CHAPTER 1

INTRODUCTION
The crystalline materials capable of absorbing energy from various sources and re-emitting it as visible or near visible radiation during or after excitation are called 'Luminors' (Leverenz 1950). Further, the phenomenon of light emission from such materials in excess of thermal radiation at a given temperature is called 'Luminescence' (Piper & Williams 1959). Luminescent emission involves optical transitions between electronic states characteristic of the radiating substance. This phenomenon can be distinguished from neighbouring physical processes such as thermal radiation since it does not follow 'Kirchoff's law' and from Raman and Compton effects, Rayleigh Scattering and Cerenkov emission by the time delay between excitation and emission which for these cases is of the order of $10^{-14}$ seconds or less while for luminescent emission is greater than $10^{-9}$ seconds.

According to the mode of excitation luminescence may be classified as follows (Gerlick 1958):

1. Photoluminescence (PL) - that produced by absorption of light photons.
2. Electroluminescence (EL) - that produced by application of an electric field (AC, DC or pulsed).
3. Radioluminescence - that produced by bombardment with high energy particles ($\alpha, \beta, \gamma$, protons etc.) or radiations ($\gamma$-rays, x-rays etc.)
Chthodoluminescence (CL) is that produced by cathode rays and is a specific case of this class.

(iv) Chemiluminescence - the emission which is accompanied with a chemical reaction.
Chemiluminescence in living organisms is called Bioluminescence.

(v) Triboluminescence - the luminescence resulting from mechanical strain and fracture of certain luminor crystals.

etc.

Thermoluminescence (TL), however, does not refer to the thermal excitation but rather to thermal stimulation of luminescent emission which is already excited by other means (UV, x-rays, y-rays etc.)

The present thesis is based mainly on the AC and DC CL of some alkaline earth sulphide luminors. Results of CL studies are also presented for comparison and understanding of the recombination process.

Luminescent emission usually originates from the spontaneous de-excitation of certain impurity sites or centres formed due to the incorporation of foreign elements into the luminor lattice or defects during preparation. The foreign elements producing this type of centres are known as 'activator' (Rothschild 1960). However, some of the luminors like Urenyl salts, Platinocyanides, tungstates, molybdates, manganous
halides and salts of rare earths (RE) show luminescence in the pure state. These materials contain certain groups which function like foreign molecules in the crystal matrix, for example \( \text{M}_2 \) in uranyl salts and \( \text{Pt(CN)}_2^- \) group in platino-cyanides (Bendall 1939). In some cases native ion vacancies create luminescence centres and a term 'self activated' or 'undoped' emission is used for such emission (Tröger & Hellingman, 1948, 1949; Brauer and Neill 1959).

The solubility of most of the activator elements in host lattice is usually limited unless another element called 'co-activator' is introduced at the same time. For example, in host lattice of \( \text{II}_B - \text{VI}_B \) compound the trivalent ion \( \text{III}_B \) or a halide ion \( \text{VII}_B \) usually acts as co-activator.

At activator centres the probability of radiative transition is greater than that of nonradiative one. However, there are some centres for which vice-versa happens and such centres are called 'killer centres' (e.g. Fe, Ni and Co in Zns). The impurities responsible for such centres are known as 'poison'.

In some materials the localized electronic states of the activator systems are well approximated by states of free activator ion which are perturbed by crystalline interactions whereas in other materials the localized states are more
approximately treated as electronic states of pure crystal which are perturbed by the activator atom. In $\text{II}_B - \text{VI}_B$ compounds the substitution of group $\text{I}_B$ activators for $\text{II}_B$ or $\text{V}_B$ group for $\text{VI}_B$ yields a series of discrete states above the valence band. In the neutral crystal, with only these impurities present, the highest state is empty consequently the activator is an acceptor. The substitution of a $\text{III}_B$ co-activator for $\text{II}_B$ or a $\text{VII}_B$ co-activator for $\text{VI}_B$ binds an extra electron in a donor state (Piper and Williams, 1958).

