# Chapter – 1

1.1 Introduction of Luminescence:

Luminescence is the emission of optical radiation (infrared, visible, or ultraviolet light) by matter. This phenomenon is to be distinguished incandescence, which is the emission of radiation by a substance by virtue of its being at a high temperature ($>5000^{o}$C) (Black body radiation). Luminescence can occur in a wide variety of matter and under many different circumstances. Thus, atoms, polymers, inorganic, organic or Organo metallic molecules, organic or inorganic crystals, and amorphous substances all emit luminescence under appropriate conditions.

The various luminescence phenomena are given their names, which reflect the type of radiation used to excite and to get the emission. 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.

1.1.1 Types of Luminescence:

Luminescence is the emission of electromagnetic radiation (photon) usually in the visible range, involving a radiative transition between energy levels of a material. According to the types of excitation, the phenomena of luminescence can be classified as:

Sr.No	Types of Luminescence	Source of excitation energy
1	Bioluminescence	Bio-chemical reaction
2	Cathodeluminescence	Electron beam
3	Chemiluminescence	Chemical reaction
4	Electroluminescence	Electric field
5	Photoluminescence	Light(UV radiation)
6	Radioluminescence	Nuclear (X & γ-rays)
7	Sonoluminescence	Sound waves (Ultrasonic)
8	Thermoluminescence	Heat
9	Mechanoluminescence 1.Triboluminescence 2. Piezoluminescence	Mechanical
10	Lyoluminescence	Pre irradiated & dissolve in water & solvent
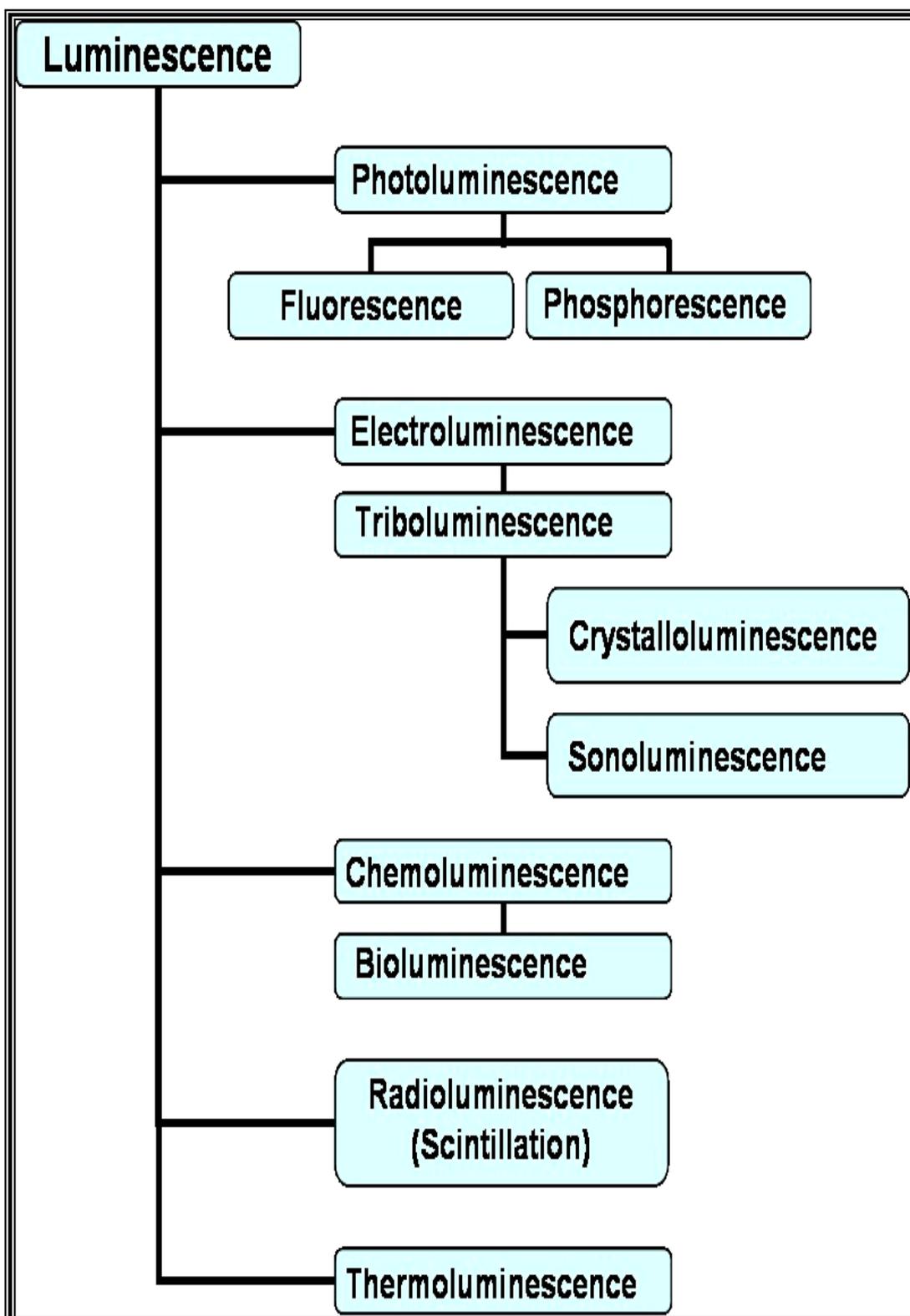
Fig.1.1.1 Types of Luminescence

