CHAPTER I - INTRODUCTION
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1.1 INTRODUCTION:

The interest in luminescence started with the gaseous medium, travelled on through liquids and arriving at solids, it seems to be finding a settling place there. Luminescence is now known to comprise important optical properties of matter in the solid state.

Solid state physics is one of the rapidly developing branches of pure and applied science. It deals with the structure of crystals. Crystals exhibit special properties on account of some deviation in the atomic arrangement of their lattices. The deviations are termed as "crystal defects or imperfections". Such defects bring extra
charge carriers into the crystal field, which disturb the periodicity of the lattice. The energy levels of the carriers either get modified themselves or modify the energy levels of the crystal as a consequence thereof.

In solids, the wave function associated with the individual atom loses its significance and hence there are two approaches to understand the electronic structure of a system in the solid phase. One approach is through the "Zone theory" and the other through the "Band theory". The former is found useful in elucidating the properties of metals where as the latter is more useful for discussing semiconductors and insulators. The luminescence phenomenon, being common to both insulators & semiconductors, has inspired men in research and industry. It arises on account of the presence of a cationic or anionic entity in crystals.

The use of luminescent materials in paints, pigments, electroluminescent panels, discharge tubes, scintillation counters etc. are immense. However, the interest in this branch of solid state physics is due not only because of its manifold applications but also due to the fact that it provides information on band structure and energy levels of impurities and imperfections in solids. A sustained effort is therefore being made in many laboratories all over the world to develop luminescent materials which would be of
theoretical or practical interest. The help of new techniques
  e.g. electron spin resonance, Mossbauer spectra, solid state
lasers, polarisation effect etc. is taken to reveal the
fundamental processes involved in luminescence. The complexities
and diversities of the luminescent phenomenon, the various
types of material that exhibit luminescence and their
characteristics often obscure some of the salient generalities.
For this reason a detailed theoretical knowledge of the band
structure and imperfections is essential. Though this provides
a basis for understanding the luminescence of materials, there
is no single, simple theory explaining the mechanism governing
the process of luminescence of inorganic solids. The theoretical
understanding of the luminescence is interwoven with the
theoretical basis of other related branches of Solid State
Physics.

Predictive contribution in the study of
luminescence has not yet been as great as in some other branches
of Solid State Physics, such as in semi-conductors. Any
prediction of this phenomenon would require a quite sophisticated
understanding of the process and the material.

1.2 THE BASIC CONCEPT OF LUMINESCENCE:

(a) Definition: Garlick (1) and Weidemann(2)
define luminescence as the emission of radiation, visible or
invisible during or after excitation by radiation, electro-
magnetic or corpuscular. According to Lenard, luminescence is
a process whereby matter generates non-thermal radiation which is characteristic of the particular luminescent material (3). Luminescence of solids is distinguished from incandescence in that it does not obey Kirchhoff's law. In general, any radiation emitted from a substance not in internal thermal equilibrium can be called luminescence. Excitation of the luminescent substance is prerequisite to luminescence emission and hence it can be classified according to the nature of the source of excitation. The luminescence excited by electromagnetic radiation of photons is called photoluminescence and that excited by cathode rays is called cathodoluminescence. Other terms such as electroluminescence, radioluminescence, chemiluminescence, triboluminescence, bioluminescence, sonoluminescence etc. can be similarly understood and explained (1,3). Thermoluminescence, however, does not refer to thermal excitation but rather to thermal stimulation of luminescence emission which was excited by other means.

(b) **Fluorescence and Phosphorescence**: These are two important aspects of the same physical process 'the luminescence'; different definitions are given to them in an attempt to distinguish by physical conditions of experiment and the physical processes.

According to Curie (4) a luminescence emission with life time of about $10^{-3}$ secs. is indisputably fluorescence and the emission that persists afterwards for longer duration
after excitation ends is phosphorescence. The interval \(10^{-8}\) Sec. is chosen as of the order of the life time of an atomic state for an allowed electric dipole transition in the visible region of the spectrum (5).

Some authors (6,7) define fluorescence as that part of emission for which the decay time is independent of excitation intensity and of temperature while phosphorescence as temperature dependent emission.

