CHAPTER I

INTRODUCTION

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CHAPTER I
INTRODUCTION

1.1 Solid State Physics and Luminescence:

Solid State Physics has acquired a very important status in recent years. In an ideal crystal the unit which may consist of atom or atoms or molecule or molecules is repeated in three dimensions according to definite geometrical patterns repeated in three dimensions and prima facie it may appear that it may be possible to interpret the physical properties of such a perfect crystal in terms of the electronic structures of the units and the pattern of repetition. However, the normal solid we come across has defects and does not consist of such regular structure as defined for an ideal crystal. Major part of the present day solid state research is devoted to the study of defect structure of solids, as this may provide a way to correlate the apparently different fields of investigation such as luminescence, electrets, conductivity, dielectric behaviour etc. Just as the spectroscopy of atoms provided basic information about atomic structure, investigations on luminescence of solids provided an important tool to investigate and to
understand the band structure and energy levels of impurities and imperfections in solids. The property of luminescence is a convenient and sensitive indication of changes of composition, structure and atomic interactions in solids and has contributed much to our improved understanding of the solid state of matter.

A side factor in the development of the field of luminescence research has been its commercial applications. Activity in the field of application has, therefore, been probably more pronounced than that in the research laboratory towards the theoretical approach. The prominent applications of luminescence in industry and science are fluorescent lamps, television and radar screens, X-ray fluoroscope, self-luminous dial markings, electroluminescent lamps etc.

However, because of the complexity of luminescent phenomena and the diversity of types of material that exhibit luminescence, it has not been possible so far to develop a unified theory of luminescence capable of explaining all the aspects. Thus it is necessary to have further information about different phosphor systems. With this in view, alkaline earth sulphide phosphors prepared under different conditions as regards the constituents and method of preparation
are receiving special attention in these laboratories.

1-2 (A) : Definitions :

(a) Luminescence:

Luminescence is a general term for the emission of visible or non-visible (ultraviolet or infrared) radiation from a substance during or following the absorption of energy in the form of ultraviolet radiation, x-rays or high energy particles or simply from the application of an electric field (1-3). The emission is not due to incandescence and so is often called "Cold Light". It can be distinguished from thermal radiation as it does not follow Kirchoff's law and from Raman and Compton effects on the basis of time delay. In the case of luminescence the time delay after excitation is greater than $10^{-9}$ sec. while Raman and Compton effects are completed in an interval of about $10^{-14}$ sec (4,5).

The general term luminescence may be subclassed according to the modes of excitation, as Photoluminescence - that produced by high energy photons, Radioluminescence - that excited by any or all radioactive disintegration products, Electro-luminescence - that produced by the application of an electric field, Sonoluminescence - that produced by ultrasonic waves, Triboluminescence - that produced by
mechanical strain and chemical luminescence - that which accompanies a chemical reaction or biological process.\( (3,5)\). 

(b) Fluorescence and Phosphorescence:

Fluorescence and Phosphorescence are the two special aspects of luminescence. Garlick (3) defines fluorescence as the emission during excitation and phosphorescence as that which persists after the excitation has ceased. The demarcation between the two may be fixed at \(10^{-8}\) sec. after the cessation of excitation as this is the time of relaxation of an ionized gaseous ion in the excited state.

On the basis of physical processes taking place during fluorescence and phosphorescence, Perrin (6) gave the following definition:

"The phenomenon is fluorescence if the emission takes place by one or more spontaneous transitions. If, on the contrary, the emission occurs with the intervention of a metastable state followed by return to the excited state due to addition of energy, then this is phosphorescence."

The distinction between the two processes is also made on the basis of the variation of the luminescence decay with temperature. The decay of fluorescence is little dependent on temperature but the decay of
phosphorescence is strongly temperature-dependent.\(^{(7)}\).

1 - 2(8) Other Terms used in Luminescence:

(a) Phosphor:

The word phosphor meaning literally "Light bearer" is commonly applied to luminescent solids prepared by a suitable heat treatment. Phosphors may be either inorganic or organic. The most interesting and useful phosphors are the inorganic ones which are generally crystalline insulators \(^{(8)}\). Phosphors are very sensitive to structural changes and are strongly influenced by chemical composition of the base compound, physical conditions of preparation and the presence of traces of impurities known as 'activators'. An efficient phosphor is that which converts a large proportion of the absorbed excitation energy into luminescence emission with inappreciable energy losses by increase in lattice vibrations or electron emission or chemical or structural changes.\(^{(5)}\).

