CHAPTER - I

INTRODUCTION

CHAPTER I

INTRODUCTION

1.1 Historical Development and General Concepts of Luminescence :-

Various kinds of luminescence emission caused by fireflies and certain sea bacteria were observed by the ancient Chinese during 1500 - 1000 B.C. Greek Aristotle (384 - 322 B.C.) had observed light being emitted from decaying fish. Regarding the knowledge of luminescence in India, some reference is found in holy writings of ancient India, 'The Vedas'.

Luminescence is the emission of light by certain materials, when they are relatively cool. We have description and find the first astounding far reaching, definition as a non - thermal light emission, in the book by Licetus, written in 1640.

In 1603, the inquisitive shoemaker, Vincenzo Cascariolo of Bologna (Italy), synthesised the first - ever luminescent materiel by heating barium sulphate with coal , which emits feable blue glow at night after exposure to day light. This 'Bolognese Stone ' (Barite material) was immediately investigated thoroughly by Mont' Albano (1634), Licetus (1640), Marsiglius (1648) and others. Some even baptized 'Bologna stone' as 'Solar egg' as it is was thought a kin to sun. Later on Robert

Boyle(1663), observed the light emitted from gem he was wearing. In 1669, the chemical element phosphorus was discovered by H. Brand. It was called phosphorus or phosphor, for the reason that it too glowed in dark when exposed to moist air. Although, phosphorus is not a phosphor in the sense in which we define it now, still the name is persisted in the present form. Meanwhile, in 1740, using the Greek title Litheosphorus, meaning stony phosphors, Fortunioliceti wrote the first monograph on the Bolognian stone. Later in 1768, Canten found a brighter material by heating calcium carbonate with sulphur. T.Sidot in 1866 discovered Zinc sulphate phosphor which emits green light. Until the middle of nineteenth century the phenomenon of light emission by solids after excitation was not subjected to systematic study. The first- ever law in this field was proposed in 1852 by stokes,[1] stating that the emitted wave-length is greater than the wave-length of the excitation radiation. At about the same time Becquerel[2] laid the foundation of experimental investigation of luminescence studies, on Uranyl salts. Lenard[3] proposed the kinetics involved in the luminescence of alkaline earth sulphides. However, early efforts at understanding of luminescence were without benefit of quantum theory and electron theory of solids and were therefore, entirely empirical.

The term luminescence was first introduced by the German physicist Wiedemann[4] in 1889. He defined luminescence as emission of electromagnetic radiations in excess of thermal radiation. The systematic study of luminescence was started by J. Becquerel and Lengard on some samples doped with impurity. The theoretical explanation for the luminescence phenomenon was given by Randall and Wilkins[5,6] and then other was proposed by Garlick and Gibson[7] due to which spectacular growth of phosphor studies could take place. Initially luminescence studies were mainly pertained to the visible range.

Sulphides were historically known material of luminescence for quite a long time. Friedrich Hoffmann[8] made much improved calcium sulphide in 1700. Oyster shells were much popular as a starting material for long time. Zinc sulphide is also one of the old known luminescent material. Among activators manganese (Mn) was well known in past.

Today luminescence is undergoing rapid advances in all fronts such as materials, methods of preparation theories and applications. The luminescence is now considered to be a down conversion energy process which involves emission of electromagnetic radiation normally in visible region by absorbing the energy of high order in one form or the other.

1.2 Review of Present Trends in Luminescence :

The study of luminescence has motivated many workers to prepare new luminescent materials, which have immense use in radar, television, cathode ray tube, infra-red detectors, fluorescence lamp etc. The field of luminescence has been a subject of scientific investigation from both theoretical and practical point of view. The scope and diversity of luminescence research have become so great that it is no longer possible to encompass the entire subject in a short review. However, attempt is made here to take review of selected representative topics of recent and timely importance.

Today the luminescence research is clearly advancing on many fronts. There is such a large number of new trends in the field that, it is difficult to single out any one, which stands above all the others. It is revealed from the recent literature that there is revival of interest in some of the old, areas of luminescence. The new trends and re-activated trends are found in experimental methods, materials, phenomena and applications.

Among the experimental techniques, opticaly detected magnetic resonance (ODMR), is active and is applied to both inorganic and organic materials, [9] . The

pico-second XRD excitation technique and photon echo-
technique[10] are outstanding trends in experimental
methods. The photo-transferred thermo-luminescence
(Pttl) technique[11], to detect deeper traps of
luminescence, is also known technique. The trends for
experiments under more and more external conditions
continues. Low temperature, high fields, intense
excitation and short-time are the examples. Thermally
stimulated luminescence and electron paramagnetic
resonance are being used widely[12] TSDC (Thermally
stimulated depolarised currents), in polymer films is
being studied recently[13]. Optical hole burning[14],
cooperative excitation[15], excimer laser excited
luminescence[16], are the techniques used recently.