According to dacay time (t) the phenomenon of luminescence is classified in to two types as **fluorescence** (if $t < 10^{-8}$ s) and **phosphorescence** (if $t > t < 10^{-8}$ s).

1.1.1a Fluorescence:
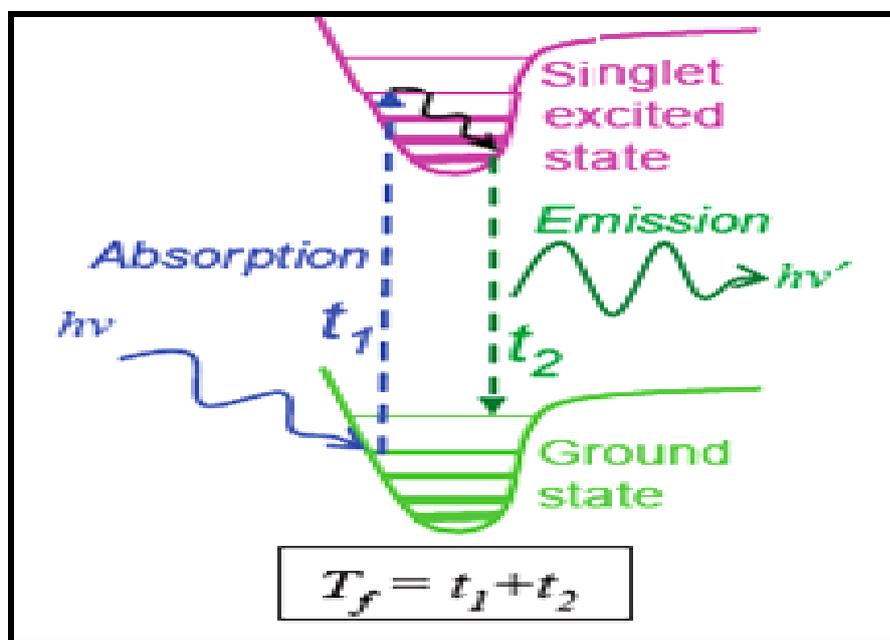
Fig.1.1.1a Fluorescence Process

The emission of light on removal of excitation, with lifetime less than 10^{-8} seconds and which is independent of the excitation intensity and temperature is known as fluorescence. 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; whereas the decay of phosphorescence exhibits strong temperature dependence. Some objects, when illuminated by light of one color, are stimulated to emit light of another color. This is called fluorescence. Common examples of fluorescence are

1) **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.

2) **The chemicals that coat the inside of fluorescent tubes.** In these tubes the UV light comes from excited mercury vapor inside the tube. The energetic UV

4

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 color.

3) **The modern machines for producing medical x-ray images**. A screen that produces a lot of visible light called fluorescence when irradiated with x-rays is used to form an image which can then be photographed with films which are sensitive to visible light. This process is more sensitive than using the film to record the x-rays directly, thus minimizing 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. The brief account of applications of fluorescence is given below.

a) **Medical application**: Fluorescence is widely used in analytical work of various compounds present in cells levers, kidney etc. The sensitivity and selectivity of PL in many micro systems facilitates 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 screen**: Different luminescent materials under exposure of ionizing 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 253.7 nm is generated through electric discharge. The phosphor absorbs the UV and through fluorescence emission it converts it in to visible light. The emission color of fluorescent lamp depends on nature of phosphor. Many varieties of fluorescent lamps are now available in market.

e)   **Forensic Science**: Luminous emission from material is highly sensitive to nature, structure and impurity (or defect) present in the specimen. PL spectrum is as good as fingerprint 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 criminals 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 lead to determine along the rotation of diffusion constant of proteins.

g)   **Fluorescence in Chemical analysis**: If the different element in the sample emits 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, thermo chrome 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 Poison and identification of strain i.e. pus, blood and urine.

