light is absorbed producing a free hole and electron
leading to conductivity.

ii) The hole and electron move in their respective bands, and eventually the hole migrates near the impurity centre.

iii) The hole is captured by the impurity centre and luminescent emission occurs leaving the centre now neutral in charge.

iv) The electron wanders through the lattice until it finally comes near the centre.

v) The electron is finally captured by the centre, and in the capture only a small amount of energy is given off as infrared radiation or as vibrational quanta.

The centre is now returned to its initial condition and the cycle can be repeated.

The essential difference between the Schön-Klassen model and Lombe-Klick model is that the former assumes that luminescence results from the capture and subsequent recombination of a conduction electron, whereas the latter assumes that luminescence results from the capture and subsequent recombination of a free hole.

4.3 Proser and Williams Model

Proser and Williams pointed out that I b activators and VII b or II b co-activators are to be recognized as acceptors and donors, respectively. The simultaneous incorporation of activator and co-activator results in the transfer of an electron from donor to acceptor, giving rise to their compensated states. They found that copper at random substitutional sites in ZnS, prepared by radioactive decay of $^{65}$Zn produced by neutron irradiation, does
not contribute to luminescence. Therefore, they considered that the association of activator and co-activator is necessary for the appearance of luminescence, and proposed that the luminescence transition is from the excited state of the donor to the ground state of the acceptor in an associated pair at second nearest or third nearest neighbour sites (see Fig. 3(C)).

5. **Efficiency of phosphors**

The efficiency of the phosphors is an important property among other properties of phosphors. Brill and Klasens\(^{14}\) have defined the radiant, quantum, and luminous efficiency as:

i) The radiant efficiency \(\eta\) is defined as the ratio of the emitted fluorescent power to the power absorbed by the phosphor from the exciting radiation (both powers to be expressed in watts).

\[
\eta = \frac{P_{\text{emitted}}}{P_{\text{absorbed}}} 
\]

ii) The quantum efficiency \(q\) is the ratio of the number of emitted fluorescent quanta to the number of the absorbed quanta.

\[
q = \frac{N_{\text{emitted}}}{N_{\text{absorbed}}} 
\]

iii) The luminous efficiency is the ratio of the emitted luminous flux in lumens to the absorbed power in watts.

Here we shall discuss their theoretical and some experimental considerations in detail.

They have assumed that the phosphor is excited by monochromatic radiation of wavelength \(\lambda_0\) and that the absorbed power is \(P_a\). If the fluorescence is emitted over a wide range of wavelength, the total power involved is \(P = \int p(\lambda) d\lambda\)
where $p(\lambda)$ is the emitted power at wavelength $\lambda$, the integration being taken over the whole range of wavelengths.

The radiant efficiency is given by

$$\eta = \frac{P}{P_a} = \frac{\int p(\lambda) d\lambda}{P_a}$$  \hspace{1cm} (x)$$

To obtain the intrinsic (or true) radiant efficiency, the measured value $\eta$ must be corrected for the absorption of the emitted fluorescence by the phosphor itself. This absorption is generally small for well prepared phosphors.

The intrinsic efficiency is approximately given by

$$\eta_i = \frac{2\eta}{1 + R_\infty}$$

where $R_\infty$ is the reflection coefficient of an "infinitely thick" layer of the phosphor for its own emission. This formula which has been used by Bril and Klaassen for cathode-ray excitation, is also valid here.

The energy of one quantum is $\hbar \nu = h c / \lambda$ where $\hbar$ is Planck's constant and $c$ is the velocity of light, so the quantum efficiency is

$$q = \int \lambda p(\lambda) d\lambda / \lambda_0 P_a$$ \hspace{1cm} (xi)$$

The ratio of quantum efficiency and radiant efficiency is therefore

$$q / \eta = q_i / \eta_i = \frac{\int \lambda p(\lambda) d\lambda / \lambda_0}{\int p(\lambda) d\lambda}$$  \hspace{1cm} (xii)$$

The lumen efficiency $L$ can be of great practical importance. It
can be written as:

\[ L = K_m \frac{\int p(\lambda) \bar{y}(\lambda) d\lambda}{P_a} = K_m \frac{\int p(\lambda) \bar{y}(\lambda) d\lambda}{p(\lambda) d\lambda} \] (xiii)

where \( \bar{y}(\lambda) \) denotes the sensitivity of the eye as a function of wavelength and \( K_m \) is the maximum value of the luminous flux per watt of radiant power i.e. 683 lm/W at \( \lambda = 555 \) nm.

The ratio

\[ y = \frac{\int p(\lambda) \bar{y}(\lambda) d\lambda}{\int p(\lambda) d\lambda} \]

is called the luminosity factor and defines the lumen equivalent \( K = \bar{y} K_m \), which is the luminous flux per watt emitted radiant power.

