CHAPTER 1

INTRODUCTION
The electro-optical properties of materials are mainly concerned with (i) conversion of electrical energy into optical energy (electroluminescence) (ii) vice-versa (Solar Cells), and (iii) detection of optical signals through electronic processes (photoconductivity). The present thesis includes studies on (i) and (iii) kinds of some II-VI compounds. The II-VI compounds form a very important class of materials, because these materials:

(a) have band gap which range throughout the visible spectrum.
(b) can be produced in the mixed crystal form and
(c) are direct band gap materials.

The phenomenon of light emission from materials in excess of thermal radiation at a given temperature is called luminescence (Piper and Williams 1958). Depending upon mode of excitation, the phenomenon of luminescence is classified into a number of classes and some important classes are mentioned below (Garlick 1958):

(a) Photoluminescence (PL): that produced by absorption of light (photons).
(b) **Electroluminescence (EL)**: that produced by application of an electric field (AC, DC or pulses).

(c) **Radioluminescence**: that produced by bombardment with high energy particles (α, β, protons etc.) or radiations (γ-rays, X-rays etc).

Cathodoluminescence (CL) is produced by cathode rays and is a specific case of this class.

(d) **Chemiluminescence**: the emission which is accompanied with a chemical reaction and such type of luminescence in living organism is called Bioluminescence.

(e) **Triboluminescence**: the luminescence resulting from mechanical strain and fracture of certain luminor crystals etc.

*Thermoluminescence (TL) however does not refer to thermal excitation but rather to thermal stimulation of luminescence emission which is pre-excited by other means (u-ν, X-rays, β-particles, γ-rays etc.)*

*Photoconductivity (PC) is phenomenon of increase in conductivity of compounds due to absorption of light*
and thus includes important processes like absorption, photogeneration and recombination.

The present thesis describes investigations on the PC and EL of some of II-VI mixed compounds. Results of PL are also included for comparison.

Because of presence of some foreign elements or the defects in host lattice during the preparation certain impurity sites or centres are produced where from the luminescent emission is usually originated. Foreign elements producing such centres are called 'activators' (Rothschild 1960). Some of the materials like uranyl salts, plationocynides and rare earth salts, etc. however show luminescence in pure states. In some cases the native ion vacancies create centres and a term 'Self' activated or 'Undoped' is used for such materials.

The solubility of most of the activator elements in host lattice is increased by the addition of another element known as co-activator. For example the trivalent III$_B$ ion or a halide VII$_B$ ion usually acts as co-activator in host lattice of II$_B$-VI$_B$ compound. In some materials
the localized electronic states of the activator systems are well approximated by states of the free activator ion which are perturbed by crystalline interactions, while in other materials the localized states are more approximately treated as electronic states of pure crystal which are perturbed by the activator atom.

In II\textsubscript{B}-VI\textsubscript{B} compounds the substitution of group I\textsubscript{B} activators for II\textsubscript{B} or V\textsubscript{B} group for VI\textsubscript{B} yields a series of discrete states above the valence bond. In the natural crystal with only these impurities present, the highest state is empty consequently the activator is an acceptor. The substitution of a III\textsubscript{B} co-activator for II\textsubscript{B} or a VII\textsubscript{B} co-activator for VI\textsubscript{B} yields an extra electron in a donor state. (Piper and Williams 1958).

In contrast to the luminescent centres there are centres at which probability of non-radiative transitions is more than that of radiative one are called 'Killer Centres' (e.g. Fe, Ni and Co in Zns) and the impurities responsible for such centres are known as 'poison'.

Sometime the imperfection in the crystal lattice results in some regions which are able to capture
electrons or holes and detain them in restricted volume such that they are prohibited from moving freely through the crystal unless supplied with thermal or optical energy. Such regions in crystal are called traps (Bube 1967). Their production is dependent upon the presence of impurities (Bube 1952, 1953), atmosphere (Garlick 1949, Kröger and Hallingman 1949, 1950; Shushan and Chandra 1984) and temperature (Kröger and Hallingman 1949, 1950) during preparation. Electron traps are having excess positive charges and hole traps are having excess negative charges surrounding the defects. Some traps are associated with impurities in which trapping involves change in effective valence of impurity ion for example Sm$^{3+}$ changes to Sm$^{2+}$. Due to the presence of traps PL emission may be delayed and such phenomenon is known as phosphorescence otherwise it is known as fluorescence.

