Chapter – I

Introduction

CHAPTER 1

INTRODUCTION

Luminescence

Herschel"s observations of the Moon, the aurora light and a TV video tube all displays the phenomenon of luminescence. The term luminescence can be applied to any object that emits light in addition to the usual reflected light. The main characteristic of luminescence is that the emitted light is an attribute of the object itself, and the light emission is stimulated by some internal or external process. This process is quite different to the incandescence seen in an ordinary light bulb filament. In this case the energy from a current of electricity is transferred directly to the metal atoms of the wire. This causes them to vibrate and hence heat up. The wire can then glow white hot, as in an incandescent light bulb. A characteristic of this type of light is that it is accompanied with a great deal of heat! The electrical energy is converted into radiation with an efficiency of about 80%, but the visible light being emitted is less than 10% of the total radiation. The remaining radiation is mainly in the form of infra-red heat. The spectrum of radiation emitted from a hot wire, or any other object, is not sensitive to the attributes of the object. All hot objects emit light and heat with very similar characteristics and this is well described by models based on a generic blackbody.

Fluorescence:

Fluorescence is the emission of light take place with a characteristic time $t_c < 10^{-8}$ sec. in which emission takes place from an excited singlet state and the phosphorescence ($t_c > 10^{-8}$ s), in which emission occurs from an excited triplet state. To clarify between fluorescence and phosphorescence is to study the effect of temperature upon the decay of the luminescence Fluorescence is essentially independent of temperature; where as the decay of phosphorescence exhibits strong temperature dependence.

Several types of luminescence can be recognised. Some objects, when illuminated by light of one colour, are stimulated to emit light of another colour. This is called fluorescence A common example is the chemical residue left behind in clothes by some types of washing powders. These powders emit visible light when stimulated by invisible ultra-violet (UV) light found in sunlight Thus the clothes containing the residues appear brighter because of the combined effect of the reflected visible sunlight and the fluorescence from the washing powder residues. Another example is the chemicals that coat the inside of fluorescent tubes In these tubes the UV light comes from excited mercury vapour inside the tube. The energetic UV light excites electrons in the fluorescent chemicals which then emit visible light (with a small amount of heat) upon decaying back to their original states. The term photoluminescence is sometimes also applied to this type of luminescence which is stimulated by light of another colour.

Another example of fluorescence is in the modern machines for producing medical x-ray images. A screen that produces a lot of visible light fluorescence when irradiated with x-rays is used to form an image which can then be photographed with film sensitive to visible light This process is more sensitive than using the film to record the x-rays directly, thus minimising the dose of x-rays to the patient. The following are few important applications of fluorescence

Applications of fluorescence:

The substances emitting the luminescence are called phosphors. Some phosphors are basically semiconductor describable in terms of energy band model. These are in biological forms. They may be in micro or macro forms. Professional have examined the PL of different materials and developed many macro and microscopic luminescence based devices. The brief account of applications of fluorescence is given below.

a) **Medical application**· Fluorescence is widely used in analytical work of various compound present in cells of lever, kidney etc. The sensitivity and selectivity of PL in many micro system facilities the professionals to estimate amino acids, proteins and nucleic acid in medico-logical works.

b) **Fluorescent Microscopy**: The microscopic components of the specimen exhibit PL on the interaction with UV or blue light Fluorescence microscopes have been developed on this premise to examine and locate fine structure of such substances.

c) **Fluorescent screens.** Different luminescent materials under exposure of ionized radiations; such as invisible alpha particles, electrons, ultraviolet light etc. display visible emission of different colors. If the screen is prepared with luminescent material. It can be used to detect the presence of radiation field. This property of phosphors has been utilized in TV screen picture tubes, watch dials etc.

d) **Fluorescent Lamp**: The phosphors are pasted on inside wall of the lamp. UV light of 253nm is generated through electric display. The phosphor absorbs the UV and through fluorescence emission it converts it in visible light The light emission of the fluorescent lamp depends on nature of phosphor. Many fluorescence lamps are now available in market.

e) **Forensic Science**: PL from material is highly sensitive to nature, structure and impurity (or defect) present in the specimen. PL spectrum is as good as finger print of the specimen. Therefore, the comparison of the PL pattern of the ideal specimen with that of specimen with defect or in different condition provides lot of information These facts are utilized in forensic science to detect and prosecution of crime etc It also evaluates physico-chemical condition of the specimen. It can be used for identification of substance in forensic science.

f) **Biological Application** Plants consists of fluorescent compounds in small concentration and distributed in specific locations The examination of the fluorescence pattern of these compounds and their careful analysis leads to new technique to detect fungus in specimen, individual fluorescent chemical compound of biological origin. In addition to this it has helped to study phenomena of photosynthesis, by inspecting the variation of chloro- fluorescent at the beginning and end of period of the exposure of the plant material to light. The measurements of fluorescence polarization under various conditions led to determine the rotation and diffusion constant of proteins.

g) **Fluorescence in Chemical analysis**· If the different elements in the sample emit their characteristics lines by electron or X-ray bombardment, then these elements may be identified by analyzing the emitting radiation and showing that specific wavelengths are present, either in qualitatively or quantitatively. Measurement of coating thickness on one chemical to another can be made by studying intensity of characteristics emission from material, Chemical behavior of liquids can also be studied by fluorescence method.

h) **Luminescent Devices as radiation services**. It includes indicator lamps, data punched type reader, position indicator, optomechanical programming, recondition equipments, motor controllers, advertisements etc.

i) **Mechanical behavior of materials through Luminescence**: Luminescence is a structure sensitive phenomenon, which is very sensitive to detect pattern inside the lattice of the materials One may find out defects, patterns in host matrix by examining fluorescence spectra.

j) **Fluorometry**: In this technique, re-emitted visible emission from the material is analyzed critically, which gives informative about the material. It is very good technique. It is used in many fields (a) Impurity analysis is done through comparison of PL spectra of specimen with that of standard spectra. This technique is widely used in tablet industry in medical field (b) The detection and assessment of several fluorescing compound in the same solution is also possible. (c) Fluorometry is also useful in biology and medicine It gives idea regarding vitamin deficiency, estimation of blood, urine and concentration of hormones. In chromatographic separation, detection of Poisson and identification of strain i e. pus, blood and urine.

Phosphorescence:

In some materials, electrons excited by the original radiation can take some time to decay back to their ground states The decays can take as long as hours or days. This type of fluorescence is called phosphorescence and the material continues to emit visible light for a while after the original radiation has been switched off If the duration is very short, around 10^{-7}s,then the material is a short persistence phosphor. If it lasts for seconds or longer it is a long persistence phosphor. Objects displaying phosphorescence are some times said to be luminous. Most luminous toys, stickers and watch dials are coated with long persistence phosphors.

Electroluminescence.

Electro-luminescence is the efficient generation of light in a non-metallic solid or gas by an applied electric field or plasmas. Another type of luminescence is that produced by some crystals when an electric current passes through them. In this case the stream (current) of electrons excites electrons that occupy energy levels involved with chemical bonds inside the crystal When the excited electrons decay back to their ground states they emit visible light This is known as electroluminescence. There are several different methods of exciting electroluminescence from a crystal. In one method, AC voltages applied to special panels produces light. About 40 years ago, it was thought this sort of light would replace ordinary light bulbs for many domestic applications. This was because electroluminescent coatings could be applied to walls, ceilings, even curtains! There was also virtually no limit to the range of colours that could be produced. Unfortunately, several practical difficulties could not be overcome, such as efficiency, and that high frequency AC was required to excite the luminescence. However, the light emitting diode (LED), operating on a different principle, has now become a widely used application of electroluminescence including the mobile displays apart from LEDs.

Chemoluminescence

Chemoluminescence is produced as a result of a chemical reaction usually involving an oxidation-reduction process The most common mechanism for such an emission is the conversion of chemical energy, released in a highly exothermic reaction, into light energy. In some chemical reactions, energy can be transferred to electrons in the chemical bonds As these electrons decay down to lower excited states, they emit light Some of these reactions proceed slowly, so the light can be emitted for a considerable time This is known as chemoluminescence. This is distinct from more vigorous chemical reactions where so much heat is released that the chemicals actually catch fire or otherwise glow red hot. This is nothing more than incandescence. Chemoluminescence is displayed by a variety of organisms and the chemical reaction usually involves the oxidation of a special light producing chemical called luciferin. This is an organic molecule with two hydrogen atoms attached, symbol LH_2 With the aid of the molecule responsible for the storage of energy in cells, adenosine triphosphate (ATP) and a special catalyst molecule (the enzyme luciferase), the luciferin is oxidized to L=O in an excited state When it changes into the ground state a visible light photon is emitted One visible light photon alone is emitted as each molecule of luciferin is oxidised, so this really is light without heat The light is typically light blue in colour, although differing chemical environments can modify the colour. It is believed that this light producing process evolved as a small side branch of the main oxidation-reduction reactions that extract energy from nutrients. Some synthetic molecules, such as Luminol (5-aminophthalhydrazide used by the detectives and police to detect the traces of blood on walls after excitation with UV source) and Cyalume are the basis of commercially available chemoluminescent products. Remarkably, some of the steps that lead to the production of light from these chemicals remain to be fully understood.

Cathodoluminescence

Cathodoluminescence is due to emission of light during electron irradiation (CRO & TV Screen Phosphors).As long ago as the middle of the last century, it was observed that invisible cathode rays, produced by electrical discharges in evacuated tubes, produced light when they struck the glass walls of the tube. The modern name for cathode rays is electrons and this type of luminescence is has retained the name cathodoluminescence. This is a very useful form of luminescence Beams of electrons are used for many applications The electron microscope employs beams of electrons to produce high resolution images of small specimens In some cases, the beam produces cathodoluminescence from the specimen This is particularly useful for the study of minerals in rocks where the presence of transition metal trace elements can cause the mineral to give of a distinctive colour light. Often the presence of the trace element cannot be detected in any other way Also, the ubiquitous video display tube also employs beams of electrons to selectively excite red, green or blue phosphors to display colour images. This is such an efficient process that despite continuing revolutions in the semiconductor industry, the video display industry remains dominated by the nineteenth century technology of the video tube.

Ionoluminescence·

A most exotic method of producing luminescence is the light produced when fast ions collide with matter This is called ionoluminescence An early application of ionoluminescence was to luminous clock dials. These relied upon a rather hazardous method of making light that involved radioactivity. A radioactive material, such as radium, was mixed with a material that displays luminescence, such as zinc sulphide As the radium decays, it emits alpha particles and other radiation This excites electrons in the luminescent material to give off light. This is very handy, since the light persists indefinitely, limited only by the half-life of the radium isotope used, ^{226}Ra, which is 1600 years! However, such clock dials are dangerously radioactive. In fact in the late nineteen twenties, several workers at a luminous dial painting factory were severely injured or killed from ingesting radioactive material as a result of licking their paint brushes to get a fine brush point.