There are two basic types of phosphors -

(i) the impurity-activated in which the luminescence is due to the addition of an activator in the form of a trace impurity e.g. CaS:Bi etc, and (ii) the so-called self-activated which show luminescence in the pure state e.g. the salts of rare earths, manganous halides, platinocyanides etc. in which the luminescence is apparently due to specific atomic groups or atoms \(^{(9)}\).
Mott (10) has classified phosphors in two groups on the basis of photo-conductivity -

(i) **Photoconducting Phosphors**:

In these, excitation raises electrons from the valence band or from the luminescence centre to the conduction band leaving behind a hole. Accordingly they exhibit strong photoconductivity. Examples of this class of phosphors are ZnS : Cu, CdS : Ag etc.

(ii) **Non-photoconducting phosphors**:

In this class, the emitting system is quasi-atomic under the usual conditions of excitation. The electron is not raised to the conduction band and consequently the photoconductivity is negligible. The typical example of this class of phosphors is KCl : Tl.

(b) **Luminescence and Killer Centres**:

Luminescence phenomenon involves initial absorption of energy, its storage and finally its re-emission. The localities in phosphor where energy is re-emitted after absorption are called luminescence centres. These centres, therefore, represent the energy levels responsible for the spectrum of the emitted luminescence. In other words, the luminescence centres represent those levels for which the probability of radiative transition is maximum. It is now definitely known that activator ions are responsible for the formation of luminescence centres in a phosphor. The
emission properties of a luminescence centre also depend on the charge of the activator ion and the bane material.

If on the other hand the probability of non-radiative transition is much greater than that for the radiative one, the centre is known as a 'Killer Centre' and the impurities responsible for such centres are called 'poisons' e.g. Fe, Ni and Co in ZnS (11).

(c) Traps:

Traps are metastable levels in the phosphor crystals capable of capturing electrons or holes within them and rendering them immobile. These can be released later by supplying an optimum amount of thermal or optical energy (12, 13). An electron thus released from a trap can either combine with a luminescence centre or be retrapped in another trap. Traps provide the mechanism for energy storage in most of the electronically active solids including phosphors and are responsible for the phenomena of phosphorescence and thermoluminescence (14). The trapping levels owe their origin to impurity atoms, preparative conditions or imperfections in the crystal lattice (15).

A normally occupied electron trap is called
a 'donor level' while a normally occupied hole trap is known as an 'acceptor level'.

1-3. Theories of Luminescence:

The basic points of difference between the luminescence spectra and the atomic spectra are - (i) Bands, (of the order of 0.1 e.v. to 1.0 e.v. wide) rather than lines are generally observed, (ii) the emission band is displaced to the low energy side of the absorption band by an electron volt or more (7).

Phosphors can emit line or band spectra or both separately or simultaneously. Band emission is usually caused by interaction between the activator and the host matrix. Line emission is, however, attributed to electronic transitions occurring within shielded electronic orbitals (within a luminescence centre) so that there is little interaction with the matrix (5).

Practically all interpretations of luminescence phenomena, including the above have been based either implicitly or explicitly on some modifications of the configuration coordinate model or the energy band model discussed below (16). The first model neglects atomic rearrangements while the second
neglects the energy transport.

(a) Configuration Coordinate Model:

This one dimensional model was first proposed by Van Hoppel and was successfully applied to problems of luminescence by Seitz (17, 18). Later, quantum mechanical modifications were proposed by Schom (19). This model is best suited to the explanation of quasi-atomic systems like KCl:Tl.