1.1.1b Phosphorescence:
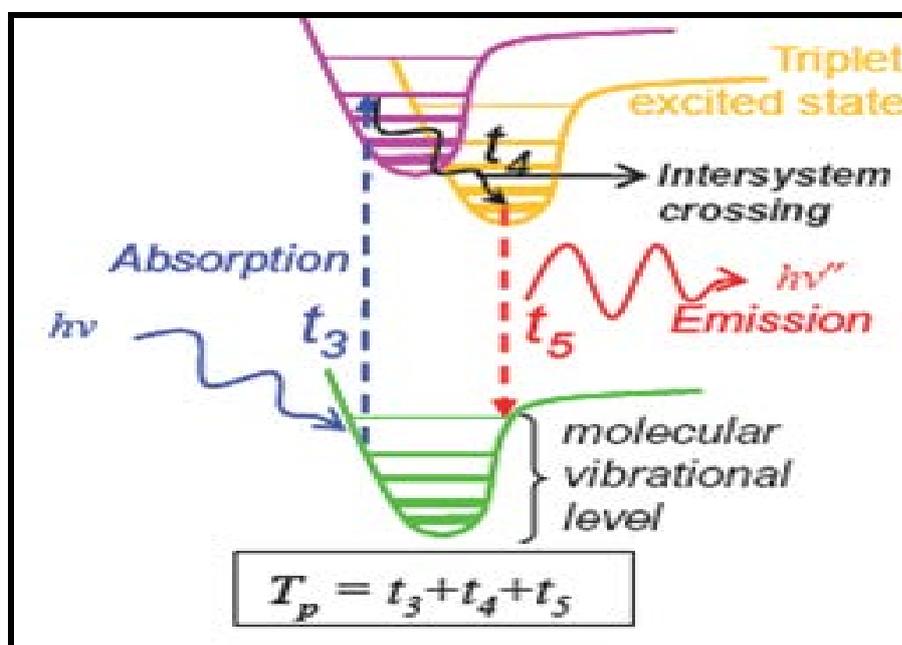
Fig.1.1.1b Phosphorescence Process

The emission of light on removal of excitation, with lifetime more than 10^{-8} seconds and which is dependent of the intensity of excitation and temperature is known as phosphorescence. 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} second, 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 sometimes said to be luminous. Most luminous toys, stickers and watch dials are

coated with long persistence phosphors. Metastable states created by the defect centers, activators, impurities, electron or hole traps present in the lattice may delay the luminescent emission causing this effect.

The luminescence of phosphors has two types.

1) **Luminescence in semiconductors**: - Luminescence of semiconductors normally occurs, after band-to-band excitation, between impurity states within the band gap.

2) **Luminescence of localized centers**: - In the case of luminescent centers, the transitions occurs between energy levels of single ions.

Phosphors are luminescent materials that emit light when excited by radiation, and are usually microcrystalline powders or thin-films designed to provide visible color emission. A phosphor is usually comprised of a host crystal material and one or more intentionally introduced impurities, called activators. The concentration of activators can be as low as tens of ppm, such as for donor-acceptors, or can be as high as 20% for rare earth dopants. The band gap of a phosphor is generally larger than 3 eV to be transparent to visible light, and so is either a wide-band-gap semiconductor or an insulator.