Radioluminescence (or scintillation) is produced by ionizing radiations. Some polymers contains organic molecules which emit visible light when exposed to such radiations as X-rays, gamma rays or cosmic rays, and thus act as detectors for high energy radiations.

Mechanoluminescence (triboluminescence or piezoluminescence) is due to the emission of light on applying an external mechanical energy It could be excited by cutting, cleaving, grinding, rubbing, and compressing or by impulsive deformation of solids.

Sonoluminescence is the emission of light due to the excitation by Sound waves including ultrasonic waves.

Bioluminescence is the result of certain oxidation processes (usually enzymatic) in biological systems like fireflies, jellyfishes etc ,

Lyoluminescence is the phenomenon of light emission during the dissolution of previously irradiated solids in suitable solvents

Optically Stimulated Luminescence (OSL) offers an alternative to conventional X-ray radiography, which consist of a photographic film and an intensifying screen. They adept to digital radiography systems which are based on the conversion of the X-ray image pattern into digital signals utilizing laser beam scanning of an optically stimulable imaging plate.

The Mechanism of Luminescence

The most important characteristic of luminescence is that it is an attribute of the material producing the light, and not the method used to excite it. The production of luminescence from a solid material can be understood from the band theory for solids. This is a theory based on elementary atomic physics and quantum mechanics. The theory is briefly introduced here.

An isolated atom carries its collection of electrons in electron orbitals surrounding the nucleus. These orbitals are analogous to the orbits of the planets around the Sun, although in that case gravity binds the system instead of the electromagnetic force as in an atom. The electrons can only occupy special orbits that allow them to orbit without loosing energy These allowed orbits may be determined from the laws of quantum mechanics. Also, owing to the fact that electrons can share their orbitals with at most one other electron of the opposite spin (the Pauli exclusion principle), some electrons may occupy orbitals far from the nucleus because the lower energy orbitals closer to the nucleus are already occupied.

Vacancies can be created in occupied orbitals by dislodging the electron occupant with a pulse of radiation such as from a photon, a fast electron or some other process. When this occurs, an electron from an outer level will fall down to reoccupy the inner, lower energy, level The excess energy is radiated away as a photon. For some transitions, this photon can be within the visible spectrum. A larger transition produces a higher energy photon which may be in the x-ray region Gases in discharge tubes that are bombarded by currents of electricity can display a spectrum characteristic of the transitions between the allowed energy levels in the solitary gas atoms.

In a solid, the situation is more complicated When individual atoms are joined together to make a solid, the atoms must be pushed relatively close together When this happens, the outer electron orbitals begin to overlap. Since no more than two electrons can occupy the same level, the energy levels begin to split into sub-levels. If six atoms are joined together to make a small lump of material, the orbital of the outermost electron overlaps with the adjacent atoms and splits into six to accommodate all electrons. These new orbitals are associated with the entire lump, rather than just a single atom. If millions of atoms are joined together to make a sizable lump of material, the outer orbitals overlap and split into millions of sub-levels, all with slightly differing energies. In practice, the energy levels are so close together, and there are so many of them, we can speak of the orbital now consisting of an energy band.

On a small scale, the solid consists of a crystal with all atoms occupying lattice sites. Some normal solids, of interest here, consist of large assemblages of microscopic crystals. The luminescent properties of the solid depends on the properties of the crystal structure.

The formation of energy bands occurs regardless if the energy levels are occupied by electrons or not. Therefore, in a typical material, the outermost electrons occupy a band called the valence band, above which is the next higher energy band called the conduction band. The energy difference between the highest energy (top) of the valence band and the lowest energy (bottom) of the conduction band is called the band gap energy

If the valence band is completely full of electrons, the material is an insulator, since to conduct electricity the electrons must pick up energy and move to a slightly higher level. Since all available levels in the valence band are full, they cannot do this, and the material is an insulator. Of course a really vigorous shall can displace an electron into the unoccupied conduction band, but the energy required to do this is greater than normally associated with the flow of electric currents.

If the valence band is only partially occupied, then the material is an electrical conductor since there are free energy levels available for the electrons to carry the electric current. Owing to the fact that the valence band is formed from the outermost occupied orbitals of the atoms, which can contain either one electron or two electrons of opposite spins, the valence band in any material is always either entirely full (insulators), or just half full (conductors).

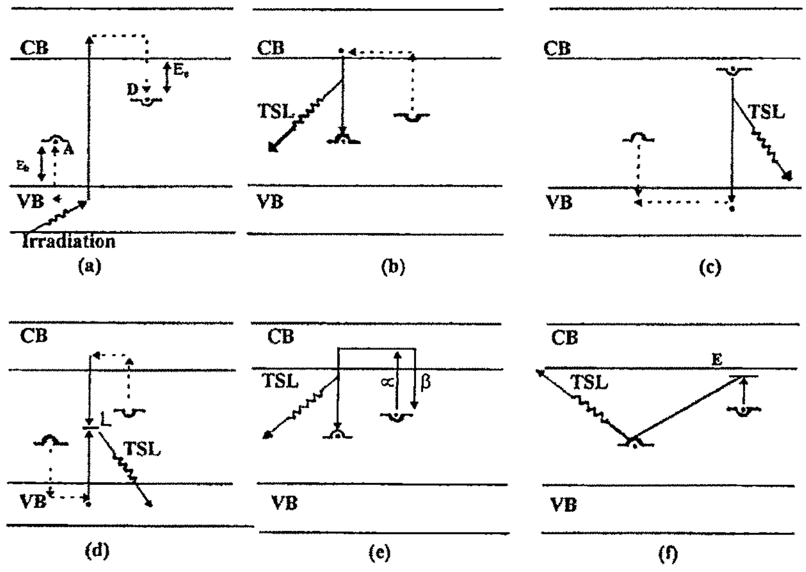


Fig 1.1 Processes involved in radiation induced electron/hole trapping and subsequent recombination on thermal stimulation with associated luminescence emission

VB- Valence band,

CB - Conduction band,

Eh - Trap depth for hole,

Ee - Trap depth for electron,

L - Luminescent center, A - Hole trap and D - Electron trap.

(a) On y - irradiation, electrons and holes are produced and trapped at electron- hole traps.
(b) On thermal stimulation, trapped e is released and recombines at trapped hole site.
(c) e-h recombination at trapped electron site
(d) e-h recombination at luminescent center site.
(e) Process of de trapping and re trapping(second order kinetics, a – de trapping probability and p- re trapping probability) ;
(f) e-h recombination via an excited state 'E' and tunneling.

In some materials, the gap between the fully occupied valence band and the empty conduction band is very narrow. So narrow in fact that ordinary heat energy at room temperature can promote electrons from the valence band into the conduction band. Such materials are called semiconductors. These are generally poor conductors compared to metals

When any solid material is excited by energetic radiation, electrons can be excited out of the valence band into the conduction band. This leaves behind a hole in the valence band The electron in the conduction band can dissipate excess energy as small amounts of heat until it reaches the lowest energy (bottom) edge of the conduction band. It can then fall back into the hole in the valence band, radiating the energy difference as a photon.

Doping:

It is known fact that few materials have band gaps where the width corresponds to the visible spectrum However, materials with a relatively wide band gap can be made to luminesce in the visible. This is possible by the addition of different atoms or creating imperfections in the crystal. The additional atoms, called dopants have a different electron orbital structure compared to the host crystal lattice. Therefore, in regions of the crystal around the dopant atom, additional energy levels are available. That is, within the forbidden band gap of the material, energy levels can exist they can accommodate electrons or holes These levels can be close to the conduction band, in which case the dopant is called a donor, or close to the valence band, in which case it is called an acceptor. Transitions between these levels can give rise to visible luminescence in which case the dopant is known as an activator In most cases, the activator is present in extremely small concentrations, ranging from as much as 1 dopant atom in 5000 host atoms down to as little as 1 dopant atom in 5 billion host atoms!

The phosphors in vacuum tube video display tubes are the phosphors formed from activators For example, ZnS doped with silver (Ag) or chlorine (Cl) produces blue light, ZnS doped with copper (Cu) or aluminium (Al) produces green light and Y_2O_3 S doped with europium (Eu) produces red light Transition metals like Ag and Cu have partially-filled 3d outer shells which make transitions highly sensitive to the surrounding crystal field. The resulting luminescence spectrum is a broad, featureless shape. On the other hand, rare earth metals like Eu have an unfilled 4f shell which is shielded from the surrounding crystal field by a filled 5s,p,d outer shell. Consequently the transitions which occur at rare earth metal impurities are sharp.

Sometimes the excited electron can find other ways to dissipate its energy Several non-radiative recombination mechanisms are possible. These are usually associated with defects in the crystal, or levels in the middle of the band gap, called deep levels, introduced by impurities called inhibitors. Still other defects in the crystal can result in shallow levels which are close to the edge of either the valence or conduction bands. Shallow levels in the band gap can trap the excited electrons. Certain characteristics of these shallow level prevent the electron from decaying immediately back into the valence band Instead the decay may only occur spontaneously after a very long time. However a small amount of heat may dislodge the electron back into the conduction band from where it can readily decay back to the valence band This is the mechanism behind the technique of thermoluminescence. Such materials can be dated by measuring how much light they produce when heated. This measures the remaining electrons trapped in the shallow levels and hence how long is has been since the original excitation promoted the electrons.

Luminescence is the emission of optical radiation (infrared, visible, or ultraviolet light) by matter. This phenomenon is to be distinguished as incandescence, which is the emission of radiation by a substance by virtue of its being at a high temperature (>5000°C black body radiation). Luminescence can occur in a wide variety of materials and under many different physical conditions. Thus, atoms, polymers, organo metallic molecules, organic or inorganic crystals, and amorphous substances all emit luminescence under appropriate conditions. The production of light in this manner is called Photoluminescence because activation of luminescence is provided by absorption of a photon The various luminescence phenomena are given their names, on the basis of radiation used to excite the material t get the emission.