Some times the imperfection in the crystal lattice results in regions which are capable of capturing electrons or holes and detain them in restricted volume in such a way that they are prohibited from moving freely through the crystal unless supplied with energy. Such regions are called traps (Rube 1960). Their production depends upon presence of impurities (Rube 1952, 1953) atmosphere (Garlick 1949; Kröger & Hellingman 1949, 1950) and temperature (Kröger & Hellingman 1949, 1950) during preparation. Some of the traps are associated with defects in the crystals i.e. due to the formation of regions with excess positive charge (electron traps) or negative charge (hole traps) surrounding the defects other kind of traps are associated with impurities in which trapping involves change in effective valency of impurity ion e.g. $\text{Sm}^{3+}$ changes to $\text{Sm}^{2+}$. 
As mentioned earlier this thesis deals with PL and EL (AC and DC) of rare earth (Er, Sm, Nd) doped CaS electro-luminors.

PL is produced by light photons and has been further classified according to the duration of emission following the removal of excitation. When excitation is removed, if there is an exponential after-glow, whose rate is independent of excitation intensity and of temperature the phenomenon is termed as 'fluorescence'. Usually there is an additional component of the after-glow which decays more slowly and with more complex kinetics. This component is known as 'phosphorescence' (Kröger 1948; Curie 1963). Fluorescence is also defined as emission during excitation and that phosphorescence as emission after excitation is removed (Garlick 1962). These phenomena are also defined in terms of physical processes (Mott & Gurney 1940; Kröger 1948; Leverenz 1950) the emission taking place by one or more spontaneous transitions is fluorescence and the emission taking place with the interaction of meta-stable state followed by a return to the excited state by the addition of energy is phosphorescence. Because thermal activation of the meta-stable states of activator or trap is prerequisite to emission, phosphorescence is markedly temperature dependent.

Since the normally observed bands of luminescent emission are attributed to interaction between emission centre
and host crystal lattice ("Leo 1984) the luminescent emission depends on the nature of the activator and its concentration in a particular host lattice. If the activator concentration is high, the activator atoms destroy the matrix resulting in quenching of luminescent emission (Kröger 1948).

"Temperature change may produce change in intensity and colour of PL emission. At a critical temperature, characteristic of the particular emission band and the material thermal quenching occurs which may be due to the nonradiative de-excitation processes becoming more probable (Williams 1960) at this temperature. With increase in temperature the emission band is normally broadened and the peak of the band may shift towards lower or higher energy side (Leverenz 1950) or remain unaffected (Kröger 1948; Studer & Gaush 1948). Colour and efficiency of PL emission are also affected by the intensity of exciting radiation (Licli 1939; Gisolf & Kröger 1939).

PL is the conversion of electrical energy into visible or near visible radiation when the luminor is subjected to a constant, pulsed or alternating voltage (Piper & Williams 1958; Ivey 1965; Kröger 1967). This kind of emission has also been observed in single crystals and evaporated films. If the light emission takes place from
luminor powders when embedded in an insulator and subjected to alternating electric field the phenomenon is called intrinsic or pure \( \Phi \) (\textit{vestrum} effect). On the other hand, light emission may also take place by the action of electric field on crystals or particles in contact with the electrodes due to injection of carriers (\textit{vestrum} and Ivey 1955). This kind of emission also occurs in \( \Phi \)-junctions (\textit{Panoo} and \textit{hetero}), metal-semiconductor (\textit{M-S}) and metal insulator-semiconductor (\textit{M-I}) structures (\textit{Panoo} 1977). In the case of intrinsic \( \Phi \) the brightness \( B \) increases more rapidly than linearly as the excitation voltage is raised. A number of empirical or theoretical relations have been proposed (\textit{Vestrum} 1947; \textit{Vestrum} & Ivey 1955; \textit{Pear} & \textit{Williams} 1955; \textit{Vorchard} 1958), but the one which is usually found to fit the results for luminors is (\textit{Alfrey} & \textit{Taylor} 1955; \textit{Selke} et al 1955):

\[
B = B_0 \exp \left( -\frac{b}{v^2} \right)
\]  

(1.1)