According to eq. (xiii) the luminescence efficiency is then given by

\[ L = \eta \bar{y} K_m = \eta K \] (xiv)

We shall now discuss some of the possible reasons for the lack of agreement between various authors:

1) Most of the measurements have been carried out using photocells or photomultipliers to detect the fluorescent radiation. The response of most of these cells decreases very rapidly at longer wavelengths, so that it is difficult to measure the response at longer wavelength with same tube or cell. The sensitivity of these cells at 750 nm is generally only of the order of 1% of the maximum sensitivity at 400-500 nm. Hence an accurate measurement of the spectral response of these cells and of the spectral energy distribution (S.E.D.) curves of the
phosphors is required.

ii) The intensity of the exciting ultra-violet radiation is usually measured after reflection from a layer of magnesium oxide. The absolute reflection coefficient of the MgO is thus required.

iii) The phosphors are generally excited by the exit beam of a monochromator so that the exciting radiation is as nearly monochromatic as possible. In principle, this is a good thing, but it means in practice that one measures with a low irradiating intensity, which may badly affect the accuracy of the measurement.

iv) The radiant efficiency is defined as the ratio of the emitted power to the absorbed power. In practice, however, only the power emitted in a certain range of wavelengths, is considered. Errors are made if radiation emitted outside this region is not accounted for.

The efficiency of the phosphors used in fluorescent lamp, for example, must be as high as possible. Parts of the emissions are, however, sometimes found in the ultra-violet or the infrared regions. It then depends on the use of suitable filters and detectors whether these parts are included in the particular efficiency measurement or not.

We have measured the efficiency of the phosphores using Spectrometer, on which the efficiency is measured directly on the drum of Spectrometer in nits.

6. Applications:

An important factor in the development of the field has been
its commercial applications. Fluorescent lighting, cathode-ray tubes for radar and television, and electroluminescent lamps call for efficient phosphors. Industrial activity in the field has, therefore, been quite large.

Electroluminescence, the new potential light source, can be used, where the space is an important consideration. The brightness and efficiency of EL light emitters is more, so EL has become a subject of great technological interest. Although the EL lamps are not efficient source of light, as compared with conventional lamps, it can no doubt, replace the need of illumination where much brightness is not essential and sometimes even not desirable, e.g. EL lamps are best suited for self-luminous objects such as instrument dial illuminations, radio and clock dials, house numbers, direction signs and similar devices for decorative purposes.

Another very important commercial application of phosphor is the electric discharges in mercury lamp. In this case, ultraviolet radiant energy generated in the discharge is used to excite a phosphor and the useful emission consists of the phosphor output plus the visible light is generated in the discharge. Phosphors are also employed in high pressure mercury-vapour (HPMV) discharges.

7. Statement of the problem:

There has been a growing interest in the last decade to study the luminescence of the II-VI compounds. It has been shown that the presence of group I activators such as silver and copper\(^15\) and lithium\(^16\) sensitizes the rare earth emission in these materials.
It has been further shown that the silver and copper as co-activators introduce an absorption band which corresponds to the photoluminescence excitation spectrum for the rare earth ions$^{15}$. In these studies it was assumed that silver and copper substitutionally replace the cations in the lattice and adopt a monovalent charge state thus acting as acceptors.

Lehmann$^{17}$ has shown that these silver and copper donor levels remain at a fairly constant depth with respect to the valence band for the mixed crystal systems of the type $\text{Zn}_x\text{Cd}_{1-x}$ but at increasing smaller depths with respect to the valence band in systems of the form $\text{Zn}_x\text{Se}_{1-x}$ as $x$ decreases.

The rare earths activated mixed $(\text{Zn}:\text{Cd})\text{S}$ phosphors have not been extensively studied. Therefore the present investigation has been undertaken to investigate the role of rare earth ion as co-activator in the mixed host. For this photoluminescence was studied and conclusions are drawn regarding the possible PL mechanism, the luminescent centres and the activator sites. The fluorescent spectral measurements were carried out at liquid air temperature and at ambient temperatures, using 365 nm, 253.7 nm and X-rays as exciting sources.

To investigate the nature of electroluminescent brightness and its relations and to determine the electron traps in host lattice we have studied the voltage and frequency dependence of the electroluminescence brightness for mixed crystals of $(\text{Zn}:\text{Cd})\text{S}$ activated with $\text{Eu}^{2+}$ and coactivated with $\text{Sm}^{3+}$. As the a.c. electroluminescence of a phosphor depends on various
parameters such as the shape, amplitude and frequency of the exciting field and the temperature of the phosphor, we have studied the brightness waveforms of these samples applying 50 Hz to 10 kHz frequencies at different voltages. Further, in order to confirm these results the EPR spectra have been analysed.

Taking into account the competitive situation in the lamp industry these phosphors were subjected to the measurement of efficiency. It was found that they can better stand to meet the needs of the lamp industry. These studies throw light on the proper choice of host and the activators to achieve the requirement of the present day lamp industry.
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MECHANISM OF ELECTROLUMINESCENCE

STATE I
Field ionization of Valence electron

Injection of Minority Carriers

Excited Crystal state

By the action of electric field localized in narrow region

STATE II
By the movement of charged carriers

By the movement of excitons

Excited Crystal state

STATE III
Collision process capture of charge carriers

Excited impurity state

STATE IV

STATE V
Intra band
Inter band
Band to impurity state

Impurity state to impurity state
Impurity state to Band

FIG 1
CONDUCTION BAND

TUNNELLING

P TYPE

VALENCE BAND

n TYPE

INTRABAND EMISSION

FIG 2A

CONDUCTION BAND

Q-F LEVEL

VALENCE BAND

n TYPE

FIG 2B