The interaction can be represented in a satisfactory manner by using a single configuration coordinate to give the distance between the luminescent ion and its nearest neighbors in the surrounding lattice. The configuration coordinate model curve is illustrated in Fig. 1-1. The total energy of the system for the ground as well as the excited states of the center including both ionic and electronic terms, is represented along the ordinate. The abscissa represents a configuration coordinate specifying the configurations of the ions around the center. On absorbing an amount of energy $h\nu$, the center is raised to its excited state at $B$, from the equilibrium position of its ground state at $A$. The transition is a vertical one (shown by the line $AB$ in Fig. 1.1) following Franck-Condon principle, according to which the
TOTAL ENERGY

GROUND STATE

EXCITED STATE

CONFIGURATION COORDINATE

CONFIGURATION COORDINATE MODEL

FIG. 1
electronic transition occurs in a time shorter than that necessary for an ion to move appreciably. After the centre has reached at $B$, the ions of the system adjust until a new equilibrium position is reached at $C$. The energy difference between $B$ and $C$ is given off as lattice vibrations. After the centre has reached at $C$, it may return to the ground state at $B$ by emitting a quantum of luminescent light $h\nu'$. The centre relaxes from $B$ to $A$ by giving off the energy again in the form of lattice vibrations. Because of these losses of energy, the emitted energy $h\nu'$ is lower than the absorbed energy $h\nu$. This shift is known as the 'Stoke's Shift'. In the case of KCl:Tl this shift is of the order of several electron volts at room temperature (20).

Nott and Gurney (21) have shown that, given sufficient thermal energy, the centre in the excited state at $C$ might reach a point such as $E$, where the curves approach each other closely. The system may then return from the excited state to the ground state by a non-radiative transition. This is known as thermal quenching of luminescence.

An alternative mechanism has been suggested by Seitz (18) to explain the absence of luminescence in a number of solids (Fig 1.2). After the
absorption of light the system in the excited state relaxes to such an extent that its minimum is shifted away from the minimum of the ground state curve. In approaching this minimum, the possibilities of radiationless transition exist at the point such as A.

The model proposed by Dexter et al. (22) (Fig 1.3) requires less lattice relaxation around a centre than does the model of Seitz.

If the transition is to a point B, the energy at which is greater than that at C - the point of close approach of the curves, immediately after the absorption act, the centre may find itself near C, increasing the probability of non-radiative transition to the ground state.

Configuration coordinate curves have been obtained experimentally by Williams and others (23-25) in the case of non-photo conducting phosphors e.g. alkali halides, tungstates etc. These curves have also been applied to doubly activated phosphors and to explain the process of sensitization (26, 27). Recently Naeda (28) on the basis of disagreement in calculated and observed values of activation energy for non-radiative transition, has proposed a multi-dimensional model in preference to the simple one.
(b) Continuous Dielectric Model:

In the configuration coordinate model, the interaction of the centre with the lattice is restricted to the first and second nearest neighbours. Rhys and Huang (29) have proposed a theory in which they ignored these short range forces and computed interaction of a centre with the phonon field of the lattice. This interaction is an electrical one and the development treats the lattice as a continuous dielectric in which the centre is embedded. In absorption, for instance, the centre experiences a difference in charge distribution when the system jumps from the ground to the excited state. This rearrangement in charge induces, in turn, a change in lattice polarization which is accompanied by the creation of lattice phonons.

(c) Energy Bond Model:

This theoretical model adopted to explain the characteristics of photoconducting sulphide and silicate phosphors was first put forward by Kiehl and Schon (30) and independently by Johnson (31) on the basis of the collective electron model originally developed by Bloch (32), to explain the energy states of a perfect lattice (Fig. 1.4).
Fig 1.4  ENERGY BAND MODEL
C - CONDUCTION BAND
E - FILLED BAND
L - LUMINESCEENCE CENTRE
T - TRAP
This model is based on the general quantum mechanical treatment of the interaction of valence electrons with the three-dimensional periodic potential of the crystal lattice. In an isolated atom the energy stages for electrons consist of discrete levels separated by regions of forbidden energies. The allowed states are defined by the Schrödinger's equation. But in a perfect crystal lattice, when the atoms or ions are arranged in an orderly manner and in close proximity, the discrete levels are disturbed by mutual interaction and consequently broadened into bands of allowed energy separated by bands of forbidden energy. In an insulator, the uppermost filled continuous energy band is called the valence band and the lowest empty continuous energy band is called the conduction band.