There has been discovery of materials and
interesting luminescent properties. The recent addition
include one - dimensional crystals, ferroelectric, rare
gas solids, some unusual glasses, certain biological
materials, rocks, polymers etc.[17-23] There has been a
revival of interest in certain old material like silicon
carbide[24], Zinc sulphide in electroluminescence,[25]
alkaline earth sulphate phosphors in dosimetry and
uranyl and Uranate compounds for their new level of
understanding.

The nonradiative processes have been
recognised in luminescence research as equal in

importance to radiative processes, because they are origin of inefficiency of luminescent materials, which is important in technological applications. There is a re-activated trends of research on the Destriau type high field electroluminescence, which was widely investigated with phosphor powders more than twenty years ago. The thin film electroluminescence display devices recently developed , use an evaporated Zn: Mn film [25]. The present trends of luminescence studies is rather application biased, for example use of sulphate and fluoride luminophors in dosimetry, use of rare earth doped phosphors in fluorescent lamps with narrow line emission, use of electroluminophors in display devices and the like are of recent origin. Moreover, the research on luminescence is used as a tool to study complex biological systems for examples, luminescence is reported to have been used to characterise both specific cancer and complexes found during cancer growth [26]. The use of thermoluminescence property of certain thermoluminophors is also made in forensic sciences, measurement of diagnostic X-ray doses, geological aging of old rocks and monitory devices to protect against radiation hazards.

1.3 Mechanism of luminescence

1.3.1 (a) General Mechanism of Luminescence :

A crystal where in transition of an atom or
ion into an excited state has occured by absorption of
radiation or otherwise; can return to the ground state
by radiating itself off the energy absorbed. The latter
is usually dissipated in the form of heat. In some
cases, however, it is re-emitted in the form of light
radiation, and the crystal exhibits luminescent
properties. It is seldom that these are exhibited by
pure (physically and chemically) substances. Randallt
suggested that a puresubstance is fluorescent if each
elementary cell of the crystal contains ions or complex
group with an unfilled valence electron layer entirely
shielded by the surrounding medium.

From theoretical point of view absorption of
a radiation quantum by a pure crystal gives rise to a
free electron and a hole. These may recombine without
emission when subjected to the effect of crystal lattice
vibrations and transfer their energy to the lattice in
the form of heat. Hence it results that the electron
transitions responsible for emission should be well
shielded off by the surrounding atomic configuration
from interactions with the crystal latice vibrations for
radiative recombination to occur. However, When the

defects are present in the lattice, the probability of recombination of electron and hole with the emission of radiation increases. The reason being that the electron and hole are better shielded off at the centers than elsewhere from the effect of lattice vibrations and thus probability for them to transfer their energy to the surrounding atoms or ions in the form of heat is lesser. The necessary defects may be created due to self activation (local defects). or may be produced by incorporating the foreign impurities (foreign defects).

1.3.1(b) **Types of defects and their role in luminescence Process :**

The phenomenon of luminescence is basically originated due to the imperfections in solids. These imperfections are of various types, and can suitably be classified as :

   i) Point defects

   ii) Line defects

   iii) Surface defects and

   iv) Volume defects.

The point defects play much more significant role in luminescence than do the other defects. The point defects in the crystal are formed by thermal quenching, chemical doping, ion implantation, high energy irradiation, non stoichiomentry etc. The different forms of the point defects are illustrated in

fig 1.1 and are listed below :

 1) positive ion vacancy.

 2) negative ion vacancy.

 3) divacancy.

 4) Schottky defect.

 5) Frenkel defect.

 6) generation of vacancy by doping of
    additional valence ion.

 7) doping of impurity ion at substitutional
    site and.

 8) doping of impurity ion at interstitial
    site.

These defects can be broadly classified into two groups.

1) Host lattice defects. (covering 1 - 5)

2) Impurity defects   (covering 6 to 8)

The impurities or lattice imperfections gives rise to discrete energy levels in the forbidden energy gap of an insulator or semiconductor. These localised discrete energy levels are classified as.

 a) Luminescence centres.

 b) killer centres.

 c) Electron traps .

 d) Hole traps and

 e) Metastable states.

1.3.2 **Basic Mechanism of Luminescence** :

The phenomenon of luminescence involve two steps :

    a) The excitation of electronic system.

    b) Emission. (radiative recombination)

a) **The Excitation**

Figs. 1.2 a,b show the energy level G and A. In the ground state G is occupied by an electron, while A is empty. But in excited state A is occupied by an electron. The excitation from G to A may take place by

    i)   Elevating electron from level G to A after absorbing the incident energy of proper frequency (fig. 1.2 a).

    ii)   Production of electron – hole pair in conduction band and valence band respectively, due to bombardment of high incident energy so that A may capture an electron and G may capture hole from conduction and valence band respectively (fig. 1.2 b).

    iii)   The exciton formation plays an important role in energy transfer.

b) **The Emission :**

A photon can be emitted when electron drops from higher to lower energy levels. These levels are either intrinsic band states or impurity levels. Fig. 1.3, represents different radiative transitions which are also stated below.

   i)   Band to Band Transitions,

  ii)   Recombination via Shallow Donor or Acceptor Levels,

 iii)   Donor Acceptor Recombination,

  iv)   Recombination via Deep Levels.

