CHAPTER I

INTRODUCTION
1.1 INTRODUCTION

Luminescence is a branch of Solid State Physics that is concerned with the phenomenon of light emission from solids in excess of thermal radiation. Crystalline luminescent solids are commonly termed "phosphors". Their emission spectra are usually bell-shaped structureless bands at longer wavelengths than their excitation wavelength. Therefore, in contrast to incandescent bodies, phosphors are quite transparent to their own luminescent emission.

Luminescence can be excited in many ways. Ultra-violet radiation, high velocity electrons and nucleons, \( \gamma \) and \( X \)-rays and electric fields excite suitable phosphors. Thus, the general term luminescence is classified according to the mode of excitation:

a) Photoluminescence produced by absorption of photons.

b) Radioluminescence produced by bombardment of a phosphor with high energy particles such as \( X \)-rays and \( \gamma \)-rays.

c) Cathodoluminescence produced by excitation of phosphors by an electron beam.

d) Electroluminescence produced by excitation of phosphors by application of an electric field.

e) Chemiluminescence and bioluminescence which accompany a chemical reaction or biological process.
1.2 PHOTOLUMINESCENCE

Photoluminescence is further divided into two classes:

a) Fluorescence: Fluorescence means luminescence which does not last more than $10^{-3}$ Sec. after the exciting radiation has been cut off (1).

b) Phosphorescence: Phosphorescence is luminescence which persists for an appreciable time after the exciting process has ceased (2-5). Time for decay to a certain fraction of the initial intensity depends upon the nature of the phosphorescing material and temperature. Phosphorescence and fluorescence can be distinguished precisely on the basis of the physical process taking place. Accordingly, the emission taking place by one or more spontaneous transitions is fluorescence whereas the emission occurring with the intervention of a metastable state followed by a return to excited state by addition of energy is phosphorescence (3, 5, 6). The first process is independent of temperature while raising of the system from metastable state to the excited state may be effected by thermal energy and, therefore, phosphorescence is a temperature dependent process.

1.3 PHOSPHORS

Phosphors are crystalline insulating materials capable of absorbing energy from various sources and reemitting it as
visible or near visible radiation during or after excitation (3). Phosphors are very sensitive to structural changes and impurities and as such they are strongly influenced by chemical composition, crystal structure, impurities present in relatively small amounts and physical conditions (e.g. temperature and type of excitation) under which they are made to luminesce.

Phosphors may be classified into two classes: those which show luminescence in the pure state and those which show luminescence on addition of small amounts of activating impurities. Luminescence in the pure state refers to the emission not affected by repeated purification (7). Some of the phosphors showing luminescence in the pure state are manganous halides, platino cyanides, tungstates, molybdates, uranyl salts, gadolinium sulphate and samarium sulphate. Some phosphors (e.g. ZnS, ZnO) show luminescence in the pure state after being given heat treatment and these are included in the latter class because the luminescence appears to be due to stoichiometric excess of Zn occupying interstitial sites.

Phosphors can be further classified into two groups:

a) Photoconducting phosphors: Photoconducting phosphors are those in which excitation raises electrons from the valence band into the conduction band e.g. ZnS: Ag, ZnS: Cu phosphors.
b) Non-photoconducting phosphors: Non-photoconducting phosphors are those in which under usual conditions of luminescence excitation the electron is not raised into the conduction band and as a result photoconduction is negligible. KCl : Tl is a typical example of this class.

According to Leverenz (8), phosphors may be classified into three main groups:

a) Phosphors exhibiting predominantly exponential decay: In such phosphors activator atoms occupy substitutional sites.

b) Phosphors having power law decay: In such phosphors activator atoms occupy interstitial sites.

c) Phosphors showing initial exponential decay followed by a strong power law decay: In such phosphors activator atoms occupy both substitutional as well as interstitial sites.

