CHAPTER I

INTRODUCTION

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INTRODUCTION :

1. LUMINESCENCE :

1.1 History :

The luminescence as a result of chemical reaction in living organisms (bioluminescence)is probably the oldest observed luminescence phenomenon. The first ever luminescent material was synthesised by Casciarolo of Bologons, Italy, in 1903 by heating barium sulphate with coal. It emitted feeble blue light at night after exposure to day light. Later in 1768, Canton found a brighter luminescent material by heating calcium carbonate with sulphur. After that, A.H.Becqueral (1) laid the foundation for experimental investigations of emission spectrum and duration of after glow. It was then followed by the contribution of Lenard and his school and J. Becqueral, who studied phosphors doped with various impurities.

In 1889, Weidmann (2) gave the first,although not accurate, definition of luminescence, however, the first Law in this field was formulated by Stokes in 1852; Mott and Gurney in 1940, proposed theories to explain the phenomenon. A novel interest in the field arose with the theor tical contribution of Randall and Wilkins (5),Garlick and Bibson (6). Since then there has been a spectacular growth of phosphor studies and novel methods are being deviced for their synthesis and new phosphor materials with improved properties are continually being added to the list. The luminescent materials, so synthesised are being used in flurorescent screen for T.V., cathoderay tubes, electron microscopes, picture display panels, dosimetery and many other solid state opto electronic devices.

The rapid development of the luminescence field is not entirely due to the technological utility of the phosphors but also because of its importance in basic research. Various theorotical models so far proposed to account the phenomenon are useful in understanding the electronic processes involved in solids at the atomic levels. Thus, luminescence continues to be an active field of scientific research from both theorotical and practical point of view.

1.2 Definitions :

1.2.1 Luminescence :

Luminescence, in broad sense, is considered as physical process of absorbing the energy in the matter and its re-emission in visible or near visible radiations. These radiations are different from the radiations emitted by an incandescent body and do not include emission and absorption of black body radiations which obey the laws of Kirchhoff and Wein (3,4) Luminescence emission is also distinguished from Raman Compton, Rayleigh scattering and Cherenkove radiation. The time delay in luminescence after excitation is longer than 10^{-9} second, where as in other process it is of the order of 10^{-14} second(7).

The luminescence phenomenon is classified according to the mode of excitation used as follows :

a) Photoluminescence : produced by absorption of ultraviolet or visible radiation.

b) Radio luminescence : Caused by bombardment with high energy particles or radiations such as X - rays, gamma rays etc.

c) Cathodoluminescence : a special case of radioluminescence, produced by cathode rays.

d) Electroluminescence : casused by applications of electric field.

e) Sonoluminescence : produced by sound waves usually of ultrasonic range.

f) Triboluminescence : produced by utilization of mechanical energy.

g) Chemiluminescence : occurs as a product of chemical reaction.

h) Bioluminescence : a chemiluminescence in living organism.

i) Galvanoluminescence : produced during electrolysis in galvanic cell.

j) Thermoluminescence: it does not refer to the thermal excitation but to the thermal stimulation of luminescent emission when the sample is excited by other means.

Often, the combinations of above type are in use and are as follows :

a) Photo-electroluminescence : refers to radiation modulated electroluminescence.

b) Electro-photoluminescence : refers to the enhancement of light intensity by the applied field.

c) Electro-thermoluminescence : refers to thermoluminescence enhanced by the applied electric field.

d) Phototransfered-thermoluminescence : refers to thermoluminescence stimulated by radiation at high temperature, usually beyond 400° c.

1.2.2 Fluorescence and Phosporescence fig. (1.1) :

The general term of luminessence is categorised either as fluorescence or phosphorescence.Garlick (6) defines fluorescence as emission of light during excitation and phosphorescence as after excitation is removed. According to Lorentz (8) and Kroger (9) a luminescence emission which lasts up to the initial 10^{-8} second after excitation, is to be called fluorescence. While the subsequent is to be referred to as phosphorescence. Phosphorescence may be of short duration or long duration according to the over lasting time of 10^{-8} second to few minutes and above respectively.

1.3 ATOMIC SUBTITUTION :

While forming a crystal as a result of ions coming close to form a regular three dimensional pattern, one ion may take place of other ion (in the crystal structure). The replacement of finding a foreign ion in the crystal structure is known as atomic substitution.

Substitution of one element by another is the rule rather than exception. Which is determined in terms of concept of solid solution or mixed crystal (10). The extent to which atomic substitution takes place is determined by nature of the structure, the closeness of correspondence of ionic radii, temperature of formation of the substance and electronegativity. Ionic size has, of course a fundamental influence on the degree of substitution, seens subsituting ion must be able to occupy the lattice position without causing distortion of the structure. From the study of many mixed crystals, it has been found that radii of substituting and substituted ion do not differ by more than 15 % (10). A wide range of substituion may be expected at room temperature.Substitution is grater at higher temperature as the added thermal energy serves to increase vibrational motion of the ions so that crystal structure expands and behaves more to learnt for foreign particles being occupied.

Crystal structure investigations have also revealed two other types of soild solutions besides that due to atomic substitution. One is known as interstitial solid solution where by atoms or ions do not replace atoms or ions in the structure but fit into interstics in the lattice. This types is common in metals. The other type of solid solution is that associated with defect lattice in which source of the atom missing, leave vacant lattice position. It is also called omission of solid solution. Since in this case total charge is compansated. The process is anologous as in the building a wall, where bricksare omitted without affecting stability of the structure.

1.4 PHOSPHORS AND THEIR CLASSIFICATIONS :

Phosphors is a term applied in industrial technology to a luminescent material. They may be either organic or inorganic but most of interesting and commercially important ones are inorganic (12).

Conventional phosphors, consist of one and some times more of the following components.

i) the host which is the major component.

ii) one or more activators (acceptors) and

iii) a co-activator or charge compensator (donor) are classified as (a) phosphors in pure form, and (b) impurity activated phosphors.