1.1.2 Terms related to the luminescence:

a) Activators: - "Small traces of impurities that are responsible for creating imperfections which give luminescence emission are termed as activators". In some cases a second impurity atom which is added to enhance the emission produced by activator is called "sensitizer".

b) Co-activators: - The impurities or imperfections that are essential for luminescence emission but have little influence on spectral distributions are known as Co-activators.

c) Energy levels or Centers: - Impurities, lattice defects and other perturbations of the ideal crystal configuration give rise to discrete energy levels in the forbidden gap. These energy levels play an important role in luminescence.

d) Luminescence centers: - Localized levels which are responsible for the luminescence emission are termed as "luminescence centers". Such levels have high electron capture cross section and a greater probability for radiative transition that for non- radiative ones.

e) Traps: - Trapping is fundamental process for energy storage in almost all electrically active solids. These are metastable levels responsible for Phosphorescence and Thermoluminescence.

f) Fluxes: - These are readily fusible inorganic salts acting as re-crystalline medium. With the use of flux, the firing temperature is lowered and the efficiency of the phosphor is increased. The most popular fluxes are alkali and alkaline earth halides, borates and sulphides.

g) Host materials: - These form the vehicles for carrying imperfections. They are normally colorless or light colored and consists of high melting point compounds which have high solubility for foreign atoms. The sulphide, selnides, phosphates, tungstates, oxides, molybdates and silicates of mainly Zn, Cd and the alkaline earths are used as host materials.

h) Killer centers: - The discrete energy levels which have large electron capture cross section but a low probability for radiative transition acts as killers. For example Fe, Ni, Co etc. act as a klillers.

1.2   Basic Mechanisms of Photoluminescence:
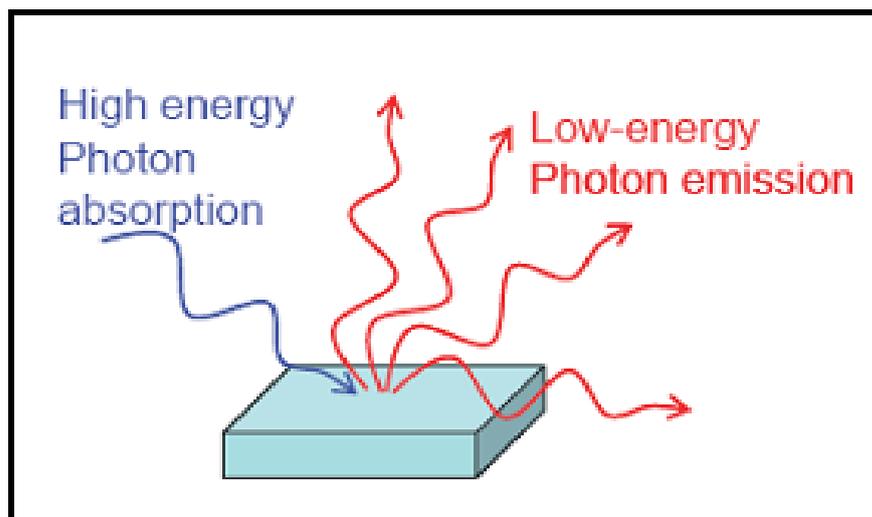
Fig.1.2 Photoluminescence process

The phenomena which involve absorption of energy and subsequent emission of light are known as luminescence. Phosphors are luminescent materials that emit light when excited by radiation, and are usually microcrystalline powders or thin-films designed to provide visible color emission. After decades of research and development, thousands of phosphors have been prepared and some of them are widely used in many areas. Excitation by absorbance of a photon leads to a major class of technically important luminescent species which exhibits fluorescence or phosphorescence.

1.2.1 Excitation and Emission Spectra:

The most common wavelength unit for describing fluorescence spectra is the *nanometer* (nm). The colors of the visible spectrum can be broken up into the approximate wavelength values

Violet and indigo	400−450 nm
Blue and aqua	450−500 nm
Green	500−570 nm
Yellow and orange	570−610 nm
Red	610 -750 nm

On the short-wavelength end of the visible spectrum is the near-ultraviolet (near- UV) band from 320nm to 400 nm and on the long-wavelength end is the near-infrared

(near-IR) band from 750nm to approximately 2,500 nm. The broad band of light from 320nm to 2,500nm marks the limits of transparency of crown glass and window glass, and this is the band most often used in fluorescence microscopy. Some applications, especially in organic chemistry, utilize excitation light in the mid-ultraviolet band (190nm – 320 nm), but special UV-transparent illumination optics must be used. There are several general characteristics of fluorescence spectra that pertain to fluorescence microscopy and filter design. First, although some substances have very broad spectra of excitation and emission, most fluorochromes have well-defined bands of excitation and emission. The difference in wavelength between the peaks of these bands is referred to as the *Stokes shift.*