In case of band to band transition, recombination of an electron in the conduction band takes place with the hole in valence band. As a result of this, a photon of energy equal or greater than the band gap energy of phosphor is emitted fig. (1.3-i). In recombination via shallow donor or acceptor levels energy emitted is smaller than band gap energy fig. (1.3- ii). The energy of photon resulting from donor-acceptor recombination fig (1.3 - iii) is given by

$$h\nu = Eg - (E_D + E_A) + e^2 / \epsilon R$$

Where,

Eg is the band gap energy

E_D and E_A are donor and acceptor binding energies respectively.

ϵ is dielectric constant of host material

R is the spatial separation between

donor and acceptor levels.

e is the charge.

In this type broad emission spectrum usually observed because of large range of separation of energy levels of impurity. The recombination via deep levels fig (1.3-iv) gives photon energy considerably smaller than band gap energy.

1.4 Types of Luminescence :

The luminescence types can be classified according to

A) The kind of excitation

B) The duration of the afterglow.

C) The energy levels.

A) Types of luminescence According to the kind of Excitation :

The excitation of luminescence material can be achieved by various exciting agencies, giving rise to different types of luminescence. The prefix denotes the means of excitation used to produce luminescence.

1) Bio- luminescence.

2) Cathodo - luminescence.

3) Chemi - luminescence.

4) Crystallo - luminescence.

5) Cando - luminescence.

6) Electro - luminescence.

7) Effuvio - luminescence.

8) Galvano - luminescence.

9) Iono - luminescence.

10) Lyo - luminescence.

11) Photo - luminescence.

12) Radio - luminescence.

13) X- ray - luminescence.

14) Sono - luminescence.

15) Theromo - luminescence.

16) Tribo - luminescence.

There are other types of luminescence in which two factors are responsible for luminescence phenomenon, the first prefix denotes the controlling factor and the second, the source of power which stimulates luminescence.

17) Electro - photo - luminescence

18) Electro - cathodo - luminescence

19) Electro - thermo - luminescence

20) Photo - electro - luminescence

21) Cathodo - electro - luminescence

22) Thermo - tribo - luminescence

23) Tribo - thermo - luminesccence

24) Radio - induced - thermo luminescence

25) Radio - induced - tribo luminescence.

26) Magneto - photo- luminescencce

B) **Types of luminescence According to Duration of After glow :**

There are two types of luminescence according to duration of after glow.

i) Fluorescence :

It is defined as emission of light during excitation. Generally the emission which lasts up to 10^{-8} sec is called fluorescence.

ii) Phosphorescence :

It is defined as emission of light after excitation is removed. The emission which lasts after 10^{-8} sec. is called phosphorescence.

C) **Types of Luminescence According to Energy Levels :**

i) Characteristic Luminescence.

In characteristic luminescence the energy levels involved are that of activator atoms.

ii) Non - Characteristics luminescence

In non- characteristics luminescence energy levels involved are of host lattice, modified perhaps by presence of activator atoms.

1.5 **Sensitised Luminescence and Energy Transfer :**

The process of energy transfer and the resulting phenomenon of sensitized luminescence can be

understood, with an aid of fig. 1.4 as follows :.

The figure shows the portion M of crystal with S and A as a group of impurity ions or ion groups incorporated in it. These S and A act as "Luminescence centres ". It is assumed that the crystal of the same composition but without S and A , is not capable of absorbing radiation. The centre A can be excited by absorbing a radiation (exc) which is followed by emission (em$_A$) and /or by dissipation of heat (non-radiative). The activator A can be excited via centre S (sensitizer) which then transfers excitation energy to A. Emission and /or dissipation from S are also possible.

1.6 Survey of Luminescence Material and Review of Studies of Alkaline Earth Sulphate Phosphors :

Materials exhibiting luminescence are known as luminophors. When the materials are inorganic in origin they are called phosphors.

Conventional phosphor consists of one and some- times more of the following components.

    i)   The host which is the major component.

    ii)   One or more activators

    iii)   A co- activator or a charge compensator (donor).

According these are classified as

        A)   Phosphor in pure form

        B)   Impurity activated phosphors.

1.6.1 Phosphor in Pure form :

A phosphor in pure form seldom shows any luminescence. The reason is that the phosphor in pure form doesnot have any energy levels, which could act as hole traps, electron traps, or recombination centres. However, it is possible to create host lattice defects in pure phosphor by giving heat treatment to the material. These host lattice defects could be freezed by thermal quenching. Thus a pure phosphor without activator may act as luminophor, even in the absence of activator. The luminescence exhibited by such phosphor is usually noncharacteristic luminescence.