Thermoluminescence (TL) or Thermally Stimulated Luminescence (TSL): TL or more specifically Thermally Stimulated Luminescence (TSL) is activated thermally after initial irradiation given to a phosphor by some other means. (∝- rays, β -rays, γ - rays, UV rays and X-rays). Thermally stimulated luminescence is (TSL) the phenomenon of emission of light from a solid which has been previously exposed to ionizing radiation under conditions of increasing temperature. Unlike other luminescence process such as Electroluminescence, Chemiluminescence, here heat is not an exciting agent, but it acts only as a stimulant. Hence it is better known as thermally stimulated luminescence (TSL). Excitation is achieved by any conventional sources like ionizing radiation, ∝ rays, β rays, γ rays and UV rays and X-rays. TSL is exhibited by a host of materials, glasses, ceramics, plastics and some organic solids. By far insulating solids doped with suitable chemical impurities, termed as activator, are the most sensitive TL materials. The band theory of solids is normally used to explain this phenomenon. When a solid is irradiated, electrons and holes are produced which are trapped at defect sites. When the solid is heated, these trapped electrons/holes get enough thermal energy to escape from the trap to the conduction band (or valance band). From here they may get re-trapped again or may recombine with trapped holes/electrons. The site of recombination is called recombination center. If this recombination is radiative, then center is called luminescence center. Alternatively a trapped hole can be released by heating which can recombine with a trapped electron resulting in luminescence. These features are shown diagrammatically in **Fig.1.1.** It is not required that all charge recombinations should result in luminescence. They can be no radiative too. The plot between the intensity of emitted light (y-axis) versus the temperature (x-axis) is known as TL glow curve. A glow curve may exhibit one or many peaks depending upon the number of electron/hole traps with different trap depths, present in the lattice. These peaks may or may not be well separated. The position, shape and intensity of the glow peaks therefore are characteristic of the specific material and the concentration of impurities and defects presents Therefore each TSL peak corresponds to the release of an electron (or hole) from a particular trap level within the band gap of the material The nature of the TL glow peaks gives information about the luminescent centers present in the material. It may be mentioned that TSL is highly sensitive to structural imperfections in crystals Defects densities as low as 10^7/ cm^3 also can give measurable. EPR and OAS are sensitive only for relatively higher defect concentrations such as 10^{12}/ cm^3. The first step towards understanding the mechanism for TSL glow peaks is the identification of the trapping center and the recombination centers for the observed light emission. Apart from being a tool for the study of defects in solids, TSL has also found widespread applications in radiation dosimetry, archeological dating of pottery, ceramics, minerals, geochronology and also meteorite research

Basic concept of Thermoluminescence [TL OR TSL]:

Thermally stimulated luminescence (TSL) is the phenomenon of light emission during warming a previously irradiated substance with uniform heating rate. When a material is exposed to ionizing radiation like, alpha, beta, gamma and X-rays or UV-rays or when it undergoes certain chemical reactions or mechanical stress, a certain percentage of the liberated charge carriers (electron and holes) maybe trapped at certain imperfections in the lattice, which are called traps If these traps are deep enough, the charge carriers remain trapped for a long time [thousands of years] before they are released by sufficient stimulation. This stimulation can be achieved by supply of optical or thermal energy to these excited solids

The return of these trapped charge carriers to a stable state due to the stimulation by external energy (e g. heat) is always associated with the release of absorbed energy (by the charge carriers), mostly in the form of heat. A small fraction of the absorbed energy is also released in the form of light during this process This form of emission of light is called Thermoluminescence (TL). The TL from the material is very sensitive to;

i) The amount and nature of impurity,
ii) Thermal history,
iii) Pre-thermal, mechanical and radiation effect,
iv) Size of material particle,
v) Crystallization history and
vi) Defect pattern present in the material

Theory demands that no electron can exist in the material with energy states falling in the forbidden gap When the material is excited by any ionizing radiations (fig.1 1 a) some electrons (originally in the valance band) are excited and they attain energy states corresponding to the conduction band. Normally, these electrons cannot remain excited indefinitely, that is the lifetime of an electron in the conduction band is very short and the electron attains its ground state immediately giving away the energy to warm up the crystal lattice or in the form of light.

However, an impurity atom (with an appropriate ionic size and charge) present in the material can have energy states in the forbidden band. These are the metastable energy states having appreciable lifetime An excited electron can find itself in this state, rather than getting back to its normal valence band state. Now, one says an electron is 'trapped'. In analogy, it is also visualized that a 'hole' (absence of an electron) is trapped at an energy state very close to the valence band. Depending upon the energy level of the electron trap with respect to the conduction band (or the hole trap with respect to the valence band) called the trap depth, the electron may remain trapped for a definite period, the greater will be the lifetime of the electron in the trapped state for a given (low) temperature

This stage corresponds to a energy storage after the initial excitation of a material .If now the material is warmed, the heat is supplied is able to stimulate the electron out of the traps (de-trapping) and the electrons return to the ground state, if the conditions are favorable (for example, the particular atom has a light emitting property) for the emission of light in this 'return process' then thermoluminescence occurs (fig 1.1 b) Alternatively, a hole may be excited into the valence band where it wanders until it combines with an electron at the trapped counter- part emitting the TSL [Fig 1.1c]

If the traps are not very deep, de-trapping and recombination may already occur at a substantial rate around room temperature resulting in a short half-life of the stored energy This is called phosphorescence but strictly speaking it is thermoluminescence at the room temperature. Only, if the traps are the deep enough i e sufficient storage stability at room temperature (half-lives of trapped electrons at least several months normally corresponding to glow peak temperature greater than about 150°C), the effect becomes of dosimetric interest .The glow curve generally exhibits many peaks, each corresponding to a trap with a different energy depth.

In many phosphors it is possible that the electrons and holes are de-trapped more or less simultaneously and they recombine at an entirely new site (fig.1.1d) called luminescence center or recombination center The TL glow curve will in this case represent an effective thermal activation energy needed by the trapped electron / hole to surmount a potential barrier between the trap and recombination center In reality, a trapped charge when de-trapped has a finite probability of getting re-trapped as in fig 1.1e When this re-trapping probability is significant, the shape of the glow curve is different from the case when it is absent Also the recombination probability for the de-trapped charge carrier may in most cases charge with time (i e. as the heating proceeds) depending on the number of available unused recombination centers. Such a process is called a second order or bimolecular process usually while the simplest case where the recombination has a constant probability with time, is called a first order or monomolecular process. There are also practical situations where the de-trapped charge carriers recombine directly without having to be excited into the conduction / valence bands. This is a, case of TL involving isolated luminescence center and process follows first order kinematics (fig 1.1f) All the foregoing discussions take into account only the ionization effects of the excitation irradiation, one should not however forget about the displacement effects resulting from elastic/inelastic collisions of the atom of the phosphors with the impinging radiation. This effect is more significant for the case of particular radiations (like alpha, beta, gamma, neutron, cosmic rays). The important thing about this displacement effect is that atoms are physically moved which results in the creation of interstitials, and vacancies. In relation to thermoluminescence, these constitute defects, which have potential to influence the trapping and emission processes.

Configuration co-ordination curve Model:

Luminescence in atomic gases is adequately described by the concept of atomic spectroscopy, but luminescence in molecular gases, in liquids and in solid introduced two major new effects, which need special explanation. One is that the emission band appears on the long wavelength (low energy) side of the absorption band, the other is that emission and absorption often show as bands hundreds of angstroms wide instead of as the line found in atomic gases Both of these effects may be explained by using the concept of configuration co-ordinate curves shown in Fig 1 2. As in the case of atomic gases the ground and excited states represent different electronic states of the luminescence centers, that is the region containing the atoms or electrons or both involve in the luminescent transition

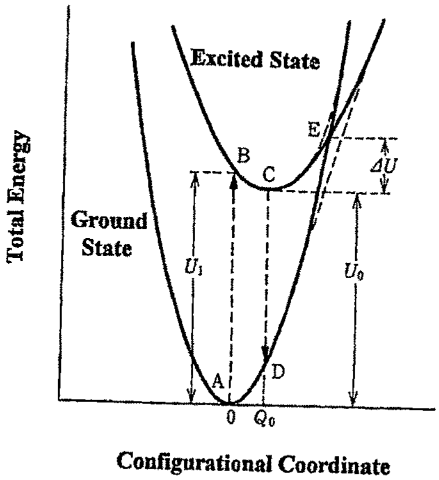


Figure 1.2 A schematic illustration of a configurational coordinate model. The two curves are modified by repulsion near the intersection (broken lines). The vertical broken lines A to B, B to A and C to D and D to C indicate the absorption and emission of light, respectively.

On these curves energy of the ground and excited states is shown to vary parabolically as some configuration co-ordinate, usually from the luminescent center to its nearest neighbors There is a value of the co-ordinate for which the energy is a minimum but this value is different for the ground and excited states because of the different interactions of the luminescent center with its neighbors. Absorption of light gives rise to the transition from A to B This transition occurs so rapidly that the ions around the luminescent center do not have time to rearrange. Once the system is at B it gives up energy to its surroundings by means of lattice vibrations and reaches a new equilibrium position at C Emission occurs when the system makes the transition from C to D and once again heat energy is given up when the system goes from D back down to A This loss of energy in the form of heat causes the energy associated with the emission C to D to be less than that associated with the absorption A to B.

When the system is at an equilibrium position, such as C of the excited curve it is not at rest but migrates over a small region around C because of the thermal energy of the system At the higher temperatures these fluctuations cover a wider range of the configuration co-ordinate As a result of emission transition is not just to point D on the ground state curve but covers a region around D In the vicinity of D the ground state curve shows a rapid change of energy, so that even a small range of values for the configuration co-ordinates leads to a large range of energies in the optical transition.

This explains the broad emission and absorption bands that are observed. An analysis of this sort predicts that the widths of the band (usually measured in energy units between the points at which the emission or absorption is half its maximum value) should vary as the square root of the temperature .For many systems this relationship is valid for temperatures near and above room temperature