In terms of the physical processes Perin (6) defines fluorescence as a emission that takes place by one or more spontaneous transitions and phosphorescence as which occurs with the intervention of a metastable state (8,9) followed by return to the excited state due to addition of energy (8-10).

(c) **Phosphor**: These are impurity and structure sensitive solid crystalline materials possessing the property of absorbing energy of a certain frequency and emitting part of the absorbed energy in the form of electromagnetic radiation in the visible or near visible region of the spectrum.

Phosphors can be obtained in three forms:

(i) Single crystal,
(ii) Thin film,
(iii) Microcrystalline powder.

(i) **Single crystal phosphor**: Techniques for obtaining single crystal phosphors have been developed comparatively recently. Being free from statistical fluctuations, where ever
possible, single crystal phosphors are preferred these days. Since precise measurement and reproducible results are more likely to be obtained with them, single crystal phosphors have been studied (11) extensively. It has not been possible to grow single crystals of alkaline earth sulphide phosphors. Only a little success has been reported in the case of SrS(12).

(11) Thin film phosphor: It is only recently that the use of thin films in luminescence work has gained impetus. Shalimova, Khirin and Korolev (13) have worked on CdS thin films. It was not the attractiveness of the sample or unique geometry that promoted this work but the promise of unusual devices like transparent and high contrast cathodoluminescent screen, optical elements with high resolving power and low voltage electroluminescent lamps. Thin films can be prepared by depositing a transparent coating on glass surface by chemical reaction of the components in vapour state (14) with relative ease, which is an important factor for practical application.

(iii) Microcrystalline powder phosphor: This is the form in which phosphors are obtained in the present work. Lenard and Klatt (15) may be rightly thought of as pioneers in initiating microcrystalline phosphor preparation. The method consists in heating a mixture of the powdered host material together with a suitable amount of fusible salt called flux along with the activator added as its salt, preferably in the form of solution. The ingredients are
thoroughly mixed and the mixture is finally fired at suitable
temperature for a pre-determined period. Thin film luminescent
devices, inspite of good transparency and easily controlled
geometry can rarely surpass or even equal the performance of
powdered phosphors in luminous intensity or efficiency because
of the acceptability and desirability of finely devided
powdered material in most of the practical applications.

The choice of method (15,16) for the preparation
of phosphors depends upon various considerations such as the
chemical and physical nature of the raw material, components
and the chemical, physical and mechanical qualities desired
in the finalised phosphor. Different phosphors thus demand
different methods of preparation.

1.3 LOCALISED ENERGY LEVELS IN THE FORBIDDEN ENERGY GAP:

Impurities, lattice defects and other perturbations
of the ideal crystal configuration and their disturbed
surroundings give rise to discrete energy levels in the
forbidden energy gap. These have been classified as follows -

(a) Luminescent Centre : (17,18) These are discrete
energy levels which have a high capture cross-section for
electrons and greater probability for radiative transitions
than for non-radiative ones. The nature of the luminescent
centre determines the luminescence spectrum.

(b) Killer Centre : Killer centres are also
discrete energy levels which have a high capture cross-section
for electrons with greater probability for non-radiative
transitions than for radiative ones (19).

(c) Traps and Trapping states : (17-21) Traps are
metastable states or levels in the forbidden gap capable of
capturing electrons and holes produced in the centre or else
where in the crystal and detaining them in a restricted
volume (3, 20) for a significant time between the excitation
and emission of luminescence. The energy storage in traps
is accomplished by a spatial localisation of excited electrons
and holes. An empty energy level close to the bottom of
conduction band can act as electron trap while a filled
localised energy level close to the valence band may act as a
hole trap. However, Joshi & Ewles have suggested that the
traps are not due to internal metastable states of impurity
ions but due to crystalline imperfections other than impurity
ions which have been identified with vacancies (22, 23),
Leverenz (21) has pointed out that multivalent impurities
which have normally occupied ground state, e.g. Cu$^{+2}$, Sm$^{+3}$ and
Sn$^{+4}$, and which can assume another occupied state, e.g. Cu$^{+}$
Sm$^{+2}$ and Sn$^{+2}$ are particularly advantageous for forming
trapping centres in phosphor crystals.