1.4 TRAPS AND TRAPPING MECHANISM

Trapping is a fundamental process for energy storage. Those regions of crystals which are able to capture electrons and holes and detain them in a restricted locality are called traps (9–11). By absorption of an optimum amount of thermal or optical energy, a trapped electron or hole is released and it is free to move until it is either
captured by a centre or retrapped. Capture by a centre is followed by a transition to ground state by either a radiative or a non-radiative process releasing the stored energy. Traps may be classified into two main types:

(a) Traps associated with particular impurities: In this, trapping involves a change in the effective valence of the impurity ion e.g. $\text{Sm}^{+3}$ changes to $\text{Sm}^{2+}$.

(b) Traps associated with defects in the crystal: It is the result of the formation of regions with an excess positive charge (electron-traps) or negative charge (hole-traps) surrounding the defects.

Production of traps in a given phosphor depends on

(a) Presence of impurities (12, 13).
(b) Temperature of preparation (12).
(c) Atmosphere during preparation (14).

1.5 LUMINESCENCE CENTRE

The localities in a phosphor where energy is reemitted after absorption are called luminescence centres (15-16). These localities contain ions or groups of ions which possess levels in which luminescence transitions take place. Crystal lattice defects such as vacancies and impurities centres act as luminescence centres. The impurity centres are created in phosphors as a result of inclusion of
some foreign constituent known as 'activator'. In most of the phosphors the activators are incorporated by heat treatment (17). The activators are supposed to be provided necessary shielding for the absorbed energy which would otherwise be dissipated in the form of thermal vibrations (6).

In the luminescence centre, the probability of radiative transition is more. If the probability of non-radiative transition is more, then it is known as a "killer-centre". In ZnS phosphor, the inclusion of impurities Fe, Co, Ni gives rise to killer centres and, hence, these are known as 'poisons'.

1.6 THEORIES OF LUMINESCENCE

To explain the phenomenon of luminescence different models have been proposed, a short resume of these models are given below:

(a) Configurational Coordinate Model.

Originally proposed by Von Hippel (18), Seitz (19) applied this model to explain the characteristic luminescence processes.

Fig. 1.1 shows the curves representing energies of the normal and excited states of the luminescence centre in relation to variation of its configuration coordinates. Absorption of radiation raises the centre from ground state A
Fig. 1.1
Configuration Coordinate Model.

Fig. 1.2
Seitz Model

Fig. 1.3
Dexter, Klick & Russel Model
to the excited state B. The energy absorbed corresponds to vertical distance AB \( (h \nu) \) according to Franck-Condon principle. At B the system is not in equilibrium and hence tries to adjust itself so as to reach C, giving off the energy difference BC as lattice vibrations or phonons. Finally, the centre returns to the ground state by emission of luminescence CD \( (h \nu') \) and, then, relaxes to A by giving up energy to the lattice. The energy of absorbed photon \( (h \nu) \) is greater than the energy of the emitted photon \( (h \nu') \). This corresponds to a shift which is known as stokes' shift.

Modifications of this model help to explain the radiationless transition. Fig. (1.2) gives the Seitz (19) model for exciton. In this model the system after excitation relaxes to such an extent that its minimum \( (A) \) lies outside the ground state curve and this increases the probability of non-radiative transition.

The other model (Fig. 1.3) was proposed by Dexter et al. (20). In this model the energy dissipated during relaxation is less than that dissipated according to the Seitz model and system comes quite close to the ground state from where the radiative transfer is not possible. In fact, this model along with its few quantum mechanical modifications successfully explains:
(i) Stokes' shift.
(ii) Width of absorption and emission bands at low temperatures.
(iii) Thermal quenching of luminescence and other temperature effects.
(iv) Monomolecular decay.
(v) F-centre luminescence
(vi) Sensitization processes in doubly activated solids (21).

Its limitations are :-

(i) It cannot be applied to the processes occurring between absorption and emission, e.g., photoconductivity.
(ii) Because of the configurational difficulties it is difficult to have precise configuration coordinate diagrams on theoretical considerations only.

(b) Continuous Dielectric Model: This model removes the defects of the above model by considering the interactions between the centre and the lattice as of a short range type. Huang and Rhys (22) have proposed a theory where they treated the lattice as a continuous dielectric in which the centre is embedded and considered long range interactions, electrical in nature. In absorption the centre experiences a difference in charge distribution resulting in a change in lattice polarization which is accompanied by the creation of lattice phonons. Extension and refinement of this work has been carried out by Lax and
Burstein (23), Pekar (24), O'Rourke (25) and Meyer (26).