1.6.2 Impurity Activated Phosphors :

The phenomenon of luminescence is better exhibited by impurity activated phosphors rather than pure ones. The impurity or foreign ion, which causes luminescence is called activator. The second impurity introduced in addition to first, to enhance the luminescence is called co-activator or sensitiser. It is observed that, due to presence of some impurities such as Fe, Co, Ni, etc., the luminescence intensity decreases, these are termed as killers or poisons.

1.6.3 **Survey of Luminescence Materials** :

Phosphors are also classified according to the use in various fields.

During last five decades there has been a dramatic progress in the field of luminescence. During this period there has been revolutionary changes in the materials, methods and concepts, that distinguish current research in the field, from those of earlier works. An important factor in the development of this field has been its commercial applications. Washington D.C. has now 48 phosphors indexed p1 to P48,[27]

    a) Photoluminescent phosphors

    b) Cathodolunimescent phosphors

    c) Thermoluminescent phosphors

    d) Electroluminescent phosphors

a) **Photoluminescent Phosphors** :-

Photoluminescent daylight phosphors, widely used in fluorescence lamps, convert all the wasteful forms of energy emitted during mercury discharge into visible light. The inorganic solid materials employed for the purpose are alkaline earth halophosphates activated by Sb, Zinc, Silicate phosphors with partial substi-tution of Zn by Be and activated by Mn . Now a days, instead of silicated and phosphote, Aluminates or

Alumino-borates, Vanadates, Oxysulphates, Stannates and Germanates are all being widely used.

b)   Cathodo - Luminescent Phosphors :

These are scintillating materials in CRT and T.V. displays. Phosphors emitting light in the visible region can be used for this purpose. However, most practical ones are based on host materials ZnS, CdS, RE oxides or Oxy- sulphides and Zinc phosponates or silicate, all activated by proper choice of metallic dopant.

c) Thermoluminescent Phosphors :

These phosphors with increasing use of nuclear energy and medical exposure of individuals to ionising radiations, are used in dosimetry (TLD) [28] . Determination of archaeological ages of rocks and use in forensic sciences are some applications of these phosphors. A few of the thermoluminescent materials are Lif, CaF. $Li_2B_4O_7$, BeO, $CaSO_4$. MgS. etc. with appropriate activators.

d) EL - Phosphors :

These are used in EL lamps, colour display panels, image intensifier, LEDS and semiconductor lasers, because of their excellent clarity and brightness. The inorganic materials used are mostly

alkaline earth sulphides and oxides doped with rare earth elements.

1.6.4 Survey of Alkaline Earth Sulphate Phosphors

This section makes a brief survey of investigations made by different investigators, about potentially useful alkaline earth sulphate phosphors Wiedemann and Schmidt[29] were perhaps the first among earlier workers to observe green thermoluminescence given off by $CaSO_4$ phosphors activated with few percent of $MnSO_4$, when exposed to condensed spark in air at a distance of a few centimeters and heated to $200^\circ C$. Later, Hoffmann[30], Laird[31], and Lyman[32] followed the work of Wiedemann and Schmidt, and suggested that the observed effect was due to X-rays from the spark and not due to ultraviolet rays of wavelength longer than 1000 A°. Purcell Tousey and Watnabe[33], used $CaSO_4 : Mn$ to detect extreme Ultraviolet and X- rays from the sun at high altitudes in earth's atmosphere by mounting the samples on V-2 rockets and exposing them to sunlight during flight. It has been observed in the studies of Dixon and Ekstrand[34] that the phosphors $CdSO_4$, $SrSO_4$, $BaSO_4$, doped; with rare earths exhibit bright TL following X- irradiation, Especially, the phosphors doped with Sm, Eu, Tb, Dy and Tm have an efficiency comparable to that of highest sensitivity phosphors available for TL dosimetry, exhibiting the glow peaks

.. 0

between 405 k to 480 k. Luthra and Gupta[35] have studied the TL, TL emission spectra, ESR and, optically excited luminescence of $BaSO_4$: Sm and $BaSo4$: Eu. They have given the possible mechanism, underlying the TL of these phosphors.

1.7 Scope of the Present Work :

In the present investigation an attempt has been made to compare the luminescence output of $BaSo4$ phosphor by choosing suitable dopants , different co-dopants and charge compensator. The comparative enhancement studies of luminescence of these phosphors have been systematically covered in three parts.

    i)   Preparation of phosphors.

    ii)   I -V and XRD studies of phosphors and

    iii)   Electroluminescence.

i) Preparation of Phosphors :

$BaSO_4$ Dy: Tb, $BaSO_4$: Dy: Pr, $BaSO_4$:Dy:Yb, BaSO4:Dy:Mn and BaSO4:Dy:Cu, phosphors were prepared in the atmosphere of sulphuric acid fumes following closely the method suggested by Mulla M.R. and Pawar S.H. for $CaSO_4$ phosphors[36,37]. The phosphors of ambient activator and co-activator concentration, with and without charge compensator were prepared. The method of preparation followed here has a special advantage of preparing a batch of 20 samples in one run.