1.4.1 Phosphors in pure form :

Certain phosphors show luminescence even when they are not intensionally activated but well purified. These are known as self activated phosphors. Heat treatments are usually necessary to make them luminescent. Some notable examples of this type are ZnO, many tungstates and molybdates diamond (13,14).

1.4.2 Impurity activated phosphors :

Impurity activated phosphors usually exibit better luminescence than the pure ones. For activation small amounts of foreign ions are added into the crystal lattices of the base compound, called host lattice or metrix material. The impurity or foreign ion, which causes luminescence is called activator. The second impurity introduced in addition to the first, to enhance the luminescence is called co-activator or sensitizer. Due to presence of some impurities (e.g. Fe, Co, Ni etc) the luminescence intensity decreases. These are termed as Killers or poisons.

1.4.3 Imperfections in solids :

The imperfection in solid gives rise to luminescent phenomenon. There are various types of imperfections. viz. point defect. line defects, surface defects and volume defects. Among these point defects play a significant role in luminescence. In the crystalline solids, the point defects are introduced by

thermal quenching, chemical doping, ion implantation, high energy radiation or nonstiochiometry etc. The impurities or lattice imperfections give rise to discrete energy levels in the forbidden energy gap of an insulator or semi conductor. These localised discrete energy levels are classified as :
(i) Luminescent, centre (ii) Killer centres (iii) Electron traps (iv) Hole traps and (v) Metastable states.

i) <u>Luminescent centre</u> :

These energy levels possess high capture crosssection for electrons and much greater possibility for radiative transitions than non radiative ones. The emission and absorption properties of these centres are characteristics of activator ion and base material.

ii) <u>Killer centres</u> :

These are distrete energy levels which possess small capture cross section for excited electrons and much greater probability for non-radiative transition than radiative ones.

iii) <u>Electron traps</u> :

These energy levels can capture an excited electron, which is produced at the luminescence contres or else where in the crystal without allowing an electron to fall directlly into a normally filled level.

Iv) <u>Hole traps</u> :

These localised energy levels just above the valence band are capable of capture of positive hole.

v) Metastable states :

These energy levels in the forbidden energy gap can be excited by high energy electron bombardment but not by photo excitation are called as metastable states. A transition from metastable state to ground state has very low probability to be radiative, i.e. transitions from metastable state to ground state are forbidden. The transition from higher energy level to metastable state are permitted. The mean life time of metastable state is found to be much longer (10^{-2} to 10^{-3} sec) than the life time (10^{-7} to 10^{-9} sec) of radiating level (11).

1.5 MECHANISM OF PHOTOLUMINESCENCE :

The mechanism of photolumenescence involves four processes (a) excitation, (2) emission (3) transfer of energy during excitation and emission and (4) storage of part of absorbed energy during excitation.

1.5.1 Excitation and Emission :

Several schemes have been proposed to explain these processes. Some of them are as follows :

A) Classical configuration co-ordinate curve Model :

The configuartion co-ordinate curve model is represented in Fig. 1.2. It was introduced by Van-Hippel (15) and was applied by Seitz (16) to explain the liminescence behaviour. In figure, the ordinate represents the total energy of the system for the ground and excited states of the centres, while abscissa the ' configuration of the ions around the centre. The equillibrium position of the centre in the ground state is represented by the point A. If the centre absorbs the light energy, it is raised to the excited state at B, The transition is vertical in accordance with the Frank-Condon principle. From B the centre releaxes to new equilibrium state C, the state corresponding to the minimum energy of the excited state. The energy difference between B and C (see Fig.1.2) is given off as lattice vibrations. Having reached centres at this new equilibrium position it returns to the ground state as D by giving luminescence emission. The centre finally relaxes from D to A again giving up energy to the lattice vibrations.

B) Energy Band Model :

The energy band model (17,18) is illustreated in fig.1.4. According to this model, the phosphors which are usually semiconductors or insulators, are describable in terms of the valence band (F) and the conduction band (C), with localised energy levels in the forbidden region between the bands. These localised levels are associated with impurities or imperfections in the host lattice. In fig. 1.3 such levels are shown. The level L represents the ground state of the luminescence centre, while the levels T_1 and T_2 represent the electron and hole traps respectively.

The act of excitation and emission takes place as follows:

Absorption of the light energy in the phosphor excites luminescence centre from its ground level (L) to the excited state (S_1) by raising the electron into the conduction band. Such excited centre then captures an electron from the conduction band and returns to its ground state by giving luminescence emmision. If the absorbed energy in the phosphor is equal to the seperation between the valence and conduction band, it also excites electrons (E) from the valence band into the conduction band creating holes (H) in the valence band. This absorption is known as the fundamental absorption band. However, such electron and hole pairs normally do not recombine radiatively (19).

C) Schon-Klassens Model!

This model was proposed by Schon (20) and elaborated upon by Klasens and his co-workers (21,22,23). Fig. 1.3 illustrates the model for the case of single luminescent centre. The ground level (L) of the luminescent centre is assumed close to the valence band. On absorption of light in the fundamental absorption band, a free electron band and a hole are created. The electron moves to the conduction band while the hole diffuses through the valence band and captures an electron from the luminescent centre. This excites the luminescent centre. The free electron after migration in the conduction band falls into the empty centre which gives emmission of light.

D) Lambe-Klick's Model :

In this model (24) the ground state of the luminscent centre (L) is assumed close to the conduction band (fig.1.6) with absorption of light photon, a free hole and electron are produced. The hole diffuses to the centre where it captures the electron from the centre. This transition gives rise to luminescence. Subsequently the electron from conduction band diffuses to the centre and gets captured there, thus completing the cycle.