1.4 Different Aspects of Luminescence :

There are three main aspects of light emission
from a phosphor. (a) absorption and excitation (b) transfer
and storage of energy (c) conversion of energy into light i.e.
emission.
(a) Absorption and Excitation: Before a phosphor can emit luminescence radiation, it has to absorb energy. This energy absorption may take place either in the host lattice or in the luminescence centre. The act of absorption of radiation by a phosphor leads to excitation of an electron from the ground state to the excited state, which only in certain cases leads to luminescent radiation. In nearly all the cases, however, some or the entire energy is dissipated as heat. The absorption and excitation characteristic of a phosphor depends on the constitution of the lattice and the nature of activator atom (7). Excitation characteristics depend on the nature of the initial and final states of electronic transitions, whereas absorption characteristics depend on the position of the excited state and the relative magnitude of various transitions. Some of the possible modes of excitation (24-26) of a phosphor system are depicted in figure (1.1).

I. Excitation by lattice absorption which produces free electron in the conduction band and free hole in the valence band.

II. Excitation of the normal valence electron produces a bound electron-hole pair called exciton.

III. Excitation of luminescence centre produces a free electron in the conduction band and a hole in the neighbourhood of the imperfection.

IV. Excitation of valence electron raises an atom to an unoccupied centre and produces free hole in the valence band.
FIG (11) ENERGY BAND MODEL FOR ABSORPTION & EXCITATION

L.1 OCCUPIED STATE OF LUMINESCENCE CENTRE
L.2 UNOCCUPIED STATE OF LUMINESCENCE CENTRE
L.3 GROUND STATE OF LUMINESCENCE CENTRE
L.4 EXCITED STATE OF LUMINESCENCE CENTRE
T. TRAPPOING STATE
V. Excitation of valence electron raises the electron into the trap and leaves a free hole in the valence band.

VI. Excitation within the luminescence centre raises an electron to the excited state. In this case no free electron is produced.

Corresponding to the above electronic transitions the absorption spectra may be described as follows.

The wavelength corresponding to the minimum energy required for the transition of an electron from the bottom of the valence band to the top of the conduction band is called the absorption edge. For light of greater energy than the minimum required, absorption is continuous and fairly constant up to a certain maximum energy.

When the excitation energy is lower than the band gap energy, then the absorption by the lattice creates excitons (27-29). This is manifested by a series of narrow absorption lines on the low energy side of the intrinsic band gap absorption (transition II) appearing in the measurement at low temperature only, since excitons are thermally dissociated at room temperature. Absorption bands with still lower energy appear which depend on the matrix or activator or both (7). These correspond to electronic transitions III, IV, V and give some structure in the tail of the absorption spectrum. Corresponding to the electronic transition VI,
bands occur at still longer wavelengths and which are due to electron transitions confined to the luminescence centre.

A further set of absorption bands have been observed in the excited powder phosphors which are due to the transition of trapped electrons to higher states (30). Defects and impurities present also give new absorption bands, mostly on the long wavelength side of the characteristic absorption. Pure lattice absorption is also observed in many compounds (31, 32).

(b) **Transfer of Storage Energy**: No mechanism for energy transfer is required for the system in which the absorption and emission of energy takes place at the same centre. However, the energy transfer in an impurity activated phosphor in which the absorption and emission of energy is not confined to the same centre, may occur in two ways (A) Energy transfer with no movement of charge carriers and (B) Transport of energy by charge carriers.

(A) **Energy transfer with no movement of charge carriers**: There are three different mechanisms for transfer of energy in such cases.

(i) **Cascade mechanism or the energy transfer by Photons**: Here the energy transfer from the absorbing to the emitting centre takes place by the emission and reabsorption of photons. The emitted radiation from the excited centre excites
in turn, the second centre. Thus for the cascade mechanism to be effective the emitting system must be an efficient activator and the spectral distribution of the primary emission must overlap the absorption spectrum of the emitting system.