In practical applications, phosphors are often excited by cathode rays, X-rays, or UV emission of a gas discharge, which correspond to applications in displays, medical imaging and lighting, respectively, such as cathode-ray-tube (CRT) color TV, X-ray fluorescent screens, and fluorescent lamps. Phosphor by co-doping with different rare earth metals Energy transfer mechanism from one dopant (sensitizer) to another (luminescent center) used to enhance the sensitivity of a phosphor. Sensitizer ions are used when the optical absorption of the activator ions is too weak (e.g., because the optical transition is forbidden) to be useful in practical devices. In such a case, energy transfer from the sensitizer ions to the activator ions has to take place. The optical absorption leading to emission can also take place by the host lattice itself (band absorption). Energy transfer from host lattice states to the activator ions (in some cases also involving sensitizers) has to take place.
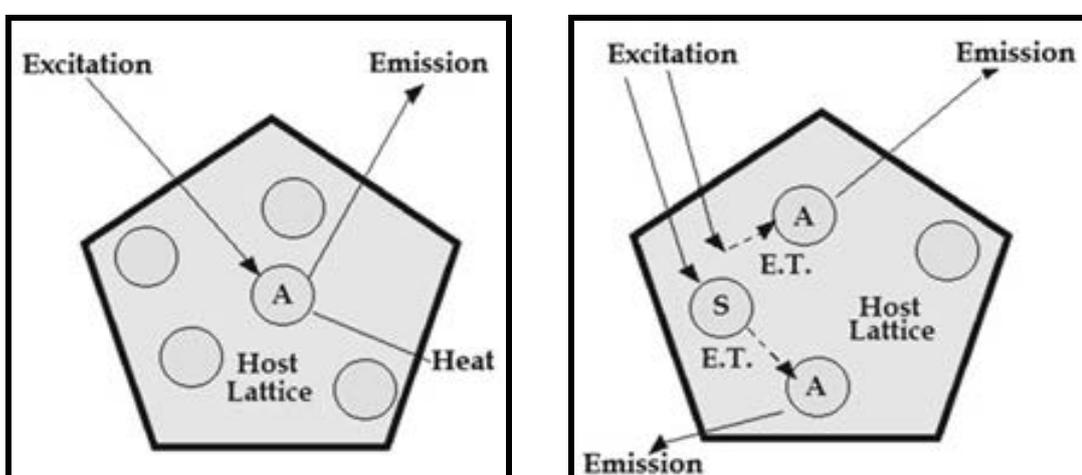
(**a**) Direct excitation of the activator   (**b**) Indirect excitation of the activator

Fig.1.2.1 Mechanism of Luminescence

Fig.1.2.1 shows basic luminescence mechanisms in luminescent centers as

(**a**) Direct excitation of the activator.

(**b**) Indirect excitation followed by energy transfer from the sensitizer or host to the activator.

In the host lattice with activator, the activator is directly excited by incoming energy; the electron on it absorbs energy and is raised to an excited state. The excited state returns to the ground state by emission of radiation.

The absorption of energy, which is used to excite the luminescence, takes place by either the host lattice or by intentionally doped impurities. In most cases, the emission takes place on the impurity ions, which, when they also generate the desired emission, are called activator ions. When the activator ions show too weak an absorption, a second kind of impurities can be added (sensitizers), which absorb the energy and subsequently transfer the energy to the activators. This process involves transport of energy through the luminescent materials. Quite frequently, the emission color can be adjusted by choosing the proper impurity ion, without changing the host lattice in which the impurity ions are incorporated. On the other hand, quite a few activator ions shows emission spectra with emission at spectral positions which are hardly influenced by their chemical environment. This is especially true for many of the rare-earth ions. Generally, luminescence of phosphors involves two processes: excitation and emission. Many types of energy can excite the phosphors. Excitation by means of energetic electrons is cathodoluminescence (CL). PL occurs when excited by photon (often ultra-violet), electroluminescence (EL) is excited by an electric voltage, chemiluminescence is excited by the energy of a chemical reaction, and so on. The process of emission is a release of energy in the form of photon.