(c) Energy Band Model: Bloch's (27) collective electron model for the energy state of a perfect crystal lattice was extended to explain the long duration phosphorescence of sulphide and silicate phosphors by Riehl and Schon (28) and independently by Johnson (29). The energy state of an electron in a crystal may be derived from the state of the individual atoms or ions which compose the crystal. The discrete energy levels in atoms or ions are broadened into bands due to interaction in a crystal lattice. These bands of allowed energy are separated by forbidden regions or zones (30) and they are either filled or unoccupied. The highest filled band is called the valence band (F) and the unoccupied band above it is known as the conduction band (C) (Fig. 1.4).

If an electron is raised from the valence band to the conduction band by absorption of energy, a positive hole is created in the valence band. There exists a nonperiodicity in the crystal lattice due to presence of impurity atoms which gives rise to localized electron states with discrete levels between the energy bands of a pure crystal. The discrete localized levels just above the valence band in the forbidden zone function as luminescence centres (L) with the ground state of each centre occupied, whereas discrete electron trapping levels (T) are provided by the vacant crystal sites or the crystal deformities just below the conduction band which are
Fig. 1.4

Energy Band Model
unoccupied levels in the forbidden zone in which electrons excited into conduction band by energy absorption can be trapped. This model was further developed by Klasens and his co-workers (31 - 33). This model involving hole migration is widely used to explain many phenomena such as trap mechanism, quenching action of impurities, function of double activators, photoconductivity and electrophospholuminescence (34 - 36). Another interesting modification has been proposed by Bube (37 - 39).

(d) Models for Luminescence Centres: Three type of models may be assumed for the centres to explain the various luminescence phenomena in a photoconducting phosphor.

(1) Schön Klasens Model: In this model Schön (40), Rose (41), Klasens (42) and Klasens with his associates (31) have proposed a hole migration theory of luminescence of sulphide phosphors activated with monovalent impurities such as Ag⁺. This model is shown in Fig. 1.5 for the case when excitation of luminescence is by absorption of light in the fundamental band of the host lattice. The sequence of events are as follows: -

(a) Light is absorbed in the fundamental absorption band producing a free electron and a hole leading to photoconductivity.

(b) The hole may migrate towards the impurity centres. If, for
Fig. 1.5
Schön - Klasens' Model
a - excitation
b - hole migration
c - hole capture
d - electron migration (Non-radiative)
e - Electron capture resulting in Luminescence

Fig. 1.6
Lambe & Klick's Model
a - excitation
b - hole migration
c - hole capture resulting in Luminescence
d - electron migration
e - electron capture

Fig. 1.7
Williams - Prener Model
I
A

II
B
C
example, the centre is due to Ag$^+$ substituted for Cd$^{++}$ in
CdS, the centre has a net negative charge and attracts the
hole with coulomb like attraction.

(c) The hole is captured by the impurity centre giving off a
small amount of energy as infra-red radiation or as
vibrational quanta.

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

(e) The electron is captured by the centre. It recombines with
captured hole and gives off energy as luminescence emission.
The electron transition may be directly from conduction band
to the ground state of the centre or may be by way of an
intermediate excited state of the centre.

After luminescence the cycle is completed and the
process may again be repeated.

By extending this model to two impurity atoms,
Schon and Klasens were able to explain the effect of poisons,
variation of luminescence with temperature of some phosphors,
the non-linear relationship between luminescence output and
the exciting intensity and similar phenomena in sulphides.

Another interesting development in the theory of
luminescence of sulphide phosphors was based on the charge
compensation theory proposed by Kröger (43). It is shown
that in ZnS it is necessary to balance each monovalent positive
ion introduced by a monovalent negative ion or a trivalent
positive ion. This principle seems to explain the role of fluxes used to prepare phosphors. In addition, it characterizes the ionic nature of impurity centres. Thus, even if the sulphide lattice is primarily covalent in character, it appears that in the vicinity of the impurities the ionic character of an impurity is decisive. Klasens has also suggested that the luminescence centre is actually a sulphur ion perturbed by the presence of the activator ion, rather than the activator itself. This modification does not essentially change the sequence of events characterized above.