Impurities introduced to produce emission centres for luminescence will usually give rise to discrete localized states (L) in the forbidden zone above the filled band (F), with the ground state of the each centre occupied, Fig. (1.4). Presence of other impurities, vacant lattice sites and other lattice defects will provide unoccupied levels in the forbidden zone (T), just below the conduction band, in which the electrons excited to the conduction band can be trapped.
If the phosphor is excited by ultraviolet or visible radiation of sufficiently high quantum energy, it may be absorbed by an atom in the crystal lattice. In this process an electron will be raised to the conduction band from the valence band represented by the transition $h\nu$ in the Fig (14) leaving behind a positive vacancy known as hole capable of moving through the lattice in an applied field. The absorption bands, due to such transitions are called 'fundamental absorption bands' of the phosphor matrix and are generally situated in the ultraviolet or near visible regions of the spectrum. The radiation of lower energy which is not absorbed by the matrix, may be absorbed by the impurity centres. Then the electron transition can take place either to an excited state of the centre or to the conduction band giving rise to additional absorption bands lying on the long wavelength side of the fundamental absorption bands.

In alkali halide crystals, although the absorption takes place in the matrix, the excited electrons are not raised to the conduction band but remain bound to their respective positive holes. These bound electron-hole pairs are known as 'excitons' (33).

The absorption of energy may also result in
the transition $E$ from the filled band directly to
the trapping states $T$ (34, 35). An important
limitation of this model is that the energy bands
and levels are characteristic of a particular atomic
configuration hence the atomic rearrangements that
occur during luminescence are ignored.

1-4. Luminescence Processes and Specific Models for
Luminescence Centre in Photoconducting Phosphors:

(a) Luminescence Processes involving Transfer of
Charge:

This type of luminescence emission is
mostly due to the recombination of electron and hole
at an imperfection. Following models have been assumed
to explain the phenomenon.

(i) Schon- Klasens' Model:

This model was proposed by Schon (36) and
developed by Klasens and coworkers (37-39) for
sulphide phosphors. This model makes use of the
energy band scheme of a solid in which the activators
(or quenchers) are supposed to cause localized
levels not far above the valence band. Fig. (1.5)
illustrates the model for the case of a single lumin-
escence centre. The sequence of events is as
follows:

(i) Absorption of light in the matrix leads to an
SCHON KLASENS MODEL

FIG. 1.5
electron in the conduction band and a hole in the valence band \((A)\).

(2) The hole may migrate towards the impurity centre \((B)\).

(3) The luminescence centre has a net negative charge and attracts the hole with a Coulomb-like attraction. The hole is captured by the impurity centre giving out infrared radiation or vibrational quanta \((C)\).

(4) The electron wanders through the lattice \((D)\) and is finally captured by the centre \((E)\) where it recombines with the captured hole giving off luminescence emission.

This model successfully explains emission in doubly activated phosphors, temperature-quenching of phosphorescence and the effects of poisons.

(ii) Lembe and Klick model:

This model assumes that the centre levels are near the conduction band (Fig 1.6). The mode of operation of the system is as follows (39,40) -

(1) Light is absorbed exciting an electron to the conduction band, leaving a hole in the valence band \((A)\).

(2) The hole and the electron move about in their respective bands and eventually the hole migrates near an impurity centre \((B)\) because of its effective negative charge.
Fig. 1.6  Lambe and Klicks Model

A - Excitation
B - Hole Migration
C - Hole capture resulting in luminescence
D - Electron migration
E - Electron capture (non-radiative)
(3) The hole is captured by the impurity centre giving off luminescence emission and the centre becomes neutral in charge (C).

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

(5) The electron is finally captured by the centre giving off a small amount of energy as infrared radiation or as lattice phonons (E).

This model nicely explains the difference in time of decay of phosphorescence as well as the photoconductivity in sulphide phosphors (41).

(iii) William - Pruner Model:

This model, also known as Associated donor - acceptor model has been proposed by William and Pruner to explain the luminescence phenomena in ZnS : Cu phosphors (42-44). (17).