Two other phenomena, which can be explained on the basis of the model described in fig. 1.2, are temperature quenching of luminescence and the variation of decay time of luminescence with temperature. On the scheme of fig 1 2 this is interpreted as meaning that the thermal vibrations become sufficiently intense to raise the system to point E From point E the system can fall to the ground state by emitting a small amount of heat or infrared radiation If point E is at an energy EQ above the minimum of the excited state curve, it may be shown that the efficiency 'η' of luminescence is given by equation 1

$$\eta = 1+C\ \exp^{(-EQ/KT)} \ldots\ldots\ \ldots\ \ldots\ldots\ .\ .(1)$$

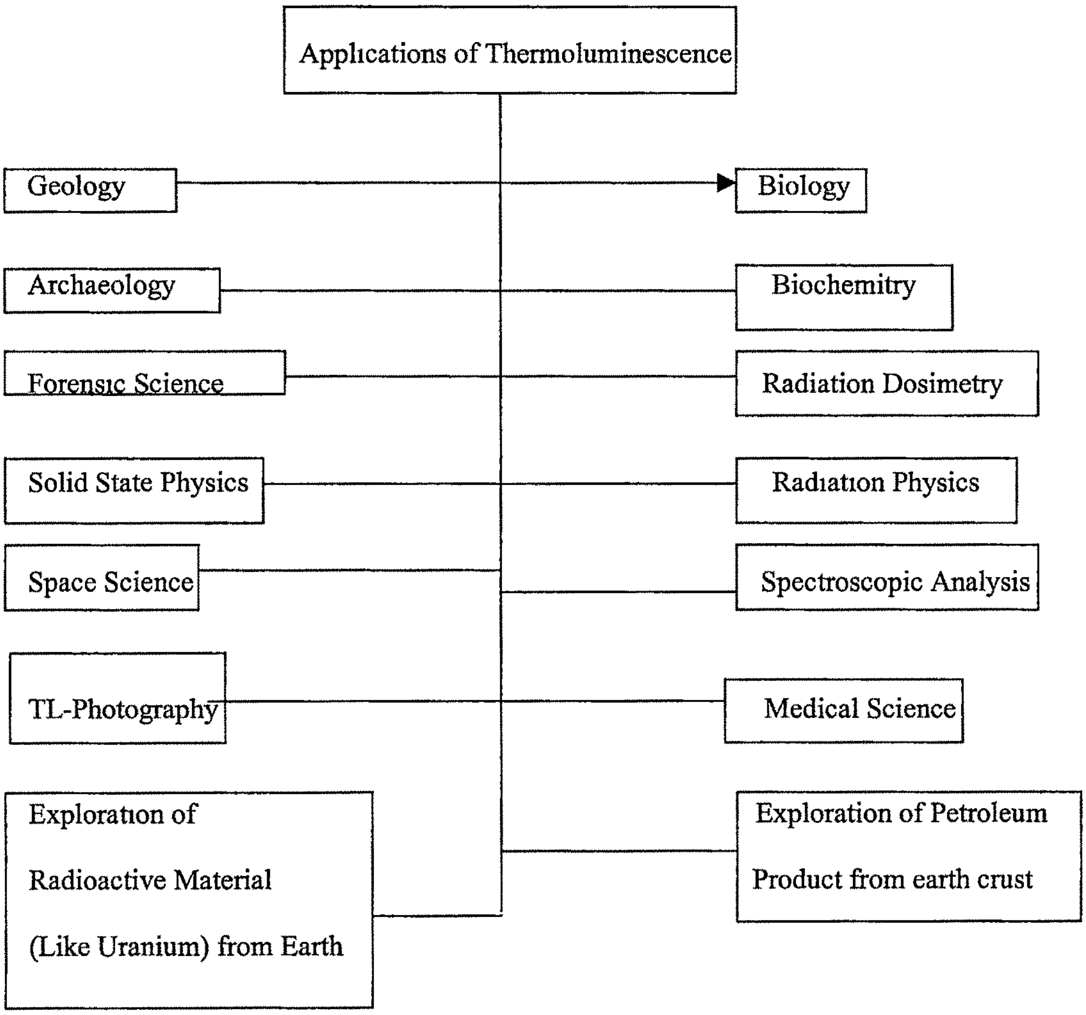
where C is a constant, K is Boltzman constant and T is the temperature on the Kelvin scale.

The temperature quenching tends to occur most strongly for centers that would have stayed in the excited state for a relatively long period of time. As a result, the decay time of the emission that occurs in this temperature region is largely characteristic of centers in which transitions to the ground state have been rapid, therefore, the decay time of the luminescence is observed to decrease

Application of Thermoluminescence:

The phenomenon of TL has been extensively studied by many investigators. The understanding of the mechanism of occurrence of thermally stimulated emission is the important field of fundamental research. Many researchers have suggested their views for TL mechanism for pure and impurity activated materials. With expanding knowledge of solid state physics, it is a matter of search to give latest approximate mechanism of TL. However, the present understanding of TL has explored very high application potential of it in various fields. The modernization and development in the instrumentation, and better understanding of TL have helped the professional to solve their problems in many fields The applications of the TL are summarized in the chart A.

Chart-A



Biology and Biochemistry. Application of TL technique in the study of biological and biochemical systems is increasingly favoured in recent years. The attempts have been successful in the study of hydroxy and aminobenzoic acids, proteins, nucleic acids, plant leaves, algae and bacteria The TL results could indicate the proper stability of the orthoform of the benzoic acid, the inter and intra molecular transfer of radiation damage in nucleic acids, proteins and their constituents could be correlated with their TL behavior; the photosynthetic electron transport routes could be correlated with TL and additional routes delineated and the interaction between salts and proteins could be understood from the TL patterns

Forensic science:

The major study in forensic sciences is to evolve and standardizes methods to compare evidentiary materials with similar materials of known origin, which are invariably available only in minute quantities and are required to be analyzed nondestructively for evidence purposes. Thermoluminescence can offer an attractive technique in selected materials that are commonly encountered in the criminal cases viz; glass, soil, safe insulation, etc . This can be used as an exclusionary evidence i.e. when the TL characteristics do not match it can be said with certainty that a particular sample has not come from a known source To reduced the probability of any coincidental matching and improve the confidence of the TL measurements whose signal to noise ratio may be bad, examination may be made of the TL glow curves from the virgin samples as well as after a heavy artificial gamma or X-ray irradiation and also of the emission spectra.

Quality control in Industry :

As early as 1938, the application of TL in the control of feldspars in ceramic products has been described. The amount of TL given out by a ceramic after artificial irradiation is directly indicative of its feldspars contains at trace levels where any other type of quantitative analysis is time consuming. Thus in ceramic industry where a particular process is repeated many number of times to produce batches of the some materials, any controllable variations in the feldspars contents can be checked quickly and efficiently

The efficiency of certain surface catalyst like Al_2O_3 can be quickly and efficiently evaluated by their TL sensitivities The lattice defects which permit the adsorption reactions might also play a role in the TL emitted by these substances and the nature and intensity of TL may be gainfully correlated with the catalytic activity. The TL glow curve in such a case could be used as criterion in controlling the preparative parameters of a desired catalyst In principle, TL method could be employed in the quality control of many of the glass, ceramics and semiconductor products; recently it has been shown in the case of textile fibers that the low temperature TL glow curve changes can be correlated with the structure differences and / or chemical tracer impurities. However these have not yet received the attention of the industries.

Archaeology:

Thermoluminescence technique has been found to be highly successful in dating ancient pottery samples This method is suitable because of the following reasons

1. It gives the exact date of kiln firings of the sample (the other methods mostly depends on the shape and style of the pottery and hence correlate with the civilization to which it belonged)
2. TL dating is possible even beyond 30,000 years, but minimum age is 50 years with an accuracy of +1 or -1 year
3. Authentication and detection of forgery can be quickly and easily done by using this method .

The dating is done by reading the TL-output from pottery sherds. The TL from the specimen is mostly due to TL sensitive mineral inclusions (mostly quartz) in the host clay matrix of the pottery. The technique of the dating pottery is very much similar to that done in geological samples. In archaeology, a more precise and definite event is the basis – the kiln firing The pottery must have fired in the kiln some time in the long past. That event is considered to be the starting of the 'TL clock ' for archaeological dating. Whatever TL has been stored earlier in the mineral inclusion due to internal and external irradiations over the geological times (since crystallization) is considered to be erased during the kiln firing.

After the on set of the 'TL clock' (kiln firing) the pottery starts building up TL due to internal irradiation from radioactive emanation of uranium (U), thorium (Th), and potassium (K), contents in the clay and external radiations from the cosmic background at the excavation site. Typically the total irradiation rate is of the order of 1 rad per year of which the major part is from internal radiations and the remaining due to soil irradiation and cosmic rays. Once an accumulated TL in the specimen has been measured and express in terms of absorbed dose by proper calibration techniques and if the total irradiation rate for the specimen could be established, the archaeological age can be obtained by simply dividing the former by the latter

$$\text{i.e Age} = \frac{\text{Accumulated dose}}{\text{Annual dose rate}}$$

But in practice many complicating factors come in the way of evaluating the age.

Geology:

Geology is one of the earliest disciplines to accept the TL technique in its fold in a variety of applications, such as dating of mineralization, igneous activities, sedimentation and evaluation of growth rate of beaches and sand dunes

The TL technique has been found useful in dating specimens of geologically recent origin where all other conventional methods fail. In a geological specimen, the TL would starts building up from the time of its crystallization and would normally continue throughout its existence due to the radioactivity present within the minerals and in the surrounding materials, till its saturates. If one selects a material with a negligible radioactivity in it (e.g. quartz) the accumulated TL mostly represents the environmental dose rate at a place from where the geological specimen was collected, it is easy to calculate age of the sample as:

TL Age = Dose to produced a TL, equivalent to the natural TL in a sample

Accumulation of TL can be affected by natural light especially its ultraviolet component. In geology the sun light bleaching is consider to be the basis for dating the geological event. The exposure of sand grains to sun light during their weathering and transport through wind and water results in bleaching of their geological TL This bleaching is effective enough to reduced thermoluminescence level to a negligible value. These bleached sand particles, once embedded in a sand dune or bleach, get shielded from further exposure to sunlight. This helps particles to acquire more TL due to radiations exposure from their new environment within the sand dune or on the seashore. At present using single grain technique age of geological samples can be estimated up to 50 million years with an accuracy of ±5%

Radiation Dosimetry:

In the present scientific world Ionizing radiations have been found very useful in nuclear engineering, medicine, science and technology. Professionals used them at every walk of life In all the applications, the exact amount of absorption of radiation energy in the exposed material is important factor to get the desired results. The better use can be achieved mostly by accurate determination of energy absorbed from the radiation field and its possible distribution of this absorbed energy within the material Measurements of these quantities form the basis of radiation dosimetry and systems used for this purpose are referred as dosimeters. Scientists have worked in this direction, investigated and standardized many analytical methods to estimate the doses of radiations. The important techniques developed and employed are as under;

1. Fluorescence technique
2. Lyoluminescence method
3. Diffused reflectance technique
4. Thermally stimulated luminescence dosimetry [TLD]
5. Optically stimulated luminescence [OSL]
6. Electron paramagnetic resonance technique [EPR dosimetry]

The main basis in the Thermoluminescence Dosimetry (TLD) is that TL output is directly proportional to the radiation dose received by the phosphor and hence provides the means of estimating unknown irradiations Also, TL can provide a perfect passive measurement i e integrated irradiation levels over extended periods of the order of even years. Thus, it finds immense use in the monitoring of doses received by radiation workers on a routine basis; weakly/ monthly /yearly depending upon whatever a situation many warrant. It should however be borne in mind that most of the TL phosphors are not tissue equivalent (in terms of energy absorption by irradiation) and hence the relevant dose which is medically significant to a radiation worker from protection point of view is not readily obtained

The application potential of TL-dosimeter is very high. They have been found very useful in many fields on account of several favorable characteristics such as high sensitivity, small size, ability to cover wide range of exposure / dose, reusability, insensitive to environmental conditions. In the past professionals had used the film badge technique.

Later on they found that TLD technique is better for many reasons. And hence during last three to four decades many TLDs are developed and established the TL technique. This became popular now-a-days prominent applications of thermoluminescence dosimetry and radiation protection including the personal monitoring of radiation workers.