(ii) Transfer of energy by non-radiative process or resonance transfer: In such cases, the energy transfer from the absorbing to the emitting centre takes place by a non-radiative process (6,10,33-37). When the emitting system is an activator the phenomenon is known as sensitized luminescence and it has been investigated by many workers (7,35,38-44). The absorbing system which transfers the energy is known as sensitizer because it sensitizes the characteristic luminescence of the emitting activator and one speaks of either host sensitized luminescence or impurity sensitized luminescence depending upon the identity of the sensitizer.

The transfer of energy may be accomplished by a quantum mechanical resonance process (6,33) by dipole-dipole (36,37), dipole-quadrupole or by exchange interaction (7,34). Transition from sensitizer to sensitizer has also been reported (35,37). This process depends on (i) the distance over which the energy is transferred and (ii) the optical transition at each centre. This quantum mechanical
resonance process is the most favoured mechanism for transfer of energy from sensitizer to activator (45,46).

(iii) **Exciton migration**: Here the excitons effectively transfer the excitation energy from one point to another by moving quickly through the lattice without contributing to electrical conductivity (37,38). They do, however, contribute to luminescent emission both in some excitation mechanisms and in some radiative recombination processes. Broser (47) and Balkanski (48) have shown that excitons can transfer energy over large distances from their point of origin. It is possible only in very pure and defect free crystals and at low temperatures.

(B) **Energy transfer with movement of charge carriers**: Excited electrons or positive holes independently can transfer energy from one point to another. Many characteristics of photoconducting phosphor have been explained on the basis of the storage action of electron traps (34,49,50). The common form of luminescence involving such a process is that in which electrons and holes recombine at an imperfection.

(C) **Conversion of stored energy as light i.e. emission**: The temporary storage of energy, at the trapping levels, in the forbidden gap by trapping of excited, quasi-excited, or free electrons, positive holes or
excitons makes the luminescence emission process complicated. An excited electron may fall into these levels releasing the balance of energy as phonons. These trapped electrons can go either to conduction or valence band. Trapping is, however, more probable in the neighbourhood of a crystal imperfection for example by producing a polaron in the host crystal (51-53). The nature of the trapping centre, is, however, a major factor in determining the behaviour of emission with time after cessation of excitation (54).

Metastable levels exist at the luminescence centre formed by the activator ions. The emission takes place when the electron is first excited to the levels from where the transitions are allowed. However, in such cases where the complete separation of electrons, or holes is achieved the storage is accomplished by a spatial localisation of these charge carriers in trapping sites. The impurities giving rise to such states, however, interact strongly with the lattice and transfer the energy and momentum associated with the charge carriers to the lattice.

(d) Concentration quenching: The increase in concentration of activator in a singly activated phosphor beyond a certain value generally results in a decrease of luminescent yield and the phenomenon is known as concentration quenching. This has been explained on the assumption that the proximity of a given activator to another or certain types of lattice defect increases the probability of radiationless
transitions. Dexter and Schulman however, have ascribed concentration quenching as due to the resonance transfer of energy from one activator atom to another until the energy reaches an imperfection which may act as an energy sink.

1.5 THEORIES OF LUMINESCENCE:

The luminescence phenomenon is often explained by means of two theoretical models, the configuration coordinate model and the band model. The two models are mutually exclusive and practically all interpretations of luminescence phenomena have been based either implicitly or explicitly on some modification of them. The configuration coordinate model ignores energy transport while the band theory ignores atomic rearrangements.

(a) Configurational Coordinate Model: The model was first proposed by Von Hippel (55) and applied to the problems of luminescence by Seitz (56) and others (57,58). The total potential energy of the ground and excited states of the centre, including both ionic and electronic terms, has been plotted as a function of the coordinate of the surrounding ions Fig. (1.2). When the centre absorbs energy, it is raised from the ground state A to the excited state B. The transition is vertical in accordance with the Franck-Condon principle. After the centre has reached the excited state, the ions of the system adjust until
FIG 12 CONFIGURATION CO-ORDINATE CURVES
a new equilibrium is reached at C, the energy
difference between B and C is given off as lattice
vibration. From the new equilibrium position C, the
centre may return to the ground state D by the emission
luminescent light. The centre then relaxes from D to A
by again giving up energy to the lattice.