E) Williams and Frener's Model :

In the model proposed by Williams (25) and Frener (26) two centres are involved (Fig.1.5). The ground level (I) of the first centre is assumed close to the valence band while the excited level (II) of the second is assumed close to the conduction band. After absorption of the energy in the fundamental absorption band a free hole and an electron are produced. The excited level II captures an electron from the conduction band while the hole in the valence band captures an electron from ground level (I) and thus leaves it empty. The emission then takes place by the transition from the level (II) to (I) (See fig. 1.5).

1.5.2 Energy Transfer :

In phosphor systems where absorption and emission of light energy takes place at the same centre, no energy transfer is involved. However, in system in which absorption and emission are not confined to the same centre, energy is transferred from absorption centre to the emission one. It occures in two ways :

A) Energy transfer with no movement of charge carriers, and

B) Transport of energy by charges carriers.

A) Energy Transfer With No Movement of Charge carriers'

There are three mechanisms for transfer energy in such cases.

i) Cascade Mechanism :

In this type of mechanism (27) one centre on absorbing excitation energy emits radiation (Primary emission). This emitted radiation is then absorbed by the second centre, which finally emits luminescence (secondary emission). This mechanism is most effective in those cases where the primary emission overlaps the absorption spectrum of the secondary emission system.

ii) <u>Responce Transfer</u> :

Here the transfer of energy from absorbing system to the emitting system is accomplished by a quantum mechanical process (28, 29) such as electric dipole field overlap, electric dipole quadrupole field overlap or by exchange interaction. The efficiency of process depends upon the distance over which the energy is transferred.

iii) <u>Exciton Migration</u> :

The non-conducting excited electron hole pairs are known as excitons. Because of their interaction with phonons they do not remain localised but migrate throughout the crystal transferring the energy. In such processes the excitons transfer excitation energy from one point to another by moving quickly through the lattice without contributing to the electrical conductivity (30).

B) <u>Energy Transfer with Movement of charge carriers</u> :

In this mechanism, energy is transferred by electron and hole migration. The process is the same as that involved in Schon-Kalsen's and Lambe-Klick's models during excitation and emission.

1.5.3 Energy storage :

Many phosphors store part of the absorbed energy during excitation. This is due to the trapping of the excited electrons in the trap levels. The energy required to liberate a trapped electron is known as the " activation energy ", and is also known as the ' trap depth ' as it is the energy difference between the trapping level and the corresponding excited level.

A) Phosphorescence Decay :

Phosphorescence decay is diminishing after glow under isothermal conditions, observed from 10^{-8} second, after removel of excitation. It arises due to the release of trapped electrons in trapping levels during excitation.

The mechanism of phosphorescence decay can be followed from the energy band model of Fig. 1.4 . An electron raised into the conduction band by absorbing light energy may according to minimum energy principle - fall into a trap (T_1) instead of immediately recombining with a centre. After some time the trapped electron returns to ground state via a conduction band giving rise to phosphorescence (process HE T_1 S_1 L).

i) Effect of Trap Distribution on Phosphorescence Decay :

The intensity and form of the decay depend upon the distribution of traps. If traps are located close to the conduction band the resulting decay is faster and hence it is of short duration. On the other hand, it is of long duration if traps are situated at a great distance from the conduction band. The intensity of the phosphorescence decay is a function of population of traps of particular depth, More the population, higher is the intensity and vice versa.

B) THERMOLUMINESCENCE :

Understanding of TL on Configurational co-ordinate (c.c) diagram :

When TL occurs within an isolated luminescence centre, the process is usually more meaningfully described on the configuration diagram fig. (1.7) (31). The energy of trapping state in interaction with the lattice is a configurational co-ordinate curve U^T (r). When the system is in the ground state and by U^L (r). When it is raised to an excited state from which luminescence transition take place. The ground state of the system before the trapping took place is represented by U^G(r). it is convenient to imagine the curve U^G(r) and U^L(r) to be representative of the potential energy of the system, trap + lattice. While U^T(r) that of the shallow excited level of the trapping state.

The entire process of excitation, trapping and thermally stimulated emission can be described as shown in fig. (1.7).

This model gives a more clear picture about the detrapping spacially regarding the thermal and optical activation energy differences . There has been arguments favoring to the use of c.c. diagrams even in the cases where the detrapped electron enters the conduction band before the luminescence transition occurs. The ionisation continuum is considered to be given by all energies lying above the curve U^L(r). Which represents potential energy of the system " trap + lattice " . When the electron has just left the trap and is in the conduction band.

Glow Curve :

A glow curve may have a single or multiple glow peaks, depending upon the presence of the trapping levels of different depths. A particular glow peak belongs to the traps of one depth, and is characterised by its own peak temperature and height. These are the functions of position of the trapping level below the conduction band and the number of electrons trapped in the level. The peak height is also a function of the rate of heating. This is because, at higher heating rate the rate of release of electrons from the traps increases and so does the TL intensity.

EFFECT OF RETRAPPING OF ELECTRONS ON PHORPHORESCENCE DECAY AND THERMOLUMINESCENCE :

The electrons escaped from traps may either recombine with luminescence centre or may be retrapped in deeper empty-traps. The presence of retrapping in the phosphorescence decay makes delay in the recombination process and thereby afffect its time constant. The retrapping also changes the form of decay as it occurs in the deeper traps.

In thermoluminescence, presence of retrapping modifies the shape of the glow curve especially its high temperature side. This is because the electrons released from the shallow traps, during early stage of thermoluminescence, are retrapped in the deeper ones. These electron are then released at high temperature and enhance the TL emission.

KINETICS OF LUMINESCENCE :

Kinetics of luminescence is concerned with the mechanism involved in recombination of electrons with luminescence centres.