ii) I - V and XRD Studies :-

The current - voltage (I-V) characteristics of phosphor system under study are obtained by applying sinusoidal voltage of high frequency to the phosphor pressed in EL cell. The I-V characteristics reveal the dependence of a.c. resistivity of phosphor on concentration and frequency. XRD studies are undertaken by automatic X - ray recording Geiger counter diffractometer. These studies not only reveal the structural properties of phosphors under study but also indicate enhancement effects of luminescence due to activator, co - activator and charge compensator.

iii) Electoluminescence Studies : -

The enhancement effect of luminescence of BaSO$_4$ phosphor with different co - activator has been thoroughly studied by measuring EL brightness at varying voltage and frequency. In this section probable mechanism of EL process of these phosphors has been dealt in detail. An appropriate mechanism underlying enhancement effect of luminescence has been discussed on the basis of proposed model.

FIGURE CAPTIONS

Fig. 1.1 Different forms of point defects.

Fig. 1.2 a) Excitation by absorption of a photon of

energy $h\gamma a$.

b) Excitation, due to electron-hole pair

production following bombardment of high

energy electrons or photons.

Fig. 1.3 Possible radiative recombination (transitions)

between,

i)   Band-band.

ii)   Via shallow donor or acceptor levels.

iii)   Donor-acceptor.