Where \( B_0 \) and \( b \) are parameters which depend upon temperature, frequency of the alternating voltage, the luminor and details of the construction of the \( \Phi \)-cell (\textit{Ivey} \& \textit{Thornton} 1961) and dielectric constant of the insulator (\textit{Roberts} 1952). This formula is interpreted by assuming the excitation mechanism as acceleration - collision one together with the fact that the maximum field strength in a \textit{Wott-Schottky} barrier varies as \( v^2 \). Departures from equation (1.1) are often observed e.g. at high
voltages (Antonov-Homenovskii 1960) at high frequency, low voltage and low temperature (Morehead 1958), for high Cu content (Kritzsche 1960) and poisoned by Co and Ni etc. (Goldberg 1959).

If a direct current is applied to a single crystal the light output is proportional to the current and increases exponentially with applied voltage. In the case of thin films the EL characteristics is shown as (Ivey & Thornton 1961):

$$ B = A \left[ \exp \left( \frac{V}{C_1} \right) - 1 \right] $$ (1.2)

It is usually found that the intrinsic EL brightness increases when the frequency of excitation is increased and is approximately proportional to the exciting-frequency of lower frequencies, saturates at sufficiently high frequency and may decrease at still high frequencies (Piper & Williams 1958). A similar characteristic is observed in the case of single crystals (Piper & Williams 1952) and thin films (Helsted &oller 1954).

Thornton (1956) by considering the recombination rate to be determined by field controlled release of electrons from traps and assuming a constant number of excited centres ($N_0$) for each half cycle of voltage gave the following
expression

$$B = N_0 f \left[ 1 - \exp \left( -1/t \right) \right]$$  \hspace{1cm} (1.3)$$

where \( A \left[ \sim \int_0^{2\pi} \exp (aV \sin x \, dx) \right] \) increases as the voltage is increased. Vale (1956) considered that the effect of voltage is to drive electrons back to the empty luminescent centres and the kinetics to be monomolecular and thus give a similar relation with \( A \) directly proportional to \( V \). The saturation effect and also the effect of voltage on the frequency dependence is accounted for by this relation.

The effect of frequency on the different bands of a multi-band system have been found to be different (Watt and Gova 1962) but in general spectral emission is found to shift towards shorter wavelength side with increase in frequency.

The temperature dependence of EL brightness is found to be different for different luminors (Thornton 1956). Changes in EL brightness occur in the temperature range where the role of traps is changing. The different effects of temperature on the EL output are: thermal quenching of luminescence at high temperature and temperature dependence of resistivity in the low field region as controlling the voltage across the barrier (Alfrey & Taylor 1956; Hase 1957), action of electron traps in the low field region in controlling the rate of return of electrons to the excitation region (Thornton 1956; Hase 1957; Morehead 1958), thermal ionization of electron
traps in the barrier region as responsible for enhancing the barrier (Johnson et al. 1956; Piper & Williams 1955), thermal escape of holes from empty activator centres as responsible for decreasing the barrier (Zalm 1956; Morehead 1958) and trapping of electrons in the low-field region as impeding the growth of the barrier (Zalm 1956).

EL efficiency follows directly from the ratio of light output to the power input (Ivey 1963) and is usually maximum for intermediate values of voltage and frequency, although the dependence on frequency may be very small in some cases (Lehmann 1955). Maximum brightness and maximum efficiency cannot be achieved simultaneously. EL efficiency also depends on the particle size of luminor powders and for this it is higher for smaller particle size (Lehmann 1958).