It may be either monomolecular (first order), bimolecular (second order) or intermediate.

i) Monomolecular Kinetics :

If the traps are situated close to the luminescence centres (less than 10^{-6} cm. away) and if a vary small movement of electrons is made to recombine with luminescence centres, the kinetics of luminescence process is said to be monomelecular (21). Under such a situation,according to minimum energy principle, there is negligible probability for an electron to be retrapped in the deeperempty traps. Thus in the monomolecular kinetics the probability of retrapping is negligible or, in other words, the process of recombination is dominent (32, 33).

ii) Bimolecular Kinetics :

In this case the traps are located away from the luminescence centres (at distance greater than 10^{-5} cms) and the elctrons have to go through large displacements for recombination with luminescence centres. Under such circumstances, according to the minimum energy principle, there is greater probability for an electron to be retraped in the deeper empty traps. Thus in bimolecular kinetics, the process of retrapping is dominent (34,35)

iii) Intermediate kinetics (36) :

Kinetics of luminescence is said to be intermediate when it is neither monomolecular nor bimolecular. Under this situation the relative location of traps from luminescence centres is an intermediate case and similar is the condition with the processes of recombination and retrapping.

C. MECHANISM OF EL :

The phenomenon of EL can be considered to comprise three sequential process, (33).

i) Excitation

ii) transfer of energy from the site of excitation to the site of emission and,

iii) recombination.

i) EXCITATION :

The excitation of EL takes place by a supply of energy (potential or kinetic or both) to the charge carries (generally electrons). The different excitation mechanisms proposed are :

i) Field ionization of valence electrons and impurities: As the break down field competes with both of these processes, activator systems having a low ionization energy in delectric phosphors (large band gaps), should be more conducive to EL by this process.

ii) Injection EL. Injection of minority carriers may occur either at an electrode contact or a P.N.Junction. In a surface contact, the interface may posses ohmic characteristics or is capable of rectification and, thus, its behavior is governed by factors like the difference in the work functions, the position of the Fermi level in the semiconductor, nature of the intermediate chemical or physical barrier layer, surface states and the concentration of the donors and the accepters. For example, in an idealized case of the difference in work function being the dominant factor, an ohmic contact is formed between a n-type semiconductor and a metal, if the work function of the metal is less than that of semi conductor. A rectifying contact, however is formed for an inverse situation. The barrier formed in the latter type of contact is known as Mott-Schottky barrier. In cases, where the work function of metal is no more than a few "kT" less than the sum of the electron affinity and the band gap of semiconductor, the Fermi level approaches the valance band in the region near the surface (P - Type) and this result in an inversion layer. In this type of a barrier, minority carriers can be injected <u>in to</u> the interior of the semiconductor. Injection EL occurs in following structures.

a) <u>P-N.Junctions</u> : As shown in [FIG.1.10 : Conditions at a P-N junction: (a) at equilibrium and (b) under forward bias. Ec, Ev and Ef represent conduction band edge, valence band edge and Fermi level respectively. V is junction voltage under forward bias. The arrow represents a band- to - band recombination]. the potential energy of electrons in the N-region is raised under a forward bias, which allows the flow of electrons in to the P - region and similarly the flow of holes into the N-region. As soon as an overlap of electrons and holes occurs, their recombination becomes possible. The Light Emitting Diodes (LED's) often have one side of the junction more heavily doped than the other. Due to this, the carriers in the larger doped side have the benefit of the reduction in the barrier height.

b) <u>Heterojunctions</u> : As shown in the FIG. 1.8 :[condi- tions at a heterojunctions (a) at equilibrium and (b) under for ward bias. $Ec._1$, Ev_1 and Eg_1 represent conduction band edge , valence band edge and band gap of material number 1 respectively.

A subscript 2 has been used for material number 2, Ef and V have their meaning as in figure 1.10] The large band gap materials act as a source of injucted carriers and that with small band gap as luminescent region.

c) Schottky barriers : (FIG.1.9: A schottky barrier for an N-type semiconductor. Symbols mean as in fig.1.10 Arrow indicate minority carrier injuction during forward bias) Shows the inversion layer in an N-type material. Under a forward bias, the band are flattened allowing the injuction of minority carriers in to the bulk matrix, where they recombine radiatively.

d) Metal-Insulator-Semiconductor (MIS) structure : In this structure the band bending can be controlled by an applied voltage and an inversion layer can be introduced by one polarity. The carrier so accumulated at the surface can be injucted by reversing the polarity of metal electrode FIG.1.11:[Light emission at a metal-insulator-semiconductor (MIS) structure (a) without bias, (b) metal (-)ively biased to form an inversion layer in which the surface (P - type) and bulk (N-type) have opposite conductivities. holes are generated in the surface region and (c) metal is (+)ively biased. The holes accumulated at the surface are injucted and recombination takes place (shown by arrow).]. If the insulator is made thin (10nm), the injuction of electrons can take place by tunnelling .

iii) Radiative tunnelling : As is shown in (FIG.1.12 radiative tunelling across P-N junction under forward bias. $h\nu_{max.}$ and $h\nu_{min.}$ show the maximum and minimum energy of emission respectively) electrons from the conduction band tunnels into the gap where it makes a radiative transition to the valance band or to an empty state in the band gap. For this process to occur, the semi conductor should be degeneratly doped on both sides, as has been observed in the case of Ga (As),

iv) Acceleration - collision EL : A process, found in most suitable materials like ZnS and is based on the acceleration of the electrons in the conduction band followed by a collision excitation of the luminescence centres. It various stages are shown in FIG.1.13 :[Acceleration-collision machanism : (1) liberation of electrons from traps by the field and/or temperature, (2) Accèleration of electrons, (3) Collision with electrons in activator centre, (iv) Ionization or excitation of activator centre (emission occurs in reversing sites of AC)] . A Mott-Schottky exhaustion barrier is suggested to account for the stability against breakdown at the field strength at which EL excitation takes place. The field in the barrier and the thickness of the barrier increase as the square root of the voltage. The source of charge carriers may be dip donors:., acceptors or traps which are field ionized. Excitation may also occur from hot carrier. Three impact processes relevant to high field EL i.e. ionization across the band gap, impurity excitation and ionization have been considered. . Carrier Acceleration may also occur in semiconductors unddr reverse bias.