1.2.1a Radiative Transition:

There are several possibilities of returning to the ground state. The observed emission from a luminescent center is a process of returning to the ground state radiatively. The luminescence quantum efficiency is defined as the number of photons emitted divided by the number of photons absorbed, and in most cases is equal to the ratio of the measured lifetime to the radiative lifetime of a given level. The processes competing with luminescence are radiative transfer to another ion and nonradiative transfers such

as multiphonon relaxation and energy transfer between different ions or ions of a similar nature. The last transfer is also named cross-relaxation.
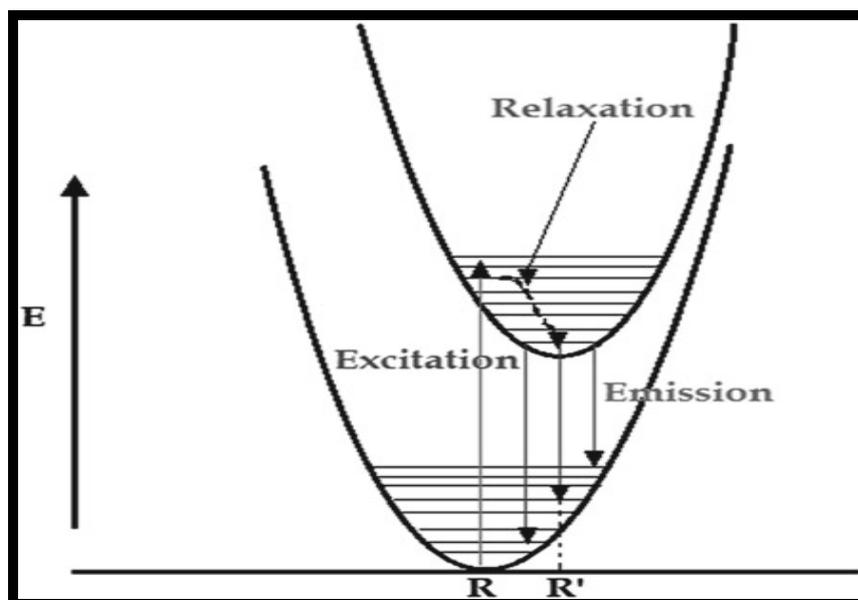
Fig.1.2.1a configurationally coordinate diagram in luminescent center.

Fig.1.2.1a shows the configurationally coordinate diagram in a broad band emission. Assumption is made on an offset between the parabolas of the ground state and the excited state. Upon excitation, the electron is excited in a broad optical band and brought in a high vibrational level of the excited state. The center thereafter relaxes to the lowest vibrational level of the excited state and give up the excess energy to the surroundings. This relaxation usually occurs nonradiatively. From the lowest vibrational level of the excited state, the electron returns to the ground state by means of photon emission. Therefore, the difference in energy between the maximum of the excitation band and that of the emission band is found. This difference is called the Stokes shift. The radiative transfer consists of absorption of the emitted light from a donor molecule or ion by the acceptor species. In order to that such transfer takes place, the emission of the donor has to coincide with the absorption of the acceptor. The radiative transfer can be increased considerably by designing a proper geometry.

1.2.1b Non radiative Transition:
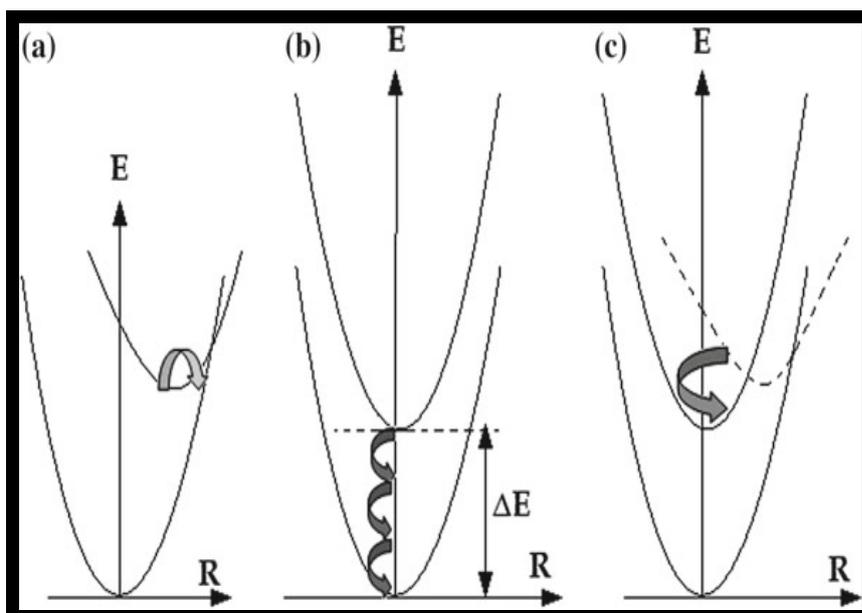
**Fig.1.2.1b configurationally coordinate diagram representing nonradiative transitions**