On account of their ability to integrate over long periods of time and measure very low exposure, they have been widely employed for environmental monitoring of doses of the order of a few micro GRAY. The TLDs have been employed in protection monitoring for measurement such as leakage radiation levels on and around source containers, air sealter measurement around open top installations, area monitoring around radiation installations etc. Rapid fading of certain phosphors such as CaSO4: Dy has been employed for the estimation of time of exposure after irradiation.

It has been found that this technique can also detect and assess the thermal and fast neutron doses Since TL phosphors insensitive to thermal neutrons are also available, combination of dosimeters can be employed for estimation of gamma and thermal neutron dose in mixed field. If UV dosimeter has sensitivity close to the thermal response of the human skin, it would provide a measure of the thermally effective value of the UV energy. On the other hand TLDs can also find useful in agriculture.

Lamps and Phosphors:

Since the birth of the incandescent lamps more than a century ago, several new lamps have been developed. Many of them are discharge lamps with far higher efficacies (lumen per watt) than the incandescent lamps. Different lamps have different possibility with regard to wattage, efficacy size, performance and color temperature. The word "Phosphor" was invented in the early 17th century with the discovery of the " Bolognian stone" in Italy. This sintered stone was observed emitting red light in the dark after exposure to sun light. Similar finding were reported from many places in Europe and these light emitting stones were named phosphors, means, " light bearer " in Greek The word Phosphorescence was derived from the word phosphor, which means light emission from a substance after the exciting radiation has ceased

The word fluorescence was introduced to denote the imperceptible short after glow of material after the excitation. In 1888, a German physicist Eilhardt Wiedemann first used the word "luminescence" which includes both fluorescence and phosphorescence. This word originates from the Latin word " lumen " which means light.

Phosphor Research Past and Present:

Research and Technology in phosphors requires a unique combination of interdisciplinary methods and techniques. Synthesis and preparation of inorganic phosphors are based on physical and inorganic chemistry. Luminescence mechanism are interpreted and elucidated on the basis of solid-state physics The research and development of major applications of phosphors belongs to the field of illuminating engineering, electronics and image engineering. Research on phosphors has a long history. Prototype phosphor ZnS phosphor for TV tube was first prepared by Theodore Sidot a young French chemist in 1886. This marked the beginning of scientific research, and synthesis of phosphors.

In early 20th century Leonard and co-workers in Germany performed active and extensive research on the phosphors. They prepared various kinds of phosphors based on alkaline earth chalcogenides and investigated their luminescence properties. Early lamp phosphors were natural fluorescing minerals, e g Willemite, Mn-activated Zinc orthosilicate, that were grinded to a powder and empirically blended together so as to obtain an approximately white field from fluorescent lamp. P.W Pohl and co-workers in Germany investigated Tl^+ activated alkali halide phosphors in details in the late 1920s and 1930s. A major turning point follows the development in 1940s with synthesis of Sb-Mn co-activated halophosphate phosphors. In a single material blue emission from the Sb^{3+} activator and the orange emission from Mn^{2+} co-activator can be adjusted such that they can produce white field corresponding to wide range of color temperature

Homboltz and co-workers at Radio corporation of America (RCA) also investigated many phosphor for application in TV tubes Their achievements are compiled in Leverenz's book. Data on the emission spectra in the book remains useful even today. After World War II, the advances in the optical spectroscopy of solids, especially those of transition metal ions help to evolve research on phosphor and solid state luminescence. In 1960 efficient rare earth activated phosphors were developed for use in color TV (Tb^{3+}- green, Eu^{3+} -red and Dy^{3+} -yellow) In 1970 tricolor lamp was introduced. Blue emission from Eu^{2+}, red emission from Eu^{3+} and green emission from Ce^{3+} - Tb^{3+} pair was used in tricolor lamp. At present a combination of halophosphate and tri-band phosphor blend is used in many lamps as a compromise between performance, phosphor cost and the lamp making cost. In phosphor area today top priority is the replacement of the high performance, but very expensive rare earth activated phosphors with good performance in expensive materials. This essentially means replacing the rare earth ions with transition metal ions or post transition ions. Now a days phosphors are used in various fields. The applications of phosphors can be classified as follows. Recently Dr. Murthy enlists the Phosphor available globally. Tables **I-VII** contain the phosphors available globally for different applications.

1. Light sources represented by various types of fluorescent lamps.
2. Display devices represented by CRTs and PDPs.
3. Detector systems represented by X-ray screens and scintillators.
4. Other simple applications such as luminous pain with long persistent phosphorescence

The fluorescent lamp is widely used as energy efficient light source, which has gone through various essential stages of development such as gas filling krypton instead of argon and the use of highly efficient phosphor coating. Compact fluorescence lamps are now replacing GLS lamps and have 8 times life than that of GLS lamps is 5 times more efficient.

Table-III: Miscellaneous Application Phosphors

Chemical Composition	Emission Peak (nm)	Emission Color	Decay	Application
ZnS: Mn	585	Orange	M	D.C.Thin-Film Electroluminescent Display Panels
ZnS : Cu	516	Green	VL	Phosphorescent Paints, Phosphorescent Plastics
CdS:Cu				Photoconductors

Table-IV : Vacuum Fluorescent Display Phosphors, Excitation Cathode Ray, UV 254nm & 365 nm

Chemical Composition	Emission Peak(nm)	Emission Color	Color Point X	Y	Decay
ZnO :Zn	505	Green	0 250	0.440	VS
ZnS: Ag+ In_2O_3	450	Blue	0.147	0.063	S
ZnS: [Zn] + In_2O_3	460	Blue	0.150	0.170	S
ZnS: Cu, Al +In_2O_3	530	Yellowish Green	0 280	0.625	S
(Zn, Cd) S: Ag+In_2O_3	545	Greenish Green	0.388	0.567	S
(Zn, Cd) S: Ag+I_2O_3	570	Greenish Yellow	0.465	0.519	S
(Zn, Cd) S: Ag+In_2O_3	595	Yellowish Green	0.535	0.457	S
(Zn, Cd) S: Ag+In_2O_3	620	Orange	0.594	0.403	S
(Zn, Cd) S· Ag+In_2O_3	655	Reddish Orange	0.627	0.371	S

Table-V: Monochrome Display & other Ray Tube Phosphors

Chemical Composition	Emission Peak (nm)	Emission Color	Color Point		Decay	Application
			X	Y		
Zn2 SiO4 :Mn	525	Yellowish Green	0.205	0.715	M	Display Tubes
ZnS:Ag + (Zn, Cd) S: Cu, Al	450, 560	White	0.251	0.291	S	Black and White Picture Tubes
ZnS: Ag	435	Bluish Violet	0.151	0.053	S	Radar Tubes
(Zn, CD) S: Cu	530-560	Greenish Yellow	0.406	0.522	M	Ditto
ZnS: Ag	450	Blue	0.147	0.098	S	Oscilloscope Tubes
Zn_3 $(PO4)_2$: Mn	636	Red	0.655	0.343	L	Low Repetition Rate Display Tubes
ZnS :Cu	530	Green	0.265	0.558	S	Display Tubes
Zn_2SiO_4 :Mn	525	Yellowish Green	0.205	0.714	L	Low Repetition Rate Display Tubes
ZnS :Ag + (Zn,Cd) S :Cu	440,555	White	0.216	0.208	M	Ditto
ZnS : Cu + Zn_2 SiO_4 : Mn	520	Green	0.225	0.660	M	Low Repetition Rate Display Tubes
Gd_2O_2S:Tb	544	Yellowish Green	0.334	0.561	M	Display Tubes
YO_2S:Tb	418,544	White	0.231	0.246	S	Ditto
$Y_3Al_5O_{12}$:Ce	535	Green Yellow	0.402	0.557	VS	Flying Spot Scanner Tubes, display tubes
Y_2SiO_5 :Ce	410	Purplish Blue	0.169	0.109	VS	Ditto
Zn, Cd) S: Ag	530-560	Yellowish Green	0.266	0.576	S	Image Tubes
ZnS :Cu, Al	530	Yellowish Green	0.282	0.620	S	Ditto
Y_2O_2S: Tb	544	Yellowish Green	0.339	0.570	M	Display Tubes
ZnS:Ag, Cu, Ga, Cl	448	Blue	0.148	0.055	M	Ditto

Table-VI : Plasma Display Panel Phosphors under Vacuum UV 146 nm Excitation

Chemical Composition	Emission Peak (nm)	Emission Colour	Decay time (ms)	Color Point		Specific Gravity
(Ba, Eu) $MgAl_{10}O_{17}$	454	Blue	<1	0.145	0.077	3.8
$(Zn, Mn)_2$ SiO_4	525	Green	14	0.233	0.702	4.2
$BaAl_{12}O_{19}$:Mn	517	Green	14	0.174	0.737	3.7
Ba, Sr, Mg) O. Al_2O_3 Mn	515	Green	14	0.145	0.747	3.7
(Y, Gd, Eu) BO_3	611	Red	11	0.641	0.356	5.1
$(Y, Gd, Eu)_2$ O_3	611	Red	4	0.642	0.344	5.1

Table- VII: Lamp Phosphors: Excitation & Emission UV – 254 nm & 365 nm

Chemical Composition	Emission Peak (nm)	Emission Color	Application
$(Sr, Ca, Ba, Mg)_{10}$ $(PO_4)_6Cl_2$:Eu	448	Blue	Tri- color Fluorescent Lamps (TcFL)
Sr_{10} (PO4)6Cl_2: Eu	447	Blue	TcFL
(Ba,Sr, Eu) (Mg, Mn) $Al_{10}O_{17}$	455,513	Blue	TcFL
(Ba, Eu) Mg, Mn) $_{10}O_{17}$	449	Blue	TcFL
$LaPO_4$:Ce, Tb	543	Yellowish Green	TcFL
Y_2O_3Eu	611	Red	TcFL
Zn_2SiO_4 :Mn	525	Green	Fluorescent Lamps
YVO_4 : Eu	620	Red	High – pressure mercury vapor Lamps

Decay of Luminescence is described by the following classification concerning time to decay to 10% of steady state brightness.

VS :Less than I µsec. S :1 µ sec. ~1msec, M:1 msec. ~ 30 msec.L:30 msec. ~1 , sec., VL:1 sec. or over

Fluorescent powder is used in discharge lamps to convert the ultraviolet radiation into useful visible radiation The powder increases the luminous flux and also changes the color rendition index of the lamp. Quantum of powder used in a lamp depends on the type of lamp. For example in popular 4ft fluorescent lamp, 4 -5 gm of powder is used. If the phosphors grain size is 4 -5 microns and 7-8 grams if the phosphors having a grain size of 10 around microns where as in 125 W high-pressure mercury vapor lamp it is in the range of 0.5. In some cases, these powders are also used to reduce glare produced by the lamp.