v) Break down luminescence : By gaining sufficient energy from the electric field, electrons and holes are multiplied and thereby form an avalanche breakdown. The pairs created in this was, recombine radiatively and such kind of emission has been observed in Si , Ge and GaAs.

vi) Luminescence from travelling high field domains :

EL may arise from travelling high field domains. However no experimental results have been reported supporting this.Several phenomena convert low applied electric field into domains of intense electric fields, which then travel through the specimen and generate high density of electron-hole pairs, either by impact excitation or by zener tunneling. In P-N junctions, the domains can cause a breakdown or injuction.

ii) ENERGY TRANSPER :

The mode of energy transfer from the point of excitation to the side of emission occurs via numerous agents. The most obvious candidates are charge carriers. The flow of energy due to the transport of charge carriers depends on the concentration gradient, the electric field intensity and the concentration of the trapping states. Hall and Shockley and Read obtained explicit expressions for the capture and recombination process occurring in a material, in which only one type of recombination centre (having one levels in the forbidden region)is present. Haynes and Hornbeck extended this analysis to the cases of a centre with more than one such level. Broser and Broser - Warminsky analysed specific types of luminophors with more than one type of centre. The theory of positive hole migration between activators has also been developed. The transport of energy from the electrically excited system to the emitting system can also occur by mechanisms not involving electronic charge carriers, i.e. by

i) Cascade transfer mechanism,

ii) Resonance transfer mechanism, and

iii) Exiton migration mechanism

These depend on the relative proximity of the centres capable of luminescing, the overlap of absorption and emission bands and dipole-dipole, multipole interactions

iii) RECOMBINATION :

In the process of recombination, various transitions take place from upper energy state to empty lower energy states. These transition can be radiative or non-radiative. Radiative transitions occur by the following processes :

i) Band to band transition : In direct semiconductors it occurs between conduction and valence bands and in the case of indirect semiconductors it requires emission or absorption of a phonon to complete the lowest energy transition across the energy gap.

ii) Travelling between baad impurity : A radiative transition can occur between an impurity state and an intrinsic band and its probability is high, if the impurity state is deep,

iii) Transition at a localized centre : In large band gap materials impurities can be excited without ionizing them i.e. without exciting their electrons to the conduction band.

iv) Transitions at isoelectronic centres : Such centres are formed by replacing an atom of the host crystal by another, but with the same valence. Radiative transitions can occur in the exciton bound to an isoelectronic centre, and,

v) Donor-acceptor transition : Efficient transitions can also occur between donor and acceptor levels and such transitions are found in LEDs (Thomas et al) and in phosphors.

Transitions from upper to lower energy states occurring without emission of photons are termed as non-radiative transitions and can occur through a number of processes such as:

i) Multiphonon emission at the intersection of the ground and excited state configuration diagram. The electron can escape the excited state and return to its equilibrium position by generation of several phonons.

ii) Auger effect, wherein a recombining electron can transfer the energy (which it would have normally radiated), to another electron in the excited state. This electron goes to a still higher energy state and returns to lower energy excited state by multiphonon emission; and

iii) Non-radiative defects such as surface recombination crystal defects providing regions, where a localized continuum of states can bridge the energy gap and cluster of vacancies (or a precipitate) of impurities can form non radiative centres.

1.6 Review of Work done by earlier workers :

i) Thermoluminescence :

Nambi K.S.V.(34) studied factors effecting TL intensity of phosphors. Nature of impurity concentration, thermal treatment, irradiating dose, stress, crystallization storage effect, thermal quenching effect, electrostatic effect and IR stimulation of $CaSo_4$(RE^{3+}) TL curve indicates multipeak structure for gamma irradiation. TL emission spectra give sharp lines and these lines do not change due to change in temperature. Nambi KSV et al (35) also found that ionic radii of Dy^{3+} and Tm^{3+} having ionic radii quite close to each that Ca^{2+} have maximum TL output, while La^{3+}, Yb^{3+} and Lu^{3+} whose ionic radii are largely different from that of Ca^{2+} do not yeild any significant increase in output. The kinetics in above phosphors is observed to be bimolecular and that TL glow peak at 200°c (by gamma irradiation dose), and $CaSO_4 : Tm^{3+}$ can be used gamma radiation detector, for measurement of gardendose (36) or environmental radiation in BARC.

In CaF_2 , $CaSO_4$ and $CaCO_3$ the impurities Mn, Pb, Dy give strong TL emission (37). The light output is affected during thermoluminescence by external electric field (38). $CaSO_4 : Dy^{3+}$ have a storage capacity (39) , cabable to detect thermal neutrons (40) . These phosphors can to used in medical dosimetry (39) radiotherapy and nuclear medicine(41).

Principle of TL dating, basic age equation can be written (42)

$$\text{Age (year)} = \frac{\text{Natural TL (aquired dose)}}{\text{(TL per rad) + (rad per year)}}$$

Patil M.G. studied Cas : Dy : Ag for which PL, TL and EL phenomenon have been reported (43) for CaS : (Fe, Co, Ni)act as effective Killer (44), while Gd is effective. Borates of composition $Ca_2\ Mg\ (BO_3) :$ RE have been studied (45). Systematic development of phosphor preparation, the TL behavior under gamma and UV radiation, Characterization of the emission spectra and associated traps and applicability of these phosphors in dosimatric applications, the origin of traps, appropriate rare earth activator and possible energy transfer are other significant out come of this work.

ii) Electroluminescence :

Electroluminescence studies of CaS : Bi : Pd have been carried out by Lawangar et al (45) found to be brightness waves are due to location of traps. In phosphor $CaSO_4$:Bi power Law relation holds good, concentration effect on EL behavior followed by concentration quenching and also $Na_2 SO_4$ change compensator is found to be enhance EL behaviour(46);The power law relation holds over a wide range of frequency for CaS : Dy : Ag and log I Vs V represent Mottshottky barrier (43). In case of CaS :Mn phosphor, $B = a (V - V_o)^n$ relation holds good with $n \simeq 5.6$ and $V_o = o$ and brightness wave form consists of two major peaks, percyle brightness is not inphase with applied voltage (48).