The energy absorbed by the luminescent materials which is not emitted as radiation is dissipated to the crystal lattice. It is crucial to suppress those radiationless processes which compete with the radiation process. In order to understand the physical processes of nonradiative transitions in an isolated luminescent center, the configurationally coordinate diagrams are presented in Fig.1.2.1b. In the figure, there is a Stokes shift between the ground state and the excited state. The relaxed-excited state may reach the crossing of the parabolas if the temperature is high enough. Via the crossing, it is possible for electrons to return to the ground state in a nonradiative manner. The energy is given up as heat to the lattice during the process. In Fig.1.2.1b, the parabolas of ground state and excited state are parallel. If the energy difference is equal to or less than four to five times the higher vibrational frequency of the surrounding, it can simultaneously excite a few high-energy vibrations, and therefore is lost for the radiation of phonons. This is called multiphonon emission. In a three-parabola diagram as shown in figure both radiative and nonradiative processes are possible. The parallel parabolas (solid lines) from the same configuration are crossed by a third parabola originated from a different configuration. The transition from the ground state to the lower excited state (solid line) is optically forbidden, but it is

allowed to transit to the upper excited state (dash line). Excitation to the transition allowed parabola then relaxes to the relaxed excited state of the second excited parabola. Thereafter, emission occurs from it. The nonradioactive processes competing with luminescence are energy loss to the local vibrations of surrounding atoms (called phonons in solids) and to electronic states of atoms in the vicinity, such as *energy transfer*, which may be resonant (including as a special case energy migration between identical systems, which may ultimately emit radiation) or phonon assisted [the excess energy being dissipated as heat, or, to a much smaller extent, the thermal reservoir supplying low-energy phonons ($kT = 210$ cm^{-1} at 300K) to a slightly higher level of an adjacent system]. Special cases of energy transfer are cross-relaxation, where the original system loses the energy *($E2 − E1$)* by obtaining the lower state $E1$ (which may also be the ground state $E0$) and another system acquires the energy by going to a higher state. Cross relaxation may take place between the same lanthanide (being a major mechanism for quenching at higher concentration in a given material) or between two differing elements which happen to have two pairs of energy levels separated by the same amount.

1.2.1c Multiphonon Relaxation:

Excited electronic levels of rare earths in solids decay nonradiatively by exciting lattice vibrations (phonons). When the energy gap between the excited level and the next lower electronic level is larger than the phonon energy, several lattice phonons are emitted in order to bridge the energy gap. It was recognized that the most energetic vibrations are responsible for the nonradiative decay since such a process can conserve energy in the lowest order. The most energetic vibrations are the stretching vibrations of the glass network polyhedra; it was shown that these distinct vibrations are active in the multiphonon process, rather than the less energetic vibrations of the bond between the R and its surrounding ligands. It was demonstrated that these less energetic vibrations may participate in cases when the energy gap is not bridged totally by the high-energy vibrations. The experimental results reveal that the logarithm of the multiphonon decay rate decreases linearly with the energy gap, and hence with the number of phonons bridging the gap, when the number of phonons is larger than two.

1.2.1d Cross-Relaxations:
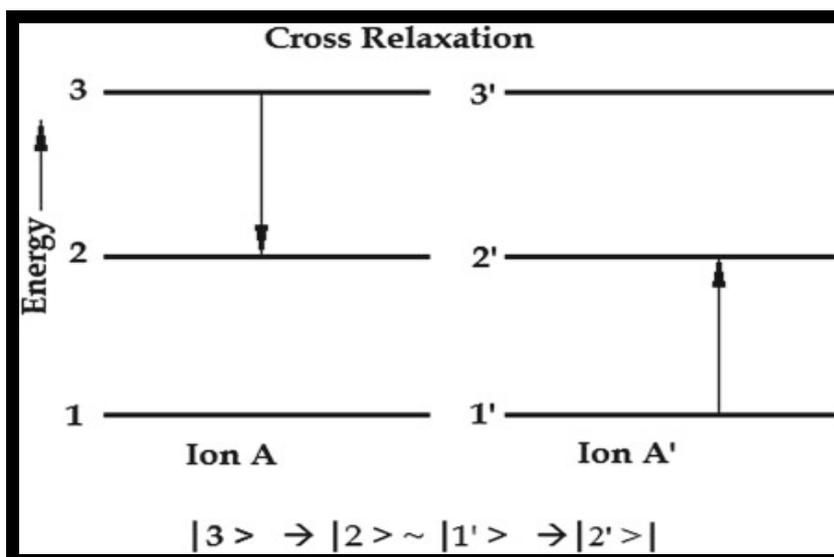
Fig.1.2.1d Cross Relaxation between two ions of same or of different nature.