The most popular powder used in India is cool day light halo phosphate powder. This phosphor is being used by the industry since its introduction in the 1940's. The quality of the phosphor has improved substantially since it was introduced **Fig1.3** This powder manufactured to give color temperature of 6500 ° K and fairly good CRI (in the range of 70) Lamp manufacturer look forward to a technology where in minimum quantity of powder is used without sacrificing the visual appearance and light output of the lamps. Average particle size and particle size distribution plays a major roll in coating process. Fine powder gives more silky finish to the lamps and narrow particle size distribution gives uniformity of the coating along the full length. Fine particle size powders are in the range of 4 -5 microns and coarser powders are above 10 microns. Lamp manufacturer prefer fine powders because these powders need not be milled and have more area coverage per gram of powder used. Another important parameter is the fluorescence yield, which is indirectly measure as the light output or luminous flux. Finer powders tend to give better light output. The trend is now changing with better technology adopted by powder manufacturer has to declare the color temperature and also sometimes CRI. Therefore, these two parameters also form an integral part of powder specification. Powders which give lower color rendition are comparatively cheaper or lower luminous flux. Another quality parameter of a discharge lamp is to maintain light level with time This lumen maintenance is decided by fluorescent powder along with many other parameters like purity, manufacturing process etc A bad powder will give poor lumen maintenance

Phosphor for fluorescent lamps consumes a major chunk, a little over 80 %, of the phosphors produced worldwide. The phosphor industry, since the introduction of first phosphor in lamps in the 1930s has undergone tremendous development. The user friendly parameters such as non-toxicity, Cost effectiveness and other lamp performance features have made the first generation phosphors viz, toxio-arsenate, beryllium compounds, willemite type Zn silicate, and the germinates (in hpmv lamps) obsolete But the Sb^{3+}, Mn^{2+} activated halo phosphates though introduced in the 1940's is still an unsurpassed phosphor system in the absence of inexpensive alternatives for fluorescent (lpmv) lamps, obviously owing to it's ease of preparation, cost factor and non-toxicity and above all wide color temperature. However, the limitations of this phosphor system are not less significant viz, moderate lumen figure (60 lumens/W) as against the theoretical maximum (120 lumens/W), lamp maintenance, poor color rendition (Ra=60) and wall load factors etc

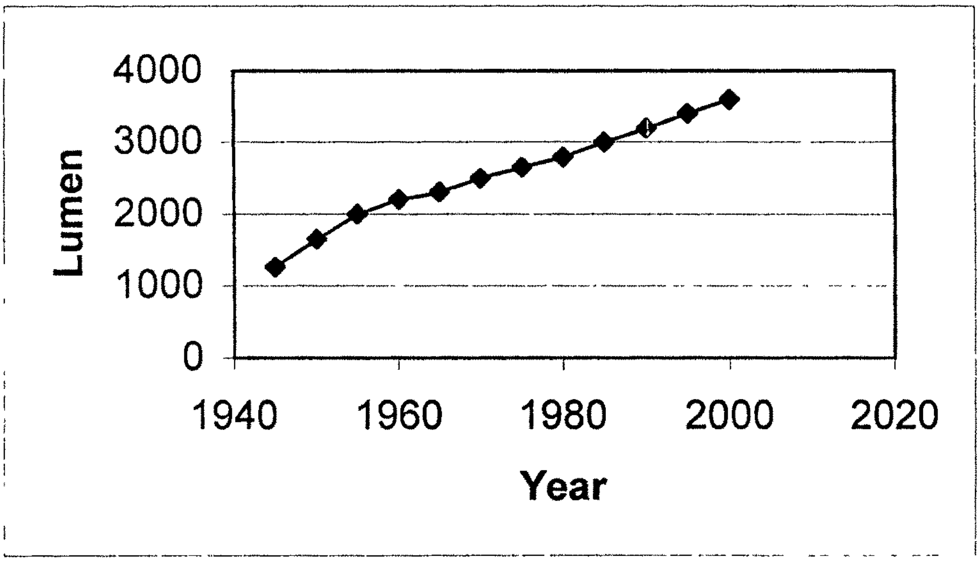
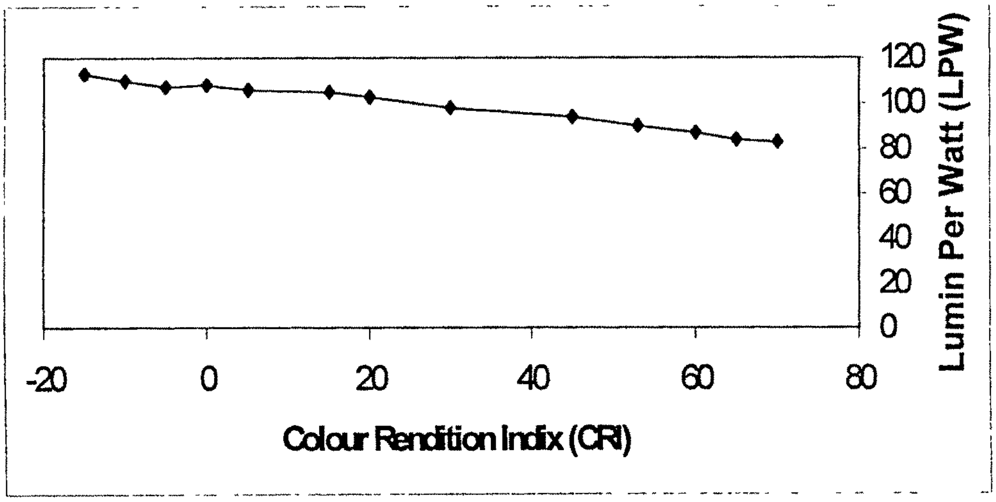


Fig. 1.3 : Lumen output progress of 40W fluorescent lamps coated with halophosphate phosphors.



Fib.1.4 : Light out put (LPW) VS Color Rendition Index (CRI) for simulated fluorescent lamps with optimum phosphor spectra.

These necessitated the search for alternatives that led to rare earths based tri-band phosphors for lamp applications in the seventies The advent of trichromatic fluorescent lamps is the corner stone in the lighting industry. The introduction of rare-earth phosphor systems for lamp applications has revolutionized the industry for it addressed to the major issues concerning the lamp performance viz; higher lumen output (90-100 lumens/W). Higher wall load factor and better color rendition index (Ra=90), in particular the high wall load –factor enabled this phosphor system to be applied in compact fluorescent lamps where stability against high-load of UV is the stringent requirement for the successful lamp performance.

Interestingly, the triband phosphor system performing near the physical limit leaves no scope for further improvement in the luminous efficiency. That's why new ways in the research are being focused on the design of in-expensive phosphor system without compromising the performance and effectively harnessing the influence of impurities to achieve the ultimate efficiency The search does not seem to be elusive. Equally important are alternate discharge mechanism (e.g. Xe discharge) paving way for higher lumen and more importantly, the concept of quantum –cutters underlying generating more than one visible photon for one UV.

New Phosphor Blends:

Because of an increased awareness of the need for efficient, i e. energy saving, lamps and the development of rare-earth-activated phosphors, new multi-component systems have been introduced and are currently receiving an increasing emphasis in the lighting industry. To illustrate the performance that is possible with optimum phosphor systems can be seen from the **Fig.1.4** which enlists the maximum candela (lumens), or light output, that can be obtained from fluorescent lamps. The numbers are calculated using simulated spectral-powder distributions (SPDs). They include the visible mercury lines and assume the efficiency of standard phosphor coatings. The X-axis is the general color rendition index (CRI) which measures the average displacement of eight test colors on a uniform chromaticity diagram from their appearance under a standard incandescent source or daylight. A CRI of 100 means that there are no color distortions. The ability of a lamp not to distort colors is important to varying degrees in different applications.

Optimum SPDs giving white light with a color temperature of 4200 K consist of two bands peaking near 575 nm and 450 nm, respectively Similar results are obtained for other white colors. When the two bands are very narrow, maximum luminous efficiency is obtained but color rendition is very poor. As the bands broaden, color rendition is improved at the expense of luminous efficiency.

Better color rendition is desired in residential lighting and certain commercial applications where good color reproduction is important. An optimum SPD having very good color rendition is achieved using three narrow bands peaking near the wavelengths 610,540 and 450 nm To utilize this principle, three component phosphor blends have been developed.

Results based mainly on simulations using different phosphor SPDs indicate that narrow red emission near 610 nm, which is available from Y_2O_3 . Eu(III), is essential to optimum efficiency and very good color rendition. However, some flexibility is possible in the choice of green and blue phosphor emissions. For example, a broad green emission provided by a strontium halo phosphate phosphor can be used with little loss in luminous efficiency Phosphor blends also used to achieve an infinite variety of SPDs for most important applications, reprographic recording, including plant growth, special color effects, etc.

Optimum phosphor blends with the narrow red emission provide 40-50 % more light output than deluxe phosphor blends previously used for applications requiring good color rendition, which contained the broad red-emitting phosphor Strontium Orthophosphate activated with Tin (II). Still other phosphor systems are used to obtain very high color rendition for color-critical applications. A CRI of 95 or higher can be obtained with phosphors or pigments that absorb some of the radiant power from the visible mercury lines in the blue violate region of the spectrum.

In many of the applications inorganic solids doped with rare earth impurities are used. To understand the how the rare earth impurities make various applications possible, it is important to know the luminescent characteristics of these materials. Most probably there are four parameters, viz excitation type and spectrum, emission intensity and the emission spectrum, relaxation to emitting state and decay time, which determine the utility of rare earth doped phosphors All these parameters are further depending on the temperature and the concentration. This dependence is equally important in context of the utility of the phosphors in various photoluminescence (PL) applications.