For a non activated phosphor CaS new type of luminescent centre with vibronic structure has been observed (49). It is also concluded that molecular anions including Oxygen and hygrogen may be responsible for the luminescence. In CaS : Nd : Cu, phosphor, temp. depends field ionisation mechanism, Usual phase lag of brightness wave does not change appreciably with change in frequency (50). Doped ZnS shows decrease of EL brightness with frequency (51, 52). The phosphor CaS :Sm does not give emission under a.c. and d.c. excitation however its PL is good , but EL brightness increases at 80°c which depends on temperature (53). The emission spectra of CaS:Sm show three bands and CaS:Dy show five band (54).

iii) Thermally stimulated electric conductivity :

Friauf, R.J.(55) determined defect that contributes electrical conductivity of the samples NaCl and KCl. The resistivity is found in the range 10^{14} and 10^{19} Ω cm between temperature range 100°c and 700°c. Through corelation studies of PL, PC,TL and TS Marwaha et al (56) arrived at charge transfer as a dominated phenomenon in case of $CaS{:}Bi^{3+}$. Electron traffic is shown to be through conduction band where as their subsequent recombination through excited state $3p_1$ accounts for characteristics of Bi^{3+}.

High band gap energies of the order of 10 eV and 12 eV are observed for CaF_2 and LiF respectively. UV radiation of wave length 200-300 n m (4 to 6 eV) can't produce electronhoee pair directly in these TL material (57). The observed TL is possibly due to direct ionisation or excitation of bound electrons of activator by UV radiation. The ionised electrons get trapped in the centre and excited electrons in the metastable state of activatcr. On heating, these electrons possibly get released from their traps and return to the ground state of the activator via excited centre, this might result in TL.

TL and TSC are assumed to be different manifestations of the same basic process of release of electrons from the trapping sides. In a photoconductors electrons reach the recombination centre from traps through conduction band as such the process of thermoluminescence would be accompanised by change of conductivity of phosphor. There is a possibility that same carrier may be responsible for TL and TSC (58). The corelation studies of TL,TSC would therefore reveal the nature of mechanism involved in the both process.

1.7 Statement of the problem :

As discussed in section 1.6(i) $CaSO_4$:RE is widely studied In the last three decades, some interest has been Found in CaS phosphors doped with metallic impurities such as Bi, Mn, Cu etc. and rare earth impurities such as Eu, Sm, Tm, Dy, Nd etc. (35,37 43,46,47,48,52,54). Most of the investigations made so far on these phosphors have been confined largely to spectroscopic studies with ulta-violet excitation and very little attension has been paid to luminescence studies with double dop ed rare earth as activator and co-activator. More over, very little is known about the nature and origin of the traps, exact mechanism of energy transfer, kinetics of luminescence and exact role of fluxes.

In order to gain information mentioned above, in present investigation CaS phosphors doped with varing concentration of activator and co-activator RE_1 and RE_2 respectively are synthesised ~~[illegible]~~ to find appropriate combination of RE_1 : RE_2 as a good pho . Fluxes of fixed amount (NaF, Na_2SO_4, $Na_2S_2O_4$) are used for sample preparation,samples are prepared in microcrystalline powder form, and their PL, TL, TSEC and EL have been studied systematically.

1) Photoluminescence :

It involve study of phosphorescence decay. The decay curves have been analysed to infer the decay law as well as kinetics of PL process. The trap depths have been calculated by ' peeling off' procedure. An attempt has been made to infer the distribution of trapping states.

2) Thermoluminescence :

The result of thermoluminescence have been examined in terms of some recent theories and an attempt has been made to investigate the effect of concentration of (RE_1,RE_2) impurities on glow curves. Using glow curves the activation energy, the frequency factor and order of kinetics in thermoluminescence process have been estimated.

iii) Electroluminescence :

A.C. electroluminescence measurements have been carried out to investigate the possible relationship between brightness voltage and brightness frequency. Effect of concentration of activator and second activator are studied and brightness-waves are obtained for typical phosphors.

iv) Thermally stimulated electric conductivity :

An attempt is made to study temperature dependent electric behaviour of phosphor (without exciting the sample) and tried to estimate band gap energy of phosphor by using four probe set up.

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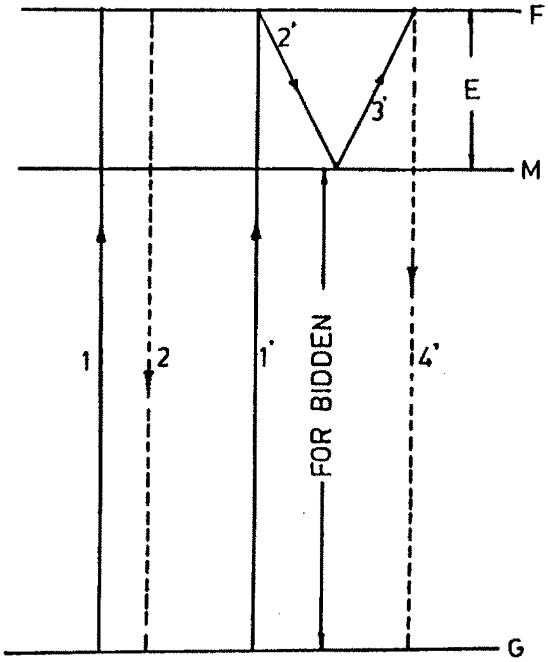
ENERGY STATES FOR FLUORESCENCE AND PHOSPHORESCENCE