In this model, centres involve a ground state I near the valence band, which has a high probability for hole capture (acceptor-level) and an excited state II near the conduction band which has a high probability for electron capture (donor-level). After the capture in each type (A and B), emission can take place by transition of the electron from level II to level I (C). The only condition to be fulfilled is that the temperature should not be very
FIG 17 WILLIAMS PRIMER MODEL
high because in that case the electrons in state II are raised to the conduction band and hence the emission is quenched (45-47).

Klasens (48) has used this model to explain photoconductivity and temperature dependence of fluorescence in ZnS phosphors.

(iv) Stimulation and Quenching:

If the emission intensity of a phosphor is increased by irradiating it with a long wavelength visible or infrared radiation, it is known as 'Optical Stimulation'. Conversely, if the intensity is diminished it is called 'Optical Quenching'. Stimulation or quenching effects can also be observed by the application of a strong electric field to a phosphor previously excited with ultraviolet radiation. Lenard and co-workers (49) have studied these effects in alkaline earth sulphide phosphors with infrared irradiation.

In stimulation, the radiation releases trapped electrons which cannot make transition to the dominant activator centres due to insufficient quantum energy while in the case of quenching, the excitation releases positive holes from empty emission centres which then migrate to traps and capture electrons in non-radiative transitions.
(b) Luminescence Processes involving Energy Transfer without Movement of Charge:

The phenomenon in which the centre responsible for emission is not the same in which absorption has taken place, is known as 'Sensitization'. The mechanism does not involve the movement of charge carriers in the transport and transfer of excitation energy from the absorber to the emitting centre. A notable example of this type of process is CaS:Sm:Bi phosphor discovered by Rothschild (50). The following mechanisms of energy transfer have been proposed -

(i) Cascade Mechanism -

After excitation one centre emits radiation which excites a second centre. This mechanism involving radiative transfer of energy between the two centres is known as 'Cascade Mechanism'. This process is better applicable to organic phosphors than to inorganic ones because in the latter case one frequently deals with activation having 'forbidden' transitions (51,52).

(ii) Resonance Transfer:

The energy absorbed by the sensitiser is transferred to the activator without any emission by the sensitiser. This is due to the resonance mechanisms by dipole - dipole or dipole - quadrupole or exchange interaction (53-55). The interaction
between the sensitiser and the activator occupies one of the nearest available cation sites surrounding the sensitiser (56). Thus, resonance transfer appears to be the most probable process of sensitised luminescence (57).

(iii) Exciton-Migration:

In this process, an electron of the sensitiser returns to the ground state while that of the activator is raised to an excited state. The return of the electron of the sensitiser creates an exciton which diffuses to the activator and is absorbed there raising an electron to the excited state. We can assume the emission of an actual exciton which can be detected by its diffusion (58,59).

Broser and Balkanski (60-61) have shown the possibility of the action of excitons at large distances from their points of creation in the case of CdS. However, this possibility is true only in pure and defect free crystals.

(iv) Transfer Leading to Quenching:

When the concentration of the activator in a singly activated phosphor is increased beyond a certain value, it is observed quite generally, that the luminescence efficiency decreases. This is known as Concentration Quenching. Johnson and Williams (62)
and Kwles and Lee (63) have assumed that quenching occurs at the centre which absorbed the excited energy initially. The proximity of a given activator to another activator or certain type of lattice defects also increase the probability of a radiationless transition. According to Dexter and Schulman (64) the degradation of energy takes place at special quenching sites in the crystal. Quenching is assumed to involve the resonance transfer of energy from activator to activator until it arrives at an activator near one of the energy sinks. Activator-quencher transfer then takes place and the energy is lost.

1-5. Properties of Phosphors:

(i) Decay Characteristics:

The fall in intensity of the phosphorescence emission with time after the excitation has ceased, is known as phosphorescence decay. It is now well established that phosphorescence in inorganic crystal phosphor arises due to the trapping of electrons in the traps lying below the conduction band. These electrons slowly escape from the traps after absorbing energy from the lattice and return to the luminescence centres via conduction band. The recombination of electrons with the luminescence centres
gives rise to phosphorescence emission. The electrons freed from traps may, alternatively, be retrapped and in this case the ultimate phosphorescence will be delayed.