iv)   Via deep levels.
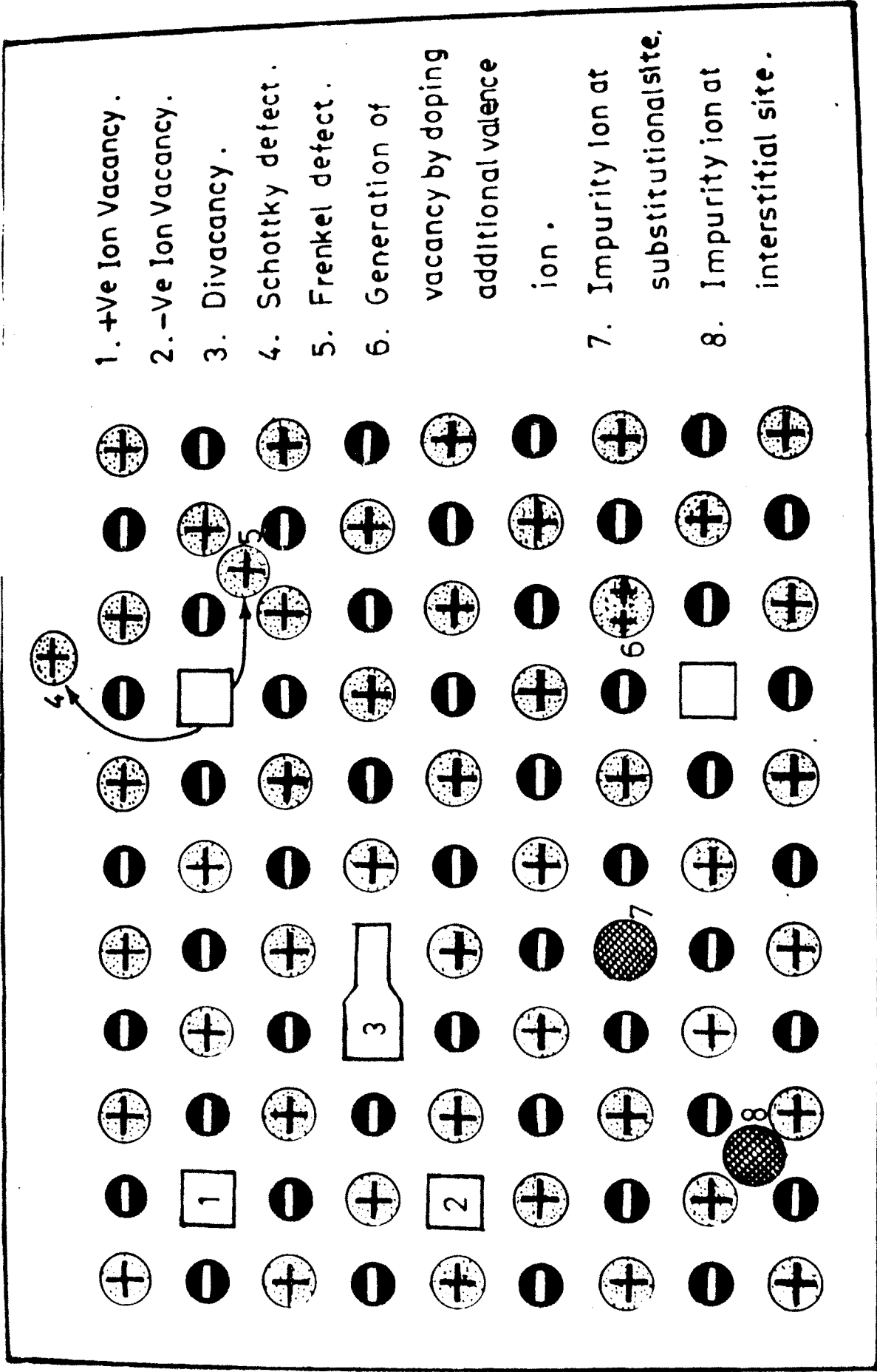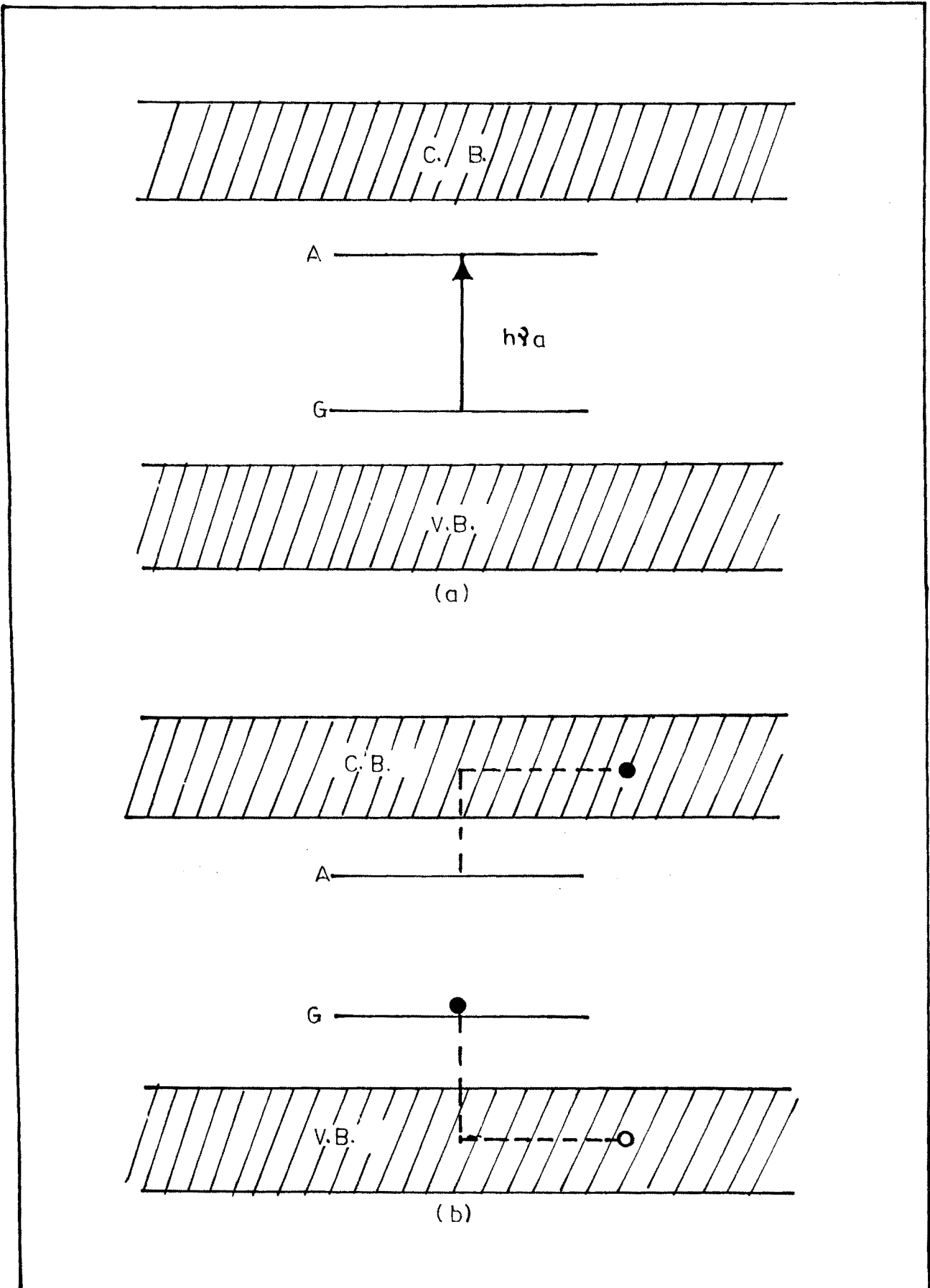
Fig. 1.4 Energy transfer and sensitised luminescence.

1. +Ve Ion Vacancy.
2. -Ve Ion Vacancy.
3. Divacancy.
4. Schottky defect.
5. Frenkel defect.
6. Generation of vacancy by doping additional valence ion.
7. Impurity ion at substitutional site.
8. Impurity ion at interstitial site.

Fig. 1·1

C. B.

A

$h\gamma_a$

G

V.B.