Energy Levels of Defects in Solids:

The energy levels of electrons in crystalline solids are determined by the interaction between the many atoms (typically 10^{19}/cm^3) that constitute the crystal. When such a huge number of atomic wave function recombines, the number of the energy levels split from any given atomic level is large. There is only very small energy difference between the levels split from one atomic level These energy level essentially form an energy continuum (or band) There is an energy separation between 1s and 2s band, 2s and 2p bands and so on. But within an given band, discrete energy levels have extremely small separation in energy The energy levels of electron crystals can be determined by the existence of a potential function that is periodic in space. The interaction of electrons with each other and this periodic potential must be considered to derive the allowed energy levels for electrons in crystals The periodic function of the lattice coupled with the wave function of a free electron when solved quantum mechanically permits only specific values for electron energies in the solids The allowed energy levels fall into a series of energy bands with the band separated by regions of forbidden energy gaps. Imperfections in a crystals give rise to localized energy states, an electron associated with the imperfection having energy level that is forbidden in perfect crystal Local deviation from the periodic potential of the perfect crystal gives rise to localized energy states characterized by wave functions that decay exponentially in amplitude with distance from the imperfection site When considered with respect to energy bands, these localized levels normally lay in the forbidden gap between the valance band and conduction bands Prominent imperfections are impurities, vacancies, interstitial or complex imperfections formed by the aggregate of the simple imperfections. Since the condition of real crystal is frequently under a thermodynamic environment favouring the existence of imperfections, such departures from the periodic potential of the perfect crystal are the rule Localized levels can also be directly associated with the impurity itself and correspond to atomic levels of the impurity as altered by the dielectric constant and interaction of the crystal. Such levels are additional levels, which are not at all present in the chemically pure crystal

RARE EARTH IONS AND THEIR LUMINESCENCE PROPRERTIES

The electronics configurations of trivalent rare-earth ions in the ground states are shown in **Table VIII**. The lanthanides from Ce^{3+} to Lu^{3+} have one to fourteen 4f electrons added to their inner shell configuration, which is equivalent to Xe. The ions with no 4f electrons i e Sc^{3+} , Y^{3+} , La^{3+} and Lu^{3+} , have no electronic energy levels that can induce excitation and luminescence process in or near the visible region In contrast the ions from Ce^{3+} to Yb^{3+} , which have partially field 4f orbital, have energy levels characteristic of each ion and show a variety of luminescence properties around the visible region. Many of these ions can be used as luminescent ions in phosphors, mostly by replacing Y^{3+} , Gd^{3+} , La^{3+} and Lu^{3+} in various compound crystals The azimuthal quantum number (ℓ) of 4f orbital is 3, giving rise to 7 (2ℓ+ 1) orbital, each of which can accommodate two electrons In the ground state, electrons are distributed so as to provide the maximum combined spin angular momentum (S) The spin angular momentum S is further combined with the orbital momentum (L) to give the total angular momentum (J) as follows

J = L – S, when the number of 4f electrons is less than 7

J = L + S, when the number of 4f electrons is larger than 7

An electronic state is indicated by notation $^{2s+1}L_J$ where L is represents S, P, D, F, G, H, I, K, L, M. Corresponding to L = 0,1,2,3,4,5,6,7,8,9, . .. ,

More accurately, an actual electronic state is exposed as an intermediate coupling state, which can be described as a mixed state of $^{2s+1}L_J$ states combine by spin orbit interaction For qualitative discussion, however, the principal L State can be taken to represent the actual state The mixing due to spin-orbit interaction is small for the levels near ground states While it is considered for excited states that have been neighboring state with similar J numbers The effect of mixing is relatively small on the energy levels, but can be large on their optical transition probabilities

The 4f electronic energy levels of lanthanide's ions are characteristic of each ion. The environment does not affect the levels much, because 4f electrons are shielded from external electronic fields by the outer $5s^2$, $5p^6$ electrons. This feature is in strong contrast with transition metal ions, whose 3d electrons, located in an outer orbit, are heavily affected by the environmental or crystal electrical field Dieke and co-workers have precisely investigated the characteristic energy levels of the 4f electrons of trivalent lanthanide ions.

The energy levels may be divided into three categories, those corresponding to $4f^n$ configuration, $4f^{n-1}5d$ configuration and those corresponding to charge transfer involving the neighboring ions

Discrete f-f transitions:

The transitions within the 4f levels are strictly forbidden, because the parity does not change (Lenore's selection rules). Besides this, there can also be spin prohibition (only $\Delta s = 0$ are allowed) Efforts were made to interpret rare earth luminescence on the basis of the magnetic dipole and electric quadruple transitions. Van Vleck shows that this hypothesis can explain only a few of the observed emissions. The emissions corresponding to Δj up to 6 were experimentally observed which could not be explained. The forbidden transitions are observed due to the fact that the interaction of rare earth ions with crystal field or with the lattice vibrations can mix states of different parities into the 4f states Although these admixtures make the transitions observable, their oscillator strengths remain relatively low (Forced electric dipole transitions) In crystals where rare earth ions occupy asymmetric sites, odd parity component of the crystal field mix states form opposite parity configuration into the $4F^n$ wave functions

In the second order, therefore, the electric dipole transition becomes parity allowed The transitions, which are not allowed as electric dipole, may take place as magnetic dipole The magnetic dipole transition obey the selection rules $\Delta L = 0$, $\Delta S = 0$ and $\Delta J = 0$ or ± 1 ($J=0 \rightarrow J=0$ is not allowed). In the spin orbit coupling weakens the selection rule on ΔL and ΔS. Interaction of rare earth ions with lattice vibrations also can mix the state of different parities into 4f states Vibronic transitions of rare earth ions are due to coupling of $4f^n$ state with the vibrational mode of the lattice In first order, coupling occurs only with IR vibrations to break the parity selection rule of the purely electronic f – f transitions

Broad Energy bands:

These bands play a vital role in excitation. These are important for emission in Ce^{3+}. The bonds are classifieds into two groups In the first group, one of 4f electrons is raised the higher 5d levels. The transition from the configuration $4f^n$ to $4f^{n-1}5d$ are allowed The second group of bands corresponds to the promotion of an electron from one of the surrounding ions to the 4f orbit of the central ion This is referred to as charge transfer state and written as $4f^n\,2p^{-1}$.

Charge transfer bands:

Charge transfer bands were first observed and interpreted by Jorgenson for trivalent Sm, Eu, Tm and Yb. These were later studied for various rare earth ions. Jorgenson also gave the theory for calculating the position of CT bands. Obviously this will depend on the ligand. It has been observed that the energy will decrease with the electron negativity of the legend ion. In case of Eu^{3+}, the CT band provides strong excitation. After this brief discussion of the general features which is necessary for understanding the peculiarities of the luminescence process, the characteristic features of luminescence of Ce and Tb which are relevant to the present work will be reviewed.

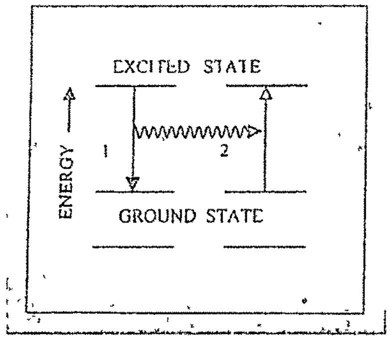


Fig.1.5 Radiative Energy Transfer Process (Schematic)

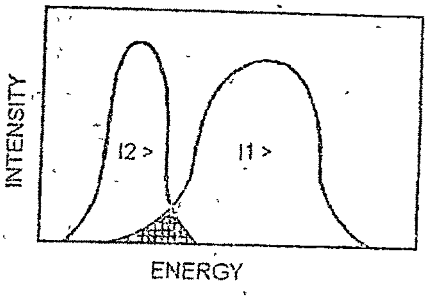


Fig.1.6 Energy Transfer by resonance Exchange

Energy transfer and sensitization of luminescence:

The energy transfer processes are often used in practical phosphors in order to enhance the emission efficiency. The process is called as sensitization of luminescence The donor is called as sensitizer. The emission intensity in Mn^{2+} activated silicate, phosphate and sulfide phosphor for sulfide phosphors for example is sensitized by Pb^{2+} and Ce^{3+} In halophosphate phosphors $3Ca_3(PO_4)_2\ Ca(FCL)_2 : Sb^{3+}, Mn^{3+}$, the Sb^{3+} plays a role of a sensitizer as well as activator. Ce^{3+} sensitizes the green emission of Tb^{3+} in many oxides, Phosphates and venadates.

Theory of energy transfer:

The energy transfer is the process of the excited state energy from donor to an activator. This transfer occurs without appearance of a photon and is the primary result of the multipole interactions between donor and activator. This process is occur, when the energy difference between the ground state and the excited state of a sensitizer and an activator are equal and suitable electrostatic or magnetic origin interaction exist between them. In addition, the emission spectrum of the sensitizer ion and the absorption spectrum of an activator ion have to show spectral overlap for the energy conservation reasons. The energy transfer has been treated by Foster and Dexter. They predicted that the rate of energy transfer is proportional. The overlap of the donor emission and the acceptor absorption spectra which is equal to R^{-6} where R is the donor to acceptor distance Generally, the energy transfer process can be represented by

$S^* + A \rightarrow S + A^*$ where the asterisk indicates the excited state.

The different mechanisms of the energy transfer are, (1) Radiative transfer, (2) Resonance exchange, (3) Spin Coupling, (4) Non-resonance process and (5) Spatial resonance.

Radiative transfer:

In radiative energy transfer process real photons are emitted by the sensitized ion and are then absorbed by any activator ions within a photon travel distance. Because of this fact, this transfer process depends on the shape of the sample. Radiative energy transfer process is schematically shown in **Fig.1.5** . Here both the oscillators are assumed to be of the same kind.

Resonance exchange:

This type of energy transfer occurs between two radiators capable of radiating at same frequency. Hence the probability of energy transfer is a direct function of the overlap of the energy states between the two sites involved. Resonance exchange process is schematically shown in **Fig.1.6**. Here 11> and 12> represent two optically active sites in a lattice. Site 11> is an excited state while site 12> is at a low energy state and hence ready to absorb energy from state 11 >. As shown in fig, there is an overlap area of energies caused by the vibronic coupling broadening of the zero phonon transition. It is this overlap of energies, which allows transfer of energy from one oscillator to another, even though several lattice plane sites separate them Resonance exchange process can be classified as electric multiple coupling (dipole – dipole or dipole – quadruple), Magnetic dipole

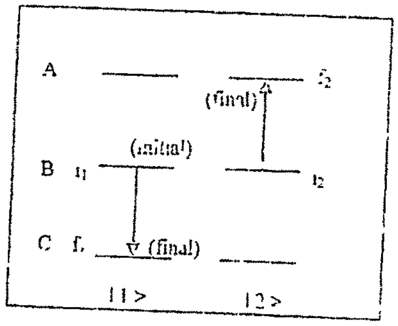


Fig.1.7 Energy Transfer by spin Exchange

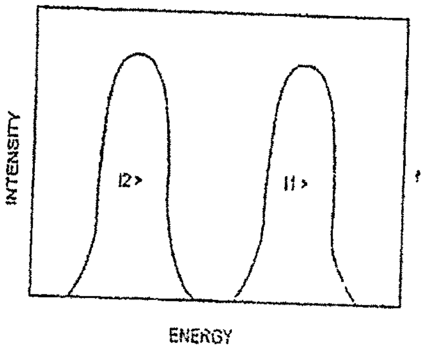


Fig.1.8 Non resonant Energy Transfer Process

coupling, direct exchange coupling and virtual phonon exchange. Direct exchange coupling and dipole – dipole or dipole-quadruple exchanges are very similar, except that the intensity is lower because of oscillator strengths. Virtual phonon exchange involves phonon wave coupling at the two sites where a Part of the energy is transmitted through lattice phonon wave.