This model accounts well the thermal quenching
of luminescence (57), Stokke's shift (59,60) and small
quantum yield at low temperature (56). The classical
picture of the configurational coordinate, though
successful in many respects, fails to explain the
variation of the width of absorption & emission bands
with temperature. In the quantum mechanical modi-
fication, the centre is considered as a simple harmonic
oscillator with quantized vibrational energy levels.
The zero point energy of the oscillator provides an
explanation of the fact that emission bands do not
sharpen up into lines at low temperatures. In addition
to the variation of width of emission and absorption
bands at low temperature (61-63) this can also account
for the process of sensitization in doubly activated
phosphors (49,64).

Though not easy to compute, configurational
coordinate curves have been attempted for non-photo-
conducting phosphors experimentally (62,65,66) and
theoretically (66). However, the disagreement between theory and experiment in the prediction of activation energy for non-radiative transition is accounted for by introducing a multidimensional model (67,68).

(b) **Continuous Dielectric Model**: In the configurational coordinate model the centre is well localised and both ground and excited states are confined to a region not much larger than the distance to the nearest neighbours. In such a case atoms other than the nearest neighbours would not influence the centre greatly and the only important interaction would be with very few atoms. In the model known as the continuous dielectric model, Huang and Rhys (69) have ignored these short range interactions and have introduced the idea of long range interaction of the centre with the phonon field of the lattice. The interactions which come into play are considered electrical in behaviour and the lattice in which the centre is embedded being a continuous dielectric. In the process of absorption, the centre experiences a change in the charge distribution when the system is raised from the ground state to the excited state. This results in a change in lattice polarization followed by the creation of lattice phonons. Further extension & refinements of this work have been carried out by many workers (70-73).
(c) **Energy Band Model** : This model has its origin in the collective electron theory of Bloch (74) for crystalline solids and was adopted by Riehl and Schon (75) and independently by Johnson (49) to explain the luminescence phenomenon. According to this model the discrete levels of electrons in atoms are disturbed by the mutual interaction in the crystal and are broadened into forbidden and allowed bands. The activator introduced generally gives rise to discrete levels in the forbidden zone above the valence band with the ground state of each centre occupied. The structure of these luminescence centres provides a shielding from the effect of lattice vibrations. Other impurities or lattice defects, if present, produce unoccupied levels in the forbidden zone close to the conduction band in which excited electrons can be trapped. Three types of models have been advanced for describing the mechanism of luminescence in photo-conducting phosphors.

(1) **Schon-Klasen's model** (Fig. 1.3) : This model was proposed by Schon (76) and developed by Klasens and his associates (77,78). Here the ground level of the centre is assumed to be close to the valence band of the crystal. Normally the level contains an electron. Absorption (A) produces a free electron and hole in the matrix. The hole diffuses to the luminescence
FIG. (13) SCHON-KLAENSEN MODEL

A. ABSORPTION
B. HOLE MIGRATION
C. HOLE CAPTURE (NON-RADIATIVE)
D. ELECTRON MIGRATION
E. ELECTRON CAPTURE RESULTING IN LUMINESCENCE
centre (B) and captures the electron located there (C) there by leaving the luminescence centre vacant. The free electron after migrating to the empty centre (D) falls into empty ground level (E) with emission of luminescence.

This model explains satisfactorily many related phenomena such as doubly activated phosphors, temperature quenching of phosphorescence and the effect of poisons (78, 79). However, a serious objection to this theory is that luminescence decay would be anticipated as being of the same order as for photo-conductivity, which is not the case (80).

(ii) Lambe and Klick's model (81-84) Fig.(1.4) : The main feature of this model is that the trapping of the hole by the centre is considered to be a large energy transition. Here the ground state of the centre consists of an electron bound in an energy level close to the conduction band. Absorption (A) produces a free electron and hole pair. The hole migrates to the filled centre (B), there gets an electron (C) accompanied by luminescence. Finally the conduction electron after migrating to the centre (D) falls into the ground state (E) and in this capture only a small amount of energy is given off (non-radiatively). In this model, it is seen that
FIG (14) LAMBE-KLICK MODEL

A: ABSORPTION
B: HOLE MIGRATION
C: HOLE CAPTURE RESULTING IN LUMINESCENCE
D: ELECTRON MIGRATION
E: ELECTRON CAPTURE (NON-RADIATIVE)
in a certain sense it is the free hole which dominates the process of luminescence.