The normally observed luminescent bands are attributed to interaction between emission centres and the host crystal lattice (Vlam 1954). Thus the luminescent emission depends upon the nature of the activator and its concentration in the host lattice. At higher activator concentration the activator atoms destroy the matrix resulting in quenching of emission (Kröger 1948).
The phenomenon of electroluminescence observed in powders, when embedded in insulator and subjected to alternating electric field, is called intrinsic or pure EL (Destriau effect). The emission may also take place with the action of d.c. electric field on crystal or particles in direct contact with the electrodes due to injection of carriers (Destriau and Ivey 1955). Emission due to injection of carriers has also been found at P-N junctions (Homo and Hetero) and in metal semiconductor (M-S) and metal insulator semi-conductor (M-I-S) structures (Fankove 1977). In intrinsic EL it is observed that the brightness (B) increases more rapidly than linearly as the excitation voltage (V) increases. The relation which is found to be mostly suitable in intrinsic EL is expressed by (Alfrey and Taylor 1955, Zalm et al 1955)

$$B = B_0 \exp(-b/V^2)$$ (1.1)

The parameters $B_0$ and $b$ depend upon temperature, frequency of alternating voltage, the compounds, details of the construction of the cell (Ivey and Thronton 1961) and the dielectric constant of the insulator (Roberts 1952). The above equation is established with the assumption that the excitation mechanism is acceleration-collision one
together with the fact that the maximum field strength in Mott-Schottky barrier varies as $V^2$. At high Voltages (Antonov-V-Romanovskii 1959), high frequency, low voltage and low temperature (Morehead 1958) this equation is, however, not obeyed. Under the excitation of constant field brightness increases exponentially with the applied voltage up to the maximum voltage at which the crystals break down. In this case the $B$-$V$ relation also depends upon the type of electrodes used (Henisch 1962).

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 DC characteristics is found as (Ivey and Thornton 1961):

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

(1.2)

All these empirical formulae tell that there is no threshold for EL effect and any apparent threshold is controlled by the instrumental arrangements (Destriaau and Domergue 1958).

The EL brightness increases with increase in frequency approximately linearly at lower frequencies,
saturates at sufficiently high frequencies and decreases at still higher frequencies (Piper and Williams, 1958). Thronton (1956) by considering the recombination rate to be determined by field controlled release of electrons from traps explained the behaviour at lower frequencies and frequencies at which saturation occurs.

The effect of frequency on the different bands of a multiband system have been found to be different (Mattler and Cevey, 1962). However in all the cases the spectral emission shifts towards the shorter wave length side.

EL efficiency is usually maximum for intermediate values of voltage and frequency (Lehmann 1955). Maximum brightness and maximum efficiency cannot be obtained under the same operating conditions. EL efficiency also depends upon particle size. In ZnS it is higher at smaller particle sizes (Lehmann, 1958).

The EL brightness is also affected by temperature change (Mattler, 1950). Particularly at higher temperatures, the traps are emptied thermally thereby enhancing the intensity of the field in the barrier regions. Similar to PL the intensity of EL falls if the temperature is raised sufficiently because emission of lattice vibrations occurs in competition with photon emission (Kröger and Hallingman, 1948; Curie 1952).
PC process involve the transition of electrons between different energy states in a substance. The high pc of compound means high photocurrent. The photocurrent can be of two types (Bube 1967) (i) Primary photocurrent and (ii) Secondary Photocurrent.

The primary photocurrent comes from the direct effect of absorption of energy whereas the secondary photocurrent results from the passage of the primary current. Primary photocurrent is found proportional to light intensity and the applied electric field for lower values of the field which saturates at high fields. The secondary photocurrent becomes more prominent for high applied fields and high light intensities. They are characterized by gains greater than unity and by a nonlinear variation of photocurrent with light intensity.

Normally with excitation intensities three kinds of variations are found (Bube 1974). The first one is called a linear variation in which change in carrier density due to photo excitations is directly proportional to excitation intensity. The second one is called a sublinear variation in which the change in carrier density depends on the excitation intensity with a power less than one. In the third case the change in carrier density depends on excitation intensity with a power greater than one and is called superlinear variation.
Incorporation of imperfection in photoconductor may have one or more of the following effects: (1) Change in the dark conductivity: Donor imperfections in n-type material or acceptor imperfections in p-type material increase the conductivity. Donors in p-type material or acceptors in p-type material decrease the conductivity.

(ii) Change in the Photosensitivity:
Imperfections acting as efficient recombination centres decrease the sensitivity. Imperfections having high probability for capturing the minority carrier with subsequent small probability for capturing a majority carrier increase the sensitivity.

(iii) Change in the speed of response:
Imperfections acting as trapping centres decrease the speed of response. Imperfections which decrease sensitivity increase speed of response.

(iv) Change in the spectral response:
Imperfection levels lying in the forbidden gap extend the spectral response to longer wave lengths.

In II-VI compounds the sensitization effect may occur due to the incorporation of impurities (Bube 1967, 1976).
For example, there is a certain proportion of incorporated halide donors for which the ratio of light conductivity to dark conductivity is a maximum. Incorporating copper acceptors reverses the effect of donors and causes a decrease in light and dark conductivity. Oxygen in II-VI compounds also acts as acceptors and thus air bake of conducting evaporated layer reduces the dark conductivity and photoconductivity but increases the ratio of light conductivity to dark conductivity exactly in the same way as copper incorporation does.