G : GROUND STATE

F : EXCITED STATE

M : METASTABLE STATE

E : ACTIVATION ENERGY

1 1' : EXITATION FLUORESCENCE

2 : FLUORESCENCE

2' : DROP IN METASTABLE LEVEL

3' : ACTIVATION THERMAL OR OPTICAL

4' : PHOSPHORESCENCE

FIG.NO.:1·1

CLASSICAL CONFIGURATION COORDINATE CURVE MODEL

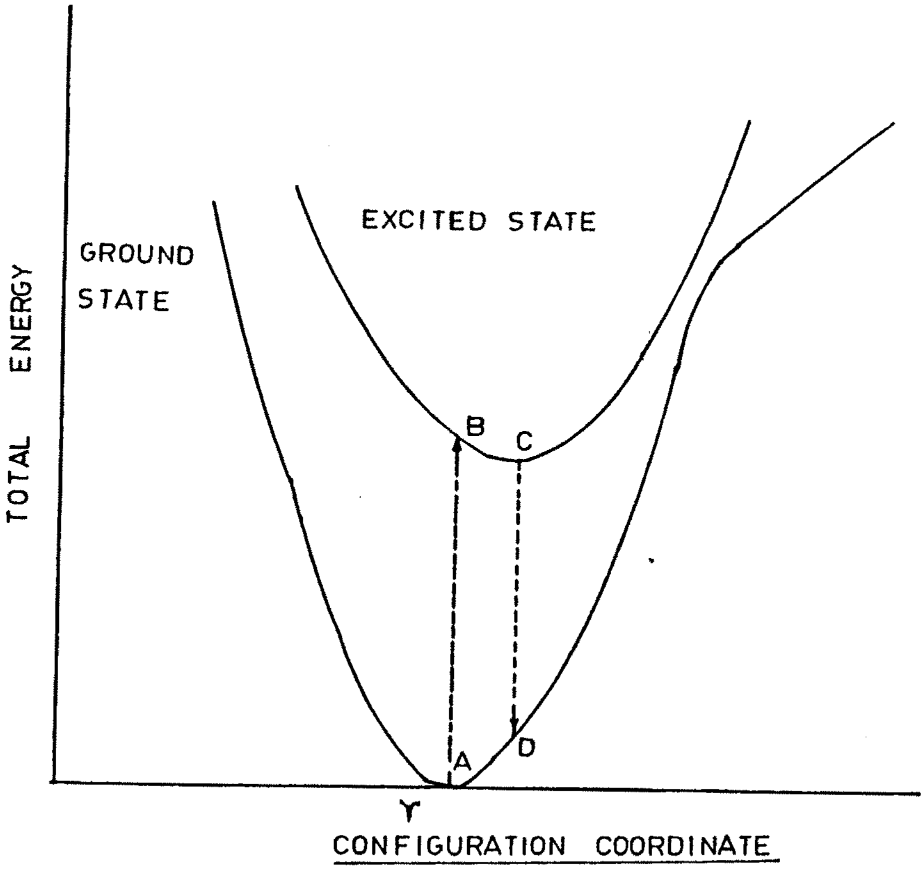


FIG.NO.:1·2

SCHON - KLASSEN'S MODEL

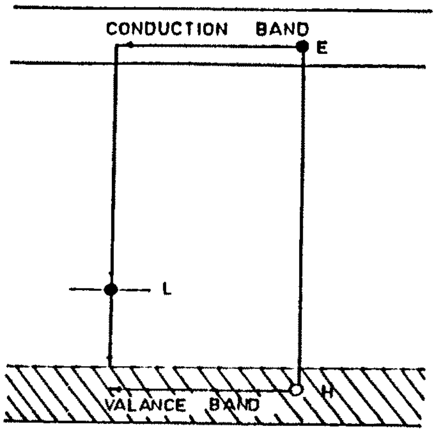


FIG. NO.: 1·3

ENERGY BAND MODEL

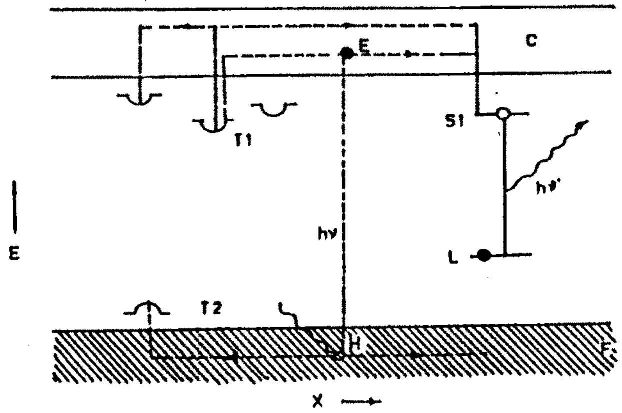


FIG. NO.: 1·4

WILLIAM'S AND PRENER'S MODEL

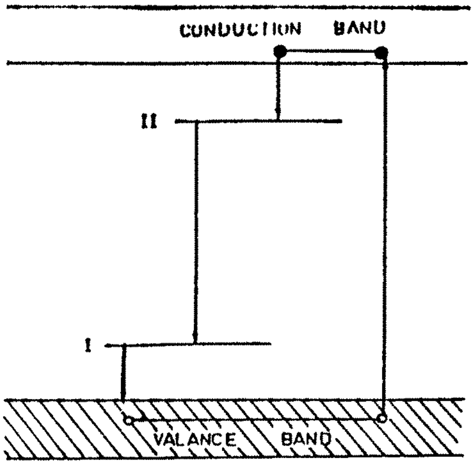


FIG. NO.: 1·5

LAMBE - KLICK'S MODEL

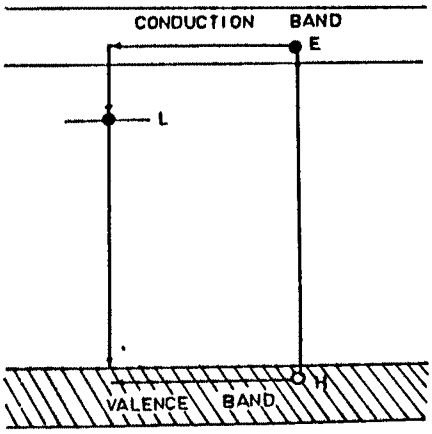


FIG. NO.: 1·6