Bacquerrel (65) was the first to study the decay of phosphorescence intensity with time. He classified the decay mechanism in two types:-
(a) Monomolecular decay, similar to monomolecular chemical reaction responsible for exponential decay curve.
(b) Bimolecular decay corresponding to bimolecular chemical reaction responsible for hyperbolic decay curve.

In exponential decay, the delay in emission is due to the time an electron spends in the luminescence centre in an excited state. This kind of phosphorescence lasts only for a few milli-seconds and is independent of temperature. In the hyperbolic decay, the delay in emission is due to an excited electron spending time in moving through the phosphor crystal from one atom to another or due to slow release from the trap after absorbing energy and its subsequent recombination with an empty centre. The phosphorescence in this case may continue for a very long time and is highly temperature dependent.
The study of decay characteristics is important as it can provide information about electronic energy levels, their distribution and movements of electrons in a phosphor (1).

(ii) Thermoluminescence:

If a phosphor is excited while cold and is then warmed, the emission it gives while warming is known as thermoluminescence. This emission is due to the release of electrons from traps by thermal activation and their subsequent return to luminescence centres. Hence this method can provide information about the trapping mechanism in a phosphor. Urbach(66) originally used this method for the study of trapping levels and their distribution in depth in a phosphor and later it was extended to the study of sulphide phosphors by Randall and Wilkins (1). The experimental method is to measure the variation of thermoluminescence intensity with the temperature obtained by warming a phosphor in the dark at a uniform rate after excitation at a low temperature sufficiently low for the traps not to lose their electrons. It is obvious that thermal activation will first remove electrons from shallow traps and then from the deeper ones. The light emission versus temperature curve known as 'Glow Curve' should then represent the distribution of traps in depths in the phosphor. The
number of traps $N_E$ of depth $E$ is proportional to the height of the glow curve and $E$ is proportional to $T_m$ the glow peak temperature (67). Garlick (3) after Wells has reported that the distribution of traps depends markedly on the activator. This method, though less precise than the decay method, is more convenient and rapid.

(iii) Photoconductivity:

Photoconductivity is the increase in electrical conductivity of a phosphor when irradiated with light which stimulates luminescence. When a phosphor is excited with energy greater than its band gap a certain number of electrons and holes become free which can move in an applied electric field, thereby making the phosphor conducting (41). The free electrons and holes finally lose their energy either by luminescence emission or by thermal dissipation. As the photoconduction arises due to the liberation of charge carriers, it should be able to provide information about the order of kinetics involved in luminescence.

The photoconductivity measurements of micro-crystalline phosphors could not be carried out successfully because of the space charge effects at the grain boundaries. However, the above difficulty has been overcome by the development of single crystals. Brosor and Warinsky (68) have made a notable
contribution from their studies on CdS and ZnS single crystals.

(iv) Photodielectric Effect:

When a phosphor, forming the dielectric of a capacitor, is excited by an electric field to give luminescence emission, an increase in the value of its dielectric constant is observed. Studies of many workers in this field reveal that this phenomenon is observed only in photoconducting phosphors (69). The variation of dielectric constant depends on the temperature and frequency of the applied field. According to Gisolf, De Groot et al (70-73) this phenomenon is due to the conduction electrons produced by the excitation. But Garlick and Gibson (67) interpret it as due to the large polarizability of the dipole system formed by the filled traps. Kallman et al (74, 75) have given the correct explanation of this effect in terms of their conducting grain theory, assuming that only those trapping states must be effective which are involved at the given grain boundaries.

(v) Electroluminescence:

Excitation of luminescence in ZnS crystals by the application of an intense electric field was observed first by Gudden and Pohl (76). The effect
was, however, transient with static fields. Sustained luminescence was first obtained by Destrieu (77) on applying alternating field to a layer of ZnS placed between two electrodes. Now this technique has been developed further for studies on more efficient single crystal as well as powder phosphors. The explanation of the above effect is put forward by Piper and Williams (75) and Curie (7). According to them the excitation raises electrons into the conduction band; some of these electrons which are accelerated by the field collide with luminescence centres causing their excitation or ionization and finally recombine with the latter to give luminescence.