(a)

C. B.

A

G

V.B.

(b)

Fig 1·2 Excitation Processes

Conduction band

Valence band

(i)   (ii)   (iii)   (iv)
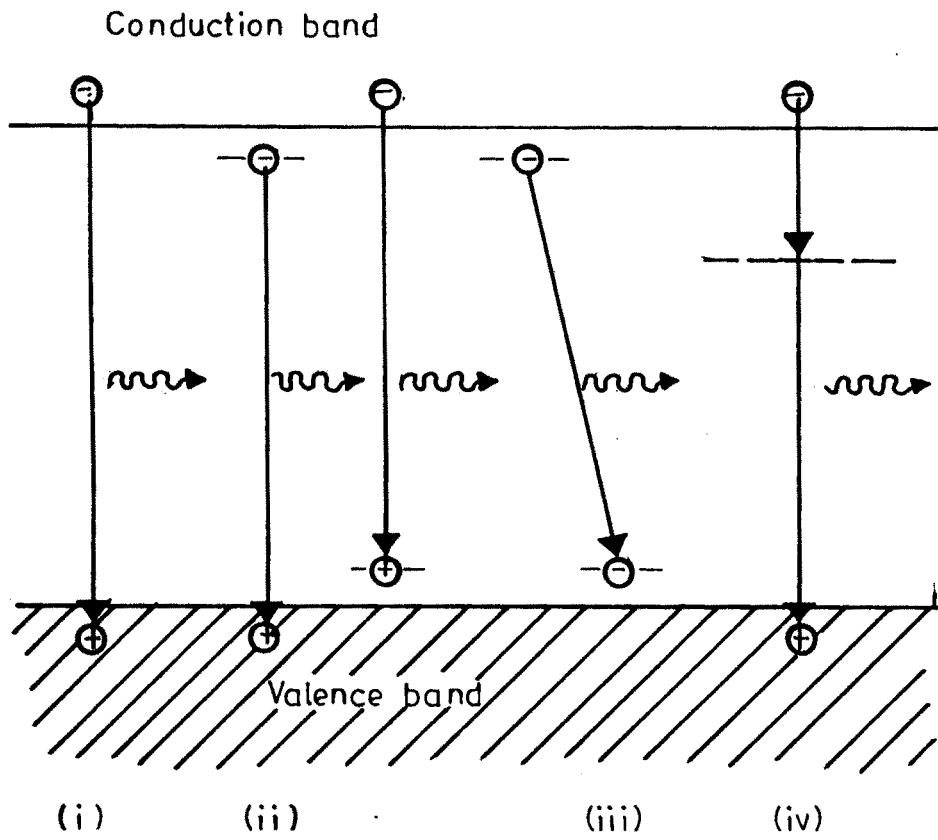
Fig. 1·3   Radiative transitions

i)   band—band.

ii)   Via. shallow donor or acceptor levels.

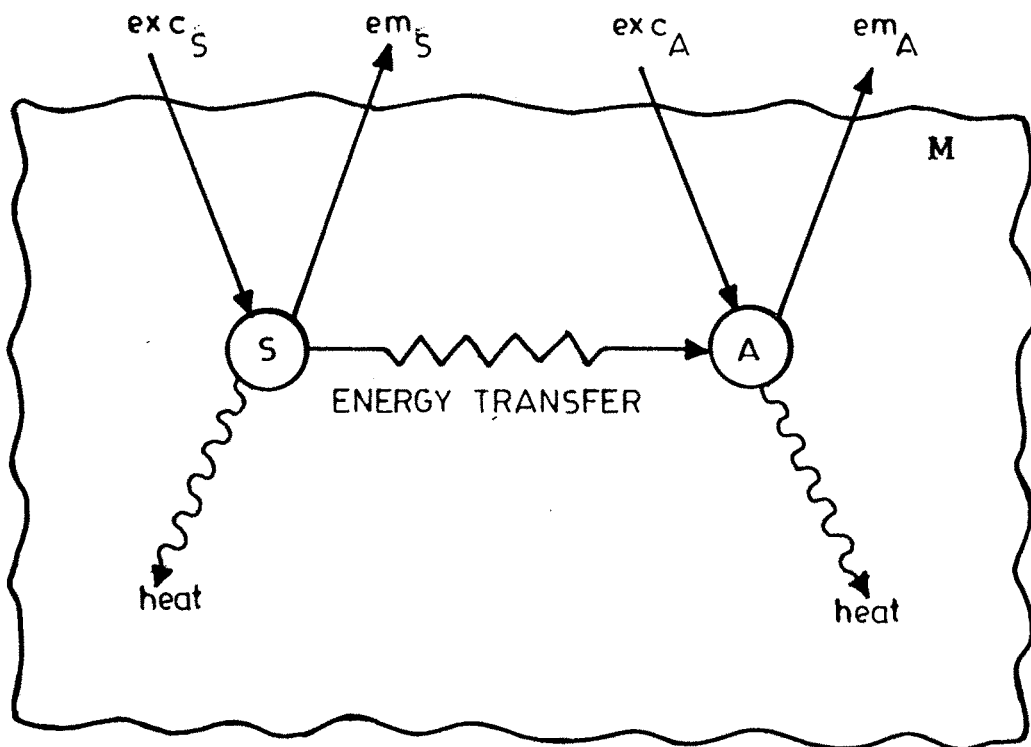iii) donor acceptor.

iv)   Via. deep levels.