Crystal defects also play an important role in determining the electrical and photo conducting properties of the materials. They can act by themselves as donors, acceptors, traps and recombination centres etc. At high temperatures the crystal defects are introduced into some materials (Mayburg 1954). Increasing temperature in some compounds decreases the photosensitivity i.e. temperature quenching of photoconductivity occurs. This result is normally related to the recombination of electrons which are thermally freed from traps with the photoexcited holes held at centres (Halperin and Garlick 1955). Increase in photocurrent (below quenching effect) with temperature is explained on the basis of impurity effect in the compound.
The thickness of layer in photoconducting compound cell also plays a major role. As the layer becomes thinner, the dark current decreases and the photocurrent increases. In surface type cell of ZnO at weak intensity saturation in photocurrent has been observed. In this case the overshoot and undershoot properties of photocurrent have also been found (Yonegawa et al 1973).

For photoconducting processes it is usually necessary to make electric contact by means of electrodes. Normally the electrodes should not produce any resistance to the flow of current, should not react chemically with the material and should remain unaffected by variation in illumination, temperature or applied field strength. The following are the causes for the formation of a barrier at metal semi-conductor contact (i) improper matching of work functions between the metal and the semi-conductors, (ii) Presence of surface states on the semi-conductor and producing an intrinsic surface barrier (iii) Presence of a thin layer of a third material such as an oxide. Butler and Moshchid (1954) showed that ohmic contact could be made to CdS crystals with a variety of metals if the contact area were first subjected to electron bombardment. Smith (1955) on the other hand found that Ag, Cu, Au, C and Pt do not make ohmic contact to CdS. Diffusion process
can also help in forming ohmic contact e.g. indium contacts to ZnS were ohmic only after heating for 600°C (Alfrey & Cooke 1956).

Photosensitivity is commonly described in three different ways. In the first method photosensitivity is related to change in conductivity per photon absorbed. Another way of representing photosensitivity is to relate it to the ratio of photoconductivity to dark conductivity. A third way of describing photosensitivity is that of gain which is defined as the number of charge carriers passing between the electrodes per photon absorbed.

The spectral response (excitation) gives very useful informations. For wavelengths much less than the absorption edge of the material, absorption is very strong and occurs near the surface of the crystal. In this range the photosensitivity is limited by the lifetime for recombination at the surface, which may be appreciably smaller than in the volume due to greater imperfection density at the surface. For wavelengths near the absorption edge, appreciable penetration of photoexcitation into the volume of the crystal occurs. For wavelengths much longer than the absorption edge, the incident radiation is only weakly absorbed and the resulting photoconductivity decreases
rapidly. Presence of impurities also affect the response by resulting in some peaks.

PROBLEM UNDERTAKEN:

Rare earth doped ZnO has been explored only recently by the earlier workers in this laboratory. The investigations reported by them include AC EL, CL (Kaza 1979, Pandey 1980 and Asre 1980) TL and the PC (Diwan 1986) Studies. Particularly a great potentiality was shown by Diwan (1986) for the rare earth doped ZnO photoconductor. Thus for the present Ph.D. thesis it was planned to study the effect of rare earth incorporation in some other strong photoconducting materials of II-VI compounds. Particularly studies on rare earth doped mixed base systems have not been investigated earlier. Therefore in the present thesis results of La and Dy doped CdSe-ZnS system have been incorporated. PC and EL studies have been done on this system. Conditions have been derived under which these materials produce the two kinds of effects.

The PC studies incorporated in this thesis include rise and decay studies as a function of temperature and atmosphere during preparation, concentration of flux and rare earths, applied voltage, intensity of excitation,
ambient temperature and pressure, different metallic electrodes and the cell thickness. Based on these results the origin of photo and dark currents have been discussed. Analysis of PC decay curves by peeling off method has resulted into the trap depth values of different traps existing in the material. Their nature has been discussed in the light of the concentrations of incorporated impurities. The nature of the ratio $I_{pc}/I_{dc}$ has been discussed in terms of the different parameters used. Nature of relative photosensitivity factor and the spectral response (excitation) has also been discussed.

The EL of this mixed base system has been observed by first preparing the ZnS electroluminor and then mixing CdSe in different proportions. The EL investigations include spectral response as a function of concentration of CdSe and those of La and Dy. Results of PL spectra are also incorporated for comparison purposes. The EL brightness studies as a function of applied voltage has given a way to understand the mechanism of excitation in these systems. The results of EL brightness due to change in frequency have also been incorporated. The general nature has been an increase in the brightness due to increase in frequency followed by a decrease at sufficiently high frequencies.