Some other properties shown by phosphors are electrophotoluminescence, electron emission, paramagnetic susceptibility, paramagnetic resonance etc. studied by various workers (79-81) to obtain information about traps and the valence state of an activator in a phosphor.

1.6 Statement of the Problem:

Alkaline earth sulphide phosphors were first synthesized and investigated in a thorough manner by Lenard (82) during the early period of this century. As these phosphors are unstable under
electric discharge and easily hydrolyse in a moist atmosphere, there was a temporary set back to their progress from practical and commercial point of view. The interest in these phosphors was revived during the World War when it was discovered that these show increased brightness on infrared stimulation and sensitization (83, 84). After the war period, a good deal of accumulated experimental results were published particularly in America.

Since last one and a half decade, the alkaline earth sulphide phosphors are being prepared and studied in the Solid State Physics Laboratory of this University. Various aspects like preparative parameters, role of single and compound fluxes, different combinations of activators (single and multiple) have been studied by various workers. It was, therefore, decided to investigate the hitherto untried phosphors CaS:Zr:Ce (Na₂SO₄) for their preparation and properties. Mention of this combination for a phosphor material has not been reported so far in any of the Science Abstracts. CaS:Zr and CaS: Ce phosphors have already been studied in this laboratory by Agnihotri-Rawat (85, 86) and Abhyankar (87) respectively. The present problem concerns the study of the simultaneous
inclusion of Zirconium and Cerium as activators. Zirconium is a transitional heavy metal while Cerium is a rare earth element and hence interesting results are expected due to their combination.

In recent years a considerable number of doubly activated phosphors have been developed and studied. They are of two classes. One is the infrared sensitive phosphor in which the role of the secondary activator is to make possible a storage of luminescence energy by such deep traps that it can be released only by stimulation with infrared. A notable example of this type of phosphor is SrS: Ce: Sm studied by Urbach (68). The second class includes those in which a secondary activator is added for the purpose of sensitizing the emission of the primary activator. Alkaline earth sulphides containing various combinations of heavy metal and rare-earth ions were the first known examples of impurity sensitized luminescence among the inorganic phosphors. One good example of this type of phosphor is CaS: Bi: Sm phosphor for which Rothschild (50) found that the emission of Sm is enhanced at the cost of Bi emission. In addition to the above, the following possibilities
can also be expected with double activation—

(i) One of the activators may evoke or intensify
a latent emission line or band of the host crystal.

(ii) One of the two activators may introduce electron
or positive hole trapping states and may act pre-
dominantly as a poison (5).

(iii) One of the activator ions may function as a
Coactivator because of its valence state (89).

(iv) The phosphor activated with a rare earth element
may prove to be an important laser material (90).

The present work which consists of the
study of phosphorescence decay and thermolumines-
cence only forms a part of the scheme to
investigate the various possibilities mentioned
above.

The phosphors were prepared in micro-
crystalline powder form after finding out the
optimum preparative parameters such as temperature,
duration of firing, amount of flux etc. Anhydrous
Sodium Sulphate was used as flux in the preparation
of the phosphors under study as it has been found
to be very efficient in the case of CaS phosphors
by previous workers (91,92). Keeping the
optimum concentration of one activator constant,
the concentration of the second activator was varied
in different samples of the two series.

Phosphorescence decay characteristics have been studied with a view to determining the decay law and the possible effect of activators on the distribution of traps.

Thermoluminescence studies were undertaken to correlate the results obtained from the decay studies. This study was carried out from the room temperature to 500°C. The glow curves are studied at two different warming rates. Trap depths calculated from glow curves and decay curves are compared to justify the assumption of monomolecular kinetics.

An attempt is also made to determine the site of activators in the host lattice.

The variation of phosphorescence and thermoluminescence intensities with the concentration of the second activator (cerium) is studied to show the high quenching action of Cerium in CaS: Zr: Ce phosphors. Fluorescence spectra of a few samples were recorded to confirm the above effect.

Finally, taking into account the results of all these studies, an attempt has been made to
determine the change in nature of the trapping levels due to double activation in CaS : Zr : Ce (Na₂SO₄) phosphors.
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