The brightness waves represent the variation of EL light emission during each cycle of excitation of varying electric field. For conventional EL cells in addition to the two main or primary peaks observed per cycle of alternating voltage there are generally minor or secondary peaks associated with them. The position of primary peaks with the applied field is found to be a function of frequency and voltage of the exciting field and the temperature (Destrieu 1947, Destrieu and Ivey 1955, Thornton 1956, Destrieu 1956, Phuschan et al. 1978, 1979, 1980). The secondary peaks are also found to be

Although DC EL has been observed in different forms like powder luminors, single crystals and thin films, a very little effort has been done on the powders probably because of difficulty in achieving it. One of the first observations of the DC EL on powders was made by Zaln et al (1954) on a binder less layer. These workers recognised the need of a copper-rich surface layer to obtain EL. The DC light output was found to vary according to the relation (1.1). Butler and Naymouth (1955) observed EL due to excitation by DC pulses from insulating layer. Nicoll and Kazan (1955) observed DC emission when high fields were applied to phosphors in cathode ray tubes. Bowtell and Bate (1956) obtained DC emission from compacted layers of ZnS phosphor-coated with a layer of an ionizable salt like potassium silicate compressed between two conducting surfaces. Thornton (1958) observed DC EL in conventional powder-plastic dispersions with high phosphor-plastic weight ratios. An increase in the AC light output of up to 250 times was recorded by the addition of DC-voltage. Kazankin et al (1959) observed DC EL in powder layers of ZnS:Cu, Mn in castor oil. They observed persistent luminescence only when Mn was present and when sufficient copper was added.
Similar characteristics were reported by Favorin and Kozina (1961) on \( \text{ZnS:Cu} \), \( \text{ Mn powder luminors in a solid dielectric resin} \). Zallen et al (1960) observed EL under DC voltage pulsed excitation and Fridkin (1961) achieved polarization of \( \text{ZnS:Cu} \), Cl powder layers which persisted for a long period of time. Quantitative brightness and efficiency of DC EL powder layers on \( \text{ZnS} \) were reported by Vecht and Ellis (1964). It was found that the firing atmosphere had a marked effect on the efficiency. The maximum efficiency was observed at lower concentration of Cu where as the brightness was maximum at higher concentration of Cu. High purity starting material and careful monitoring of the level and nature of Mn and Cu were required to obtain reproducible DC EL properties. Presence of chloride resulted in rapid loss in efficiency and the maximum efficiency and brightness were observed at room temperature (Vecht et al 1969). Further, the copper coated phosphors exhibited a 'forming process' in which the initial high current falls during the first minute of voltage application if sufficient power is dissipated in the layer. The fall in current is accompanied by the onset of DC EL emission. Narrow band luminescence from rare earth centres in \( \text{ZnS} \) powders were reported by Waite and Vecht (1971). The EL spectra was found to be different compared to those of PL spectra. Recently Vecht et al (1981) have claimed that the alkaline earth sulphide phosphors may provide alternative and
more versatile systems for DC EL than the established ZnS: Cu, Mn.

Problem undertaken:

Although alkaline earth sulphide luminors have been known since Lenard's (1928) time but have been neglected probably due to their low light emission. However, Lehmann (1971, 1972) based on his work on CL of CaS has shown that CaS and related luminors are extremely attractive for fundamental luminor research as well as from applicational point of view. According to him quantum efficiencies of about 80% or more are routinely possible. Further as mentioned earlier alkaline earth sulphide phosphors may provide alternative systems for DC EL than the established ZnS:Cu, Mn. Thus it would be worthwhile to undertake detailed study of CaS doped with different rare earths. With this view for the present thesis CaS doped with different rare earths (Er, Sm, Nd) has been selected. The various studies done on EL concern with (1) AC EL brightness as a function of voltage and frequency of the applied field, temperature, brightness waves as a function of voltage and frequency of applied field and the temperature; spectra as a function of frequency of applied field and various activators used; the current through the cell and the efficiency as a function of applied voltage,
(ii) DC EL brightness as a function of voltage of the applied field and the temperature; spectra as a function of various activators used; current passing through the cell and efficiency as a function of applied voltage. The mechanism of DC EL has so far been a matter of controversy. From the present work on the DC and AC EL of rare earth doped CaS, it has been possible to conclude that a Mott-Schottky barrier is effective and a transport process of Schottky emission type is effective. In terms of this process the experimental results of efficiency are well explained. Results of PL spectral studies and the dependence of brightness on temperature have also been included for comparison and knowing the recombination process of luminescent emission. The phosphorescence decay studies (where ever observed) have also been done.