This model requires no additional centre to account for the rates of luminescence and photovoltaic decays. Hole trapping and luminescence occurs first, which has a large capture cross-section owing to coulomb attraction. Subsequent trapping of electrons with much smaller capture cross-section leads to the development of photo-conductivity which will persist for a longer period. The recombination process is essentially the annihilation of a hole and an electron, in Schon - Klasen's model it is a bound hole by a free electron while in Lambe Klick's model it is a bound electron by a free hole.

(iii) Williams and Prener's model (85-89) Fig.(1.5) : In this model the centre has the ground state I near the valence band and an excited state II near the conduction band. Level I has a high capture probability for valence band hole which level II has a high capture probability for conduction electron. After the formation of free electron and hole pair the capture of hole and electron occurs in levels I and II respectively. The luminescence emission is then due to the transition from II to I.

In this model the probability of the radiative
emission is much greater than in the above two models provided the temperature is not too high. At high temperature electrons from level II are raised into the conduction band before radiative emission. This explains the quenching of luminescence. This model explains satisfactorily the temperature dependence of fluorescence (90) and photo-conductivity. The steady state of luminescence of ZnS phosphors has been explained by Rebane (91).

1.6 Allied Properties and Related Topics:

The study of allied properties associated with luminescence are important since they provide additional information about the mechanism involved in the luminescence process. A few such properties are discussed here.

(a) Photo-conductivity: Photoconductivity is the increase of electrical conductivity of a crystal caused by the radiation incident on it. But its measurements are difficult with powder phosphors due to space charge effect at the grain boundaries. This increase of conductivity arises from the liberation of charge carriers during excitation and it can be used to correlate evidence of the order of reaction kinetics involved. However, the systematic study of photoconductivity in phosphors began with the development of single crystals because space charge
effects encountered in microcrystalline powders are eliminated (92,93). The study of its different aspects e.g. decay of photoconductivity and the increase in conductivity of pre-excited phosphors on heating helps in the determination of the lifetime of the charge carriers and distribution & density of trapping states (54,94,95).

(b) Photodielectric effect : When a photoconducting phosphor used as a dielectric of a capacitor, is excited to give luminescence, an increase in dielectric constant is observed. This has been explained by early workers (96-98) as due to the production of conduction electrons by the excitation. Garlick and Gibson (99) made extensive study of this effect along with luminescence. They have suggested that the dielectric changes are due to large polarisability of the dipole system formed by these trapping states which are coupled by electrons. This change has also been explained by assuming the existence of space charge at grain boundaries in the phosphor and the electrons involved to be localised in traps (100). Gisolf and many others (97,101) have considered the photodielectric effect as another manifestation of photoconductivity. They argued that the presence of photoconductivity decreases the distance between the plates due to presence of
electrons produced by the excitation and thus increases the capacitance and the apparent dielectric constant. The study of this effect adds new information to our knowledge of trapping processes.

(c) Electrophotoluminescence: This is the phenomenon of stimulation (102) or quenching (103) of phosphorescence emission by an applied electric field. To explain this effect it has been suggested that it is due to the release of trapped electrons and holes by the action of applied electric field. Investigations have been made to make a precise study of the release of trapped electrons by an applied electric field in powder phosphors (104) and in single crystals (105). This study is useful for studying shallower traps (106) since for deep traps a strong electric field is required at which breakdown occurs.

(d) Electroluminescence: This is a phenomenon in which a direct transformation of electrical energy into light takes place (107). In older literature (108) electroluminescence was used to describe the emission resulting from the passage of current through a gas or vapour. According to Payne, Mager and Jerome (109) certain materials when placed in a fluctuating electric field under proper condition
give luminescence and continue to emit light as long as the exciting field is maintained. It has been observed in CaS and SrS phosphors also (110, 111). Piper and Williams have explained this phenomenon by arguing that electrons injected into the conduction band in the presence of a high electric field from the donor level or occupied traps too deep to be ionised thermally, have an appreciable property of attaining enough kinetic energy to excite or ionise an activator system by means of inelastic collisions.