Energy exchange by spin coupling:

If two ions are on adjacent sites (no further than 2 – 3 lattice sites apart), than a direct energy exchange can occur through the coupling of electron spins. The spin exchange process can be illustrated by using the band model and is shown in Fig 1.7. Consider two ions, both initially in an excited state In this case, one ion at site 1 spin couples to another ion at site2. In the diagram refers to the initial state of each and f the final state. Thus, the " **2** ion " goes from the level B to the level A. While the " **1** ion " simultaneously transforms from the level B to level C. Thus from two excited ions, one end up with one in the ground state and the other in an energy state double that of the initial state This process has been observed in rare earth activated phosphors, which can absorb IR radiation and convert it to visible light (an anti Stoke's process). This process occurs only between nearest neighbors and is not a special process The spin exchange process is strong in many lattices and may even be equivalent to dipole- quadruple process found in many phosphors

Energy transfer by non-resonant process:

This type of an energy transfer process occurs when there is a large mismatch of the energy of oscillators Non-resonant energy transfer process is schematically shown in Fig 1.8 Here even through there is no overlap of vibronically – coupled energies, the energy transfer occur as a dipole-dipole, dipole-quadruple, or Exchange interactions, through the coupling of each state to the lattice via phonon exchange This involves emission of a virtual phonon at site 1 (which is an excited state) to the lattice, which is immediately absorbed at site 2, with simultaneous special transfer of resonant energy by an allowed multiple process In other words two mismatched multiples can readjust their energy states, so that a resonant energy transfer process can occur. This type of energy transfer has been observed experimentally.

Energy transfer by special process:

In this process, the energy exchange occurs over a rather long distance in the lattice and is executed as an excited energy state carried by a phonon wave to the receiving site Dixter first developed this energy mechanism in 1962 By far the most frequently observed mechanism is dipole – dipole transfer This coupling is strongest if the corresponding dipole transition in the donor and acceptor are allowed In these transitions the donor and acceptor are coupled not only to the electromagnetic field, but also to each other The entire energy transfer consists of five stages: (1) absorption of photon of energy ~ Eo by the sensitizer, (2) relaxation of the lattice surrounding the sensitizer by an amount such that the available energy E1<E0, (3) transfer of energy E1 to the activator, (4a) relaxation around the activator such that the available energy in a radiate transition is E2<E1, (4b) relaxation around the sensitizer to a state similar to it's original unexcited state and (5) emission of energy E2. Process 2 occur in about 10^{-13} seconds or longer, the excess energy being dissipated to the lattice by phonons This is the process associated with the Stoke's shift Process 3 requires a time, which depends on the distances to the surrounding activators, that is on the activators concentration, Xa. If these distances are too large, the energy reappears. as (a) a photon which May or may not be absorbed by an activator atom depending on its absorption cross section and on the total number of activators in the crystal, (b) a photon which may be reabsorbed by another sensitizer, depending on whether or not the absorption and emission bands of the sensitizer overlap and upon the total number of sanitizers in the crystal, (c) an excitation energy E1 on a different sensitizer atom

without a photon as, intermediary depending on the concentration of the sensitizer Xs and on the overlap between emission and absorption bands of the sensitizer, or (d) thermal energy following a non radiative transition. Process (4) requires a time>10^{-3} s and process (5) a time 10^{-8} s or much longer, depending on the forbiddingness of the transition.

Killers of luminescence or Quenchers:

Cations having unpaired electron spins function as quenchers of luminescence, e g Fe, Ru, Co, Ti etc These cation may be optically active in proper valance state, however they function as quencher when in the wrong valance state, they become and energy traps and dissipaters of excitation energy. The cations are essentially acceptors even for resonant energy transfer Since they cannot under go an excitation transition, because of the ground state coupling to the local phonon modes they function opposite to the luminescence process. Many of them exhibit strong absorption bands at the frequencies of radiation commonly used for excitation of the phosphors. They for excitation energy is dissipated to the lattice by phonon processes, once this type of site has captured it. Therefore, to obtain a phosphor having high degree of luminescence efficiency, it is important to exclude all transition metals from the host crystals i e. high degree of purity is mandatory if one is to obtain a phosphor with high-energy efficiency and high quantum efficiency. In the phosphor however these killers are intentionally added for the purpose of reducing the emission decay time, thereby obtaining a fast decay phosphor at the expense of emission intensity. Another factor, which results in quenching of the luminescence, is the

Table VIII. Electronic configurations of trivalent rare-earth ions in the ground state.

At. No.	Ions	E	4f electron							S Σs	L $\Sigma \ell$	J $\Sigma(L+S)$
21	Sc^{3+}	Ar								0	0	0
39	Y^{3+}	Kr								0	0	0
57	La^{3+}									0	0	0
58	Ce^{3+}	Xe	↑							1/2	3	5/2
59	Pr^{3+}	Xe	↑	↑						1	5	4
60	Nd^{3+}	Xe	↑	↑	↑					3/2	6	9/2
61	Pm^{3+}	Xe	↑	↑	↑	↑				2	6	4
62	Sm^{3+}	Xe	↑	↑	↑	↑	↑			5/2	5	5/2
63	Eu^{3+}	Xe	↑	↑	↑	↑	↑	↑		3	3	0
64	Gd^{3+}	Xe	↑	↑	↑	↑	↑	↑	↑	7/2	0	7/2
65	Tb^{3+}	Xe	↑↓	↑	↑	↑	↑	↑	↑	3	3	6
66	Dy^{3+}	Xe	↑↓	↑↓	↑	↑	↑	↑	↑	5/2	5	15/2
67	Ho^{3+}	Xe	↑↓	↑↓	↑↓	↑	↑	↑	↑	2	6	8
68	Er^{3+}	Xe	↑↓	↑↓	↑↓	↑↓	↑	↑	↑	3/2	6	15/2
69	Tm^{3+}	Xe	↑↓	↑↓	↑↓	↑↓	↑↓	↑	↑	1	5	6
70	Yb^{3+}	Xe	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑	1/2	3	7/2
71	Lu^{3+}	Xe	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	0	0	0

E- Elements

Table- IX: Properties of rare earth and non –rare earth elements used in the present thesis

Sr No.	Properties	Europium (Eu)	Cerium (Ce)	Praseodymium (Pr)	Manganese (Mn)	Neodymium (Nd)
1	Atomic radius (A°)	1.98	1.83	1 82	1.12	1.81
2	Ionic radius (A°)	95	1.03	1.01	.80	1.00
3	Electronic Configuration	[Xe] $4f^7$	[Xe]$4f^1$ 5d1	[Xe] $4f^3$	[Ar]$3d^5$ $4s^2$	[Xe] $4f^4$
4	Atomic number	63	58	59	25	60
5	Atomic weight	151 965	140.115	140.90765	54.908	144.24
6	Crystals structures, (stable below or stable above, ^{0}C	Bcc	fcc<-148dcph> 148 and <139 fcc <139 and <726 bcc>726	dcph<795 bcc>795		dph<863 bcc>863
7	Density, g/cm^3 at 24 ^{0}C	5 244	8.16	6.773	1245	7.008
8	Valance in aqueous solution	3 2	3 4	3		3
9	Color in aqueous solution, RE^{+3}	Colorless	Colorless	Yellow green		rose
10	Color of oxide, RE_2O_3 natural (artificial)	colorless 2(16)	Off white(CeO_2) 4(15)	Yellow green 1(14)		rose 7(7)
11	Ionization potential, eV/g. atom	5.67	5.65	5 76		6.31
12	Melting point, ^{0}C	822	798	931	4195	1021
13	Boiling point, ^{0}C	1597	3426	3512	906	3068

[Xe] $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^6$, [Ar] $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

About the Present Work

In the last two decades considerable interest has been directed towards the synthesis and characterization of economical and efficient rare earth doped phosphors using different hosts has been developed for various applications. The red [$^5D_0 \rightarrow {}^7F_2$] and orange emission [$^5D_0 \rightarrow {}^7F_1$] of Eu^{3+} and green emission of Tb^{3+} [$^5D_4 \rightarrow {}^7F_5$], is usually used in these phosphors. These phosphors find applications in fluorescent lamps, color TV screen, cathode ray tubes, Plasma Display Panels, discharge lamps etc. These phosphors are not commercially synthesized in India, and are imported Also no systematic efforts were made towards studying the use of indigenous chemicals for the synthesis of these phosphors In this direction the display materials laboratory at Applied Physics Department , Faculty of Technology and Engineering, M.S University of Baroda is working since a decade

The doping of $BaMgAl_{10}O_{17}$ (BAM) with Eu $^{2+}$, Mn $^{2+}$ yields highly efficient luminescence phosphors which are widely used as display phosphors mostly PDP's, Mercury low pressure and Xe low pressure discharge lamps The excellent stability of the BAM phosphors makes it possible to develop very high loading fluorescent lamps such as compact fluorescent lamps (CFL's) and high loading photocopying lamps.

The chemical composition of BAM originally proposed as $BaMg_2Al_{16}O_{27}$, but a true single phase was later found to take the form $BaMgAl_{10}O_{17}$. The later showed better maintenance performances, both in lamp manufacturing process and in lamp operation The work presented in this thesis consists of the experimental results of the phosphors synthesized in the laboratory By considering the application potential of these phosphors (BAM) with different dopant concentrations the present work was under taken for this thesis Since the CFL's are the present day energy saving lamps which are widely used globally therefore it is considered the present phosphor synthesis will help the local industry to use the indigenously developed materials

The synthesized phosphors i e. $BaMgAl_{10}O_{17}$: Eu, Mn, Pr, Ce, Nd were prepared using high temperature solid state reaction method with different Eu, Mn, Pr, Ce, Nd concentrations. The physical properties of dopants used in the present investigation are enlisted in Table VIII The Photoluminescence (PL) and Thermoluminescence (TL) characteristics of developed phosphors are presented in the thesis. High reaction temperature and long processing time is always a bit problem with solid state diffusion process, therefore required quantities of $BaCl_2$ and AlF_3 were used as a flux in the synthesis of the phosphors Optical properties were studied by recording TL emission spectra of the powder samples. The PL spectra were recorded at room temperature using the Shimadzu RF-5301 PC Spectrofluorophotometer. Thermoluminescence of the synthesized phosphors are also studied with beta and gamma radiations using Nucleonix TLD auto ranging reader system. The results are analyzed in the context of available theories and literature on the phosphor material The main aim of the present research work is to develop an indigenous phosphor for Compact Fluorescent Lamps and PDP's. An attempt is made in this direction. For easy comparison the properties of rare earth and non rare earth materials used for the present are enlisted in Table IX.

Phosphors having a small particle size and high efficiency would be most useful. By considering this phenomena TL of different particle sizes are also studied

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