According to Schön Klasens' model, it would be expected that the decay time of luminescence and photoconductivity would be approximately alike, since the capture of an electron leads both to luminescence and to a decrease in conductivity. However, it has been found that in many cases the decay of luminescence is much more rapid than the decay of photoconductivity, unlike what is expected from Schön and Klasens' model. Some attempts have been made to explain this phenomenon (44). A model proposed by Lambe and Klick (45) for CdS:Ag reconciles in a simple way observations on luminescence and photoconductivity, the two closely related features in the material.

(ii) Lambe - Klick Model: This model is shown in Fig. 1.6. The mode of operation of this system is as follows:

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

(b) The hole and electron move about in their respective bands and eventually, the hole migrates near impurity centre (activator ion).

(c) The hole is captured by the impurity centre, and luminescence emission occurs, leaving the centre effectively neutral in charge.

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

(e) The electron is captured by the centre, resetting the centre for the next cycle of the operation. In the capture, a small amount of energy is given off as infra-red radiation or as lattice phonons.

The essential difference between the two models is that the luminescence results from the capture and subsequent recombination of a conduction electron in the former case and in the latter the luminescence results from the capture and subsequent recombination of a free hole.

(iii) Williams - Prener Model: The luminescence of ZnS elements phosphors containing of IB and VB group of the periodic table as activators and elements of group IVB or VIIIB of the periodic table as co-activators, involve localized states that can be more appropriately treated as perturbed states of the band structure for the pure crystal. The energy level structure of ZnS type phosphors can be deduced from semiconductor theory (46 - 48). The substitution of group IB activator for Zn or VB for S yields a series of discrete
states above the valence band. In a neutral crystal with only these impurities present, the highest state is empty. Hence the activator is an acceptor. The substitution of group III B co-activator for Zn or VII B for S yields a new series of discrete states below the conduction band. In a neutral crystal with only co-activator impurities present, the extra electron is bound in these discrete states. The co-activator is, therefore, a donor.

Photoluminescence excitation and emission of ZnS(Cu)-Cl phosphors in which halide flux (Cl) is used during preparation is summarized in Fig. 1.7. Absorption takes place from ground state of acceptor (level I) to an excited coulomb state of nearest donor (level II). Level I has a high hole capture probability whereas level II has a high electron capture probability. For emission, transition takes place from level II to level I if the temperature is not high. Otherwise the electron is freed by activation from level II before actual transition takes place. The above model is due to Williams and Prener (46-48).

1.7 CONCENTRATION QUENCHING

The increase in the activator concentration usually increases the luminescence efficiency until an optimum concentration is reached. Any further increase in the concentration of activator may decrease the luminescence
efficiency until the emission is quenched. This phenomenon of concentration quenching has been explained by assuming that an activator centre is non-luminescent if there is another centre at the nearest point of the surrounding lattice (49-51). The value of the parameter differs from one phosphor to another. It is defined as the number of lattice positions (whether substitutional or interstitial or both) surrounding the given activator such that if any of these sites is occupied by another activator, the luminescence is quenched.

According to the assumption of Dexter and Schulman (52), the degradation of energy occurs at special quenching sites in the crystal. Quenching has been attributed to resonance transfer of energy from one activator to another, until it arrives at an activator near one of the energy sinks.

1.8 LUMINESCEENCE WITHOUT MOVEMENT OF CHARGE

Calcium phosphate activated by Mn emits red fluorescence when excited by electron beam but no excitation is found by a u.v. source of 250 nm. The latter falls outside the characteristic absorption band of Mn$^{2+}$ ion. Calcium phosphate activated by cerium alone produces an u.v. fluorescence of 350 nm by u.v. excitation due to transition in Ce$^{3+}$ ion. In calcium phosphate phosphor with Ce$^{3+}$ and Mn$^{2+}$ activators, u.v. excitation produces both u.v. emission of Ce$^{3+}$ and red emission of Mn$^{2+}$. The 250 nm absorption is by Ce$^{3+}$ ions but is followed by a transfer of energy from Ce$^{3+}$ ions to Mn$^{2+}$ ions which occurs
by a resonance process.