(e) Paramagnetic resonance: Electron paramagnetic resonance was first observed in the year 1945. The substances investigated were crystalline paramagnetic salts. Most of the paramagnetic solids are ionic compounds containing elements from one of the transition groups of the periodic table. The magnetic properties of the solid originate in a net electronic angular momentum of the unfilled inner electron shell of the ions. The electrons and nuclei of atoms have magnetic properties much like tiny bar magnets which when placed in a constant magnetic field and subjected also to a small time-varying magnetic field of the correct frequency, absorb energy from the time-varying field. The condition under which this energy absorption occurs makes possible a detailed statement about the interaction of these tiny magnets with their magnetic
environment.

The paramagnetic results for a given ion reflect faithfully the symmetry properties of the particular crystal lattice. So paramagnetic resonance is a means of studying not only the energy levels of the paramagnetic ions in solids, but also the detailed crystalline structure of these solids.

Thus, this phenomenon is a powerful tool for detecting and characterising the defects and impurities in phosphors (112,113) the localised electron at trapping sites at a particular temperature (20,114) and the kinetics of fluorescence & phosphorescence processes (115).

1.7 **STANDARD OF PROBLEM**

The alkaline earth sulphide phosphors are among the earliest known impurity activated phosphors(116). These phosphors which have been extensively studied particularly by Lenard and his school, fell into oblivion because of their instability under excitation or atmospheric conditions and the advent of other phosphors with far better characteristics. However, with the discovery of infra-red stimulation, sensitization, magnetic properties, and electroluminescent nature of these phosphors a good deal of interest has been rejuvenated.
Much work has been done and is still being continued in our laboratories on alkaline earth sulphide phosphors. Starting from preparative parameters, the role of fluxes (single and compound), effect of different activators (singly and in various combinations), many detailed studies have been carried out. In the present investigation four activators from the IV group of the periodic table have been chosen and SrS:Zr, SrS:Sn, SrS:Ba and SrS:Th phosphors have been prepared with the view that a systematic determination of the effect of activators of the same group on the various luminescence characteristics in the same host may help in understanding the role of activators in this phosphor system. The chemical similarities existing between these four activators we expect ad might present interesting possibilities and it may be possible to infer to what extent these activators differ from each other in influencing the characteristics of the phosphors.

CaS:Zr and CaS:Th have already been tried in our laboratories (117, 118). These activators incorporated in SrS lattice could provide complementary studies. By a fortuitous circumstance Sn and Pb have not been tried extensively as activators in this phosphor system.

Moreover, the precise nature of traps in alkaline earth sulphides has been uncertain. Therefore, to investigate the effect of Zr, Sn, Pb and Th, on the nature and distribution of trapping states, phosphorescence decay in
conjunction with thermoluminescence is studied. The decay is studied at room temperature for the period from a second after cessation of excitation to the time when intensity is reduced to a negligibly small value. An attempt is made to analyse the decay curves into different exponentials and thus evaluate the trap depths and also to find out the decay law and the effect of variation of concentration of activator in each series of phosphors.

Thermoluminescence studies as used by Randall and Wilkins (54) and others (119,120) for the interpretation of phosphorescence are also carried out in order to have a picture of the spread of trapping levels and to know how far it is affected by the variation of activator concentration. The range of study is from room temperature to about 550°C. The trap depths are calculated from the peak temperatures of the glow curves and are compared with the values obtained from decay studies.

Study of fluorescence which serves to give information concerning the energy levels of the phosphors has also been carried out. The effect of activator on the fluorescence intensity and peak wave length is investigated and an attempt has been made to account for the occurrence of bands.

These studies, however, form only part of a total scheme. It is hoped that when other studies like absorption, excitation, electroluminescence and magnetic
behaviour, which are in progress in these laboratories are complete a better understanding of the nature of luminescence in this system would be obtained.
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