THERMAL AND OPTICAL ACTIVITION OF A TRAP AND TL EMISSION, ON A CONFIGUATION CO-ORDINATE DIAGRAM

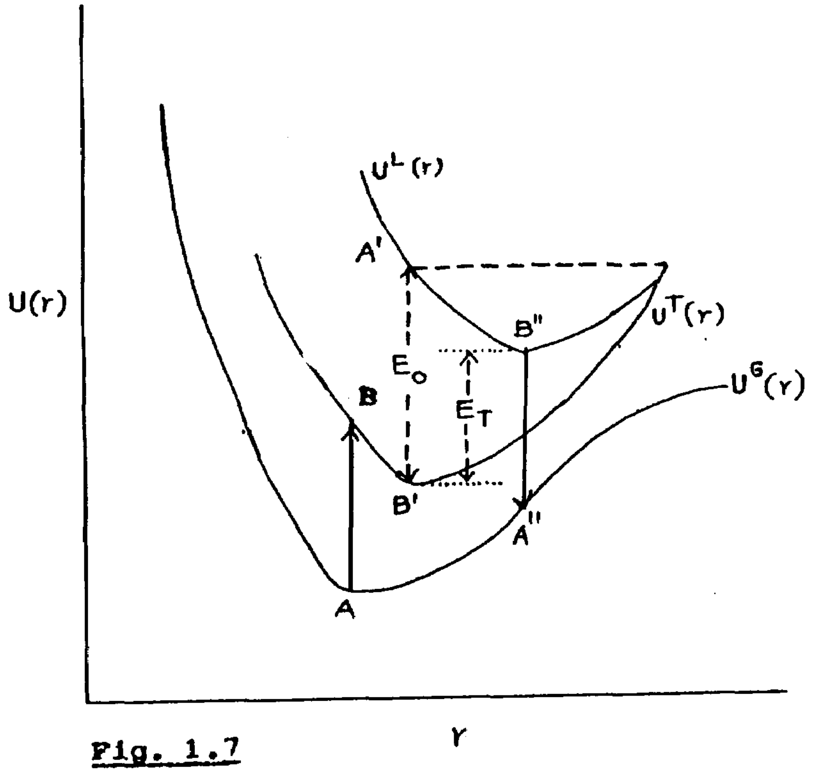


Fig. 1.7

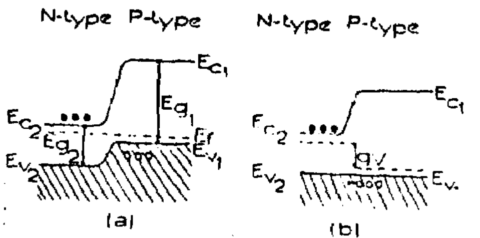
AB excitation leading to trapping at B'

B'A forbidden transition

E_o activation energy trension

E_T thermal activation energy

B" A" - TL emission



Under equilibrium

Under Forward bias

FIG.1.8: HETEROJUNCTION

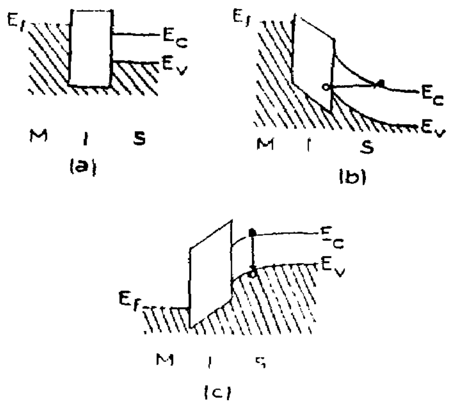


FIG. 1.11

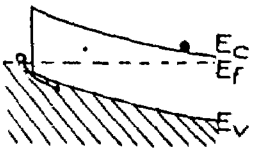


FIG. 1.9

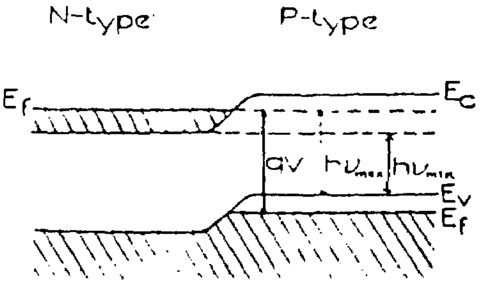
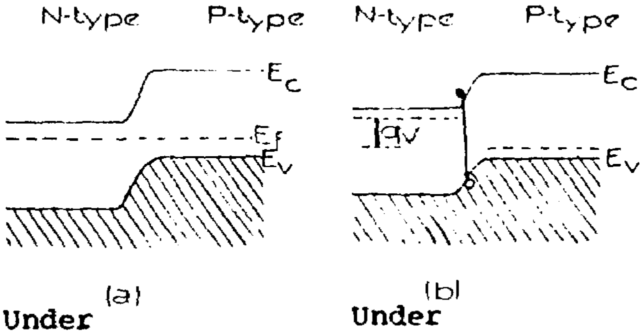


FIG. 1.12



Under equilibrium

Under Forward bias

FIG.1.10 : P.N.JUNCTION

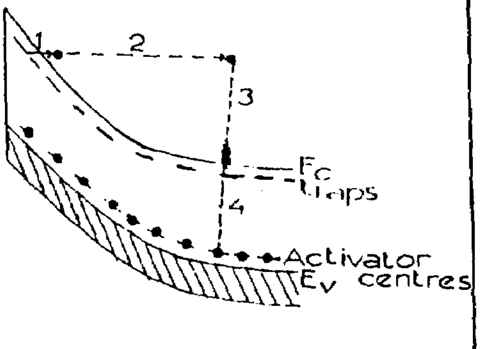


FIG.1.13

EL Mechanism