Thus, energy transfer in luminescence during absorption by one activator (primary) and emission by another (secondary) is also possible by transfer of energy. This process is called sensitization. The important activators in primary class have either $d^{10}s^2$ or $d^{10}$ configurations; they include monovalent Ga, In, Ti; divalent Ge, Sn, Pb and trivalent As, Sb and Bi with the first configuration and monovalent Cu and Ag with the second.

The major secondary activator is divalent Mn with $d^5$ configuration. Another activator with the same configuration is trivalent Fe ion. This has received little attention because of the ease of reduction to a divalent state. Divalent Fe is a poison because close grouping of energy levels allows ready radiationless loss of energy.

The sensitization effect was discovered by Tomашек (53) and Rothschild (54). Since then different types of sensitized phosphors have been found out and related studies have been made (55 - 62).

Double Activator: A theory of energy transfer between primary and secondary activators in phosphors like calcium fluophosphate activated by both Sb and Mn is proposed by Dexter (63). The major requirement is that the virtual photon emitted by primary activator must match the absorption of secondary activator. While this criterion is
satisfactory for fluophosphate and a number of other phosphors, the alkaline earth pyrosilicates are an exception (64). There is no indication of transfer from \(\text{Pb}^2+\) to \(\text{Mn}^2+\) in these materials. It would be seen that site symmetry and decay time for two activator ions also enter the picture. Also, transfer of energy between primary and secondary activators in various sites may be forbidden and for manganese there are strong indications that transfer of energy between closely spaced levels within a single ion may not occur. Therefore, it may be pointed out here that energy transfer in doubly activated phosphors is still a problem requiring further work. The phenomenon of luminescence is quite complex but great progress has been made in the last thirty five years in the discovery of new phosphors and measurement of their properties.

1.9 PRESENT STUDIES

Luminescence of oxygen dominated lattices has been observed since long in nature as phosphates, carbonates, silicates in the mineral form. It was only when they were used as fluorescence lamp phosphors in the middle of thirties that serious attention was given to develop and study the properties of these phosphors. Since then hundreds of papers have been published on the subject including that of McKeeag and Ranby (65), Jenkins and co-workers (66) on white phosphors, the halophosphate \(\text{Ca}_3(\text{PO}_4)_3\) : \(\text{Sb}^{3+}\), \(\text{Mn}^{2+}\). Good control is also possible on color by varying activator concentration in this
system of phosphors. Other oxygen dominated phosphors are used in fluorescent lamps to give special colors or color rendition, in high pressure mercury lamps for color correction and in cathode ray tube screens.

Alkaline earth oxides constitute the simplest compounds among oxygen dominated lattices with the generic formula $M_{x}O_{y}$. Though the possible combinations of simple oxides and activators are small in number, it is surprising that new phosphors in this group continue to be found. The oxides are known to have a comparatively higher temperature of quenching which is an important factor in its application. Among the alkaline earth oxide phosphors, CaO phosphors have been widely studied but published reports on CaO phosphors do not agree with each other and many early publications have been outdated.

The alkaline earth oxides also exhibit selfactivation due to oxygen vacancies. This itself contributes an interesting study from a theoretical point of view but it usually interferes with activator emission and investigation may be necessary to control this emission for practical applications. Not many studies of the phenomenon of sensitization have been made in this class of phosphors, though individual conventional activator emission characteristics have been studied (67).

In view of the above discussion the present investigation involves the preparation of CaO phosphors with Sb and Mn as activators and a study of the luminescence properties of these
phosphors. In the reflection spectra of CaO powder an onset of strong optical absorption observed at about 6.4 eV (56). It seems that the part of absorption may be due to lattice defects obscuring the true band gap of 7.7 eV. In either case, CaO phosphors cannot be excited optically using 254 nm radiation. Therefore, the source of excitation used in the present studies for these phosphors have been either X-rays or an electron beam.

The following studies have been carried out with CaO (Sb and Mn) samples prepared by the author:

1. Phosphorescence decay characteristics (X-rays and electron beam excitation).

2. Thermoluminescence studies (X-rays excitation).

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