Fig.-1·3

Fig.-1·4

REFERENCES

1] Stokes, G.Q. On the Change of refrangibility of light. Phil. Trans. Roy Soc. London A 142, II,463, (1852).

2] Becquerel, E., "La Lumiere, Ses Causes at ses effects," Gauthier. Villars, Paris (1867).

3] Lenard, P., Phosphoreszenz and fluoreszenz" Akad. Verlagsges, Leipzing, (1928). See also Handbuch der Experimental Physik 23, pt.1 and 2 (1928).

4] Wiedemann, E, Ueber Fluorescenz and Phosphorescenz, I. Abhandlung, Ann. Physik U. Chemic, 34,446(1988).

5] Randall, J.T. and Wilkins M.H.F., Procedings of the Royal, A, Vol. 184, (1945).

6] Randall J.T. and wilkins M.H.F., Communicated by Oliphant M.L., F.R.S. Received 6, November (1940).

7] Garlick, G.F.J. and Wilkins M.H.F., Communicated by Mott. N.F. F.R.S. Received 4 August (1942). Received 13 May (1943).

8] Hoffmann, H-Chymia rationaliset experimentalis, Berlin, (1784).

9] Caventt, B.C. J. Lum, 18/19, 846, (1979).

10] Dawson, P and Caventt, B.C. J.L., 18/19, 853(1979).

11] Bhasin, B.D. and Kathuria S.P. Proc.

Thermoluminescence and it's applications 182, (1992).

12] Sheshagiri, T.K., et.al.: Proc. Thermoluminescence and it's applications, 108 (1992).

13] Narsimharao, V.V.R. and Subharao B., Proc. Thermoluminescence and it's applications, 213,(1992).

14] Holiday, K. and Manson N.B. Proc. International Conference on Luminescence, Beijing, China, (1987).

15] Pelletier, N-Allard, Pelletier, R,Proc. International Confernce on Luminescence, Beijing, China (1987).

16] Richard, H. Clarke and Jeffrew, M.Isner, Proc. International Conference on Luminescence, Beijing, China, (1987).

17] Morita, M. and Sakuta, N. J. Lum. 18/19, 801 (1979)

18] Zimmer, G; J. Lum. 18/19, 875 (1979).

19] Hagarty, J. and Yen, W.M., Weber, M.I. and Black burn, D.H.J. Lum 18/19, 657 (1979).

20] Boulon, G. Moine B. and Bourcet, J.C., Reisefeld R and Kalisky Y., J. Lum, 18/19, 924 (1979).

21] Szabo, A.G., Lynn, K, Krajcarski, D and Rayner, D.M., J. Lum., 18/19, 582 (1979).

22] Amesz, J. and de Grooth, B.G. J. Lum, 18/19, 598, (1979).

23] Limaye, M.A., et.al. Proc. Thermoluminescence and

its applications, Baroda 150 (1992).

24] Bimberg, D. Sander, L M., Skolnick, M.S., Rossler, U. and Choyke, W.J.J. Lum. 18/19, 542, (1979)

25] Abdalla, M.I., Godin, A and Noblanc, J.P., J. Lum, 18/19, 743, (1979).

26] Vigny, P., and Duquesne, M.J.Lum. 18/19 587, (1979).

27] Bote, P.R., Ph.D. thesis, Shivaji University Kolhapur (1980).

28] Mc. Dougal, R.S. and AXt, J.C. Health Phys. (G.B.) 25,6,612-13 (1973).

29] Wiedemann, E. and Schmidt, G.C., Wied. Ann. 54,604, (1895).

30] Hoffmann, M.W. Wied. Ann. 60,269 (1897).

31] Laird, R.E., Phys. Rev., 30, 293, (1910).

32] Lyman,T. Phys. Rev., 48, 149, (1935).

33] Purcell, J.D., Tousey. R. and Watnabe, k. Phys. Rev., 76, 165, (1949).

34] Dixon, R.L. and Extrand, K.E., J. Lum, 8, no. 5, 583-590, (1974).

35] Luthra, J.M. and Gupta, N.M., J. Lum, 9, No. 2, 94-103, (1974).

36] Mulla, M.R. and Pawar S.H. J. of Luminescence 31 and 32, 239-241 (1984).

37] Mulla, M.R. and Pawar S.H.

Proc. International Conference on Luminescence, held at Beijing, China (1987), J. Lum. 40 and 41, 179-180 (1988)