A special case of energy transfer is cross-relaxation, where the original system loses the energy $(E_3 - E_2)$ by obtaining the lower state E_2 (which may also be the ground state E_1) and another system acquires the energy by going to a higher state E_3 may take place between the same lanthanide (being a major mechanism for quenching at higher concentration in a given material) or between two differing elements, which happen to have two pairs of energy levels separated by the same amount. The cross-relaxation between a pair of R ions is graphically presented in Fig.1.2.1d. The two energy gaps may be equal or can be matched by one or two phonons. Cross-relaxation has been measured in a variety of ions and it is a dominating factor in nonradiative relaxations at high concentration. The nonradiative relaxation rates can be obtained by analysis of the decay curves of R fluorescence using the formula of the general form where the population number of state i, Ni, is proportional to the intensity of emitted light.

1.2.1e Up-Conversion:
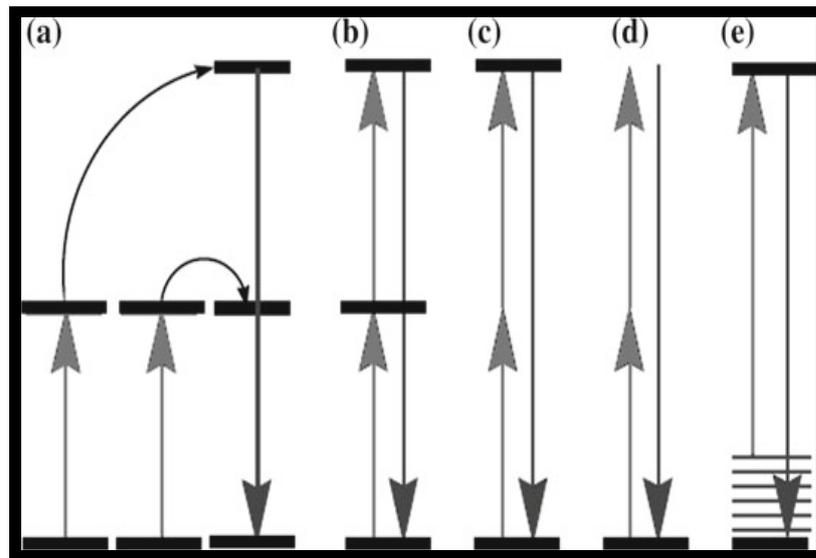
Fig.1.2.1e Up-conversion process.

Up-conversion in its most general sense is the phenomenon whereby one or more photons of lower energy are absorbed by a material, and re-emitted as a higher energy photon. Materials able to cause this effect are known as up-converters. A main attraction is that they can be tuned to respond to near IR energy near 980nm from commonly available and cheap diode lasers, and emit a range of photon energies at visible wavelengths. A major type of up-converter is based on rare earth-(RE)-doped salts of various metals, usually fluorides, in solid crystal or glass matrices.

Figure 1.2.1e shows diagrammatically some of the absorption–emission processes which lead to up-conversion. The vertical arrows represent absorption or emission of a photon, while the curved arrows represent energy transfer between species (usually ions).

❖ Mechanism (a) is the most common in RE systems. Here, two photo excited RE ions (same species or different) each transfers its energy to a third ion which emits from the higher energy state. Ytterbium as Yb^{3+} is commonly used as a primary absorber of input photo radiation, and this transfers energy to emitter ions, commonly Er^{3+} and Tm^{3+}. The efficiency of this energy transfer up-conversion (ETU) is surprisingly high and, of the five mechanisms shown in figure, this is the most efficient. Three-photon ETU is also well-known.

17

❖ In mechanism (b), initial absorption leads to an intermediate excited state, which lives long enough to allow ready absorption of a second photon to give a higher excited state, hence its name of 2-step absorption. Emission from this clearly gives a higher energy, up-converted, and photon. This process is about two orders of magnitude less efficient than (a).

❖ Mechanism (c) is two-photon absorption, this time without a real intermediate excited state. This implies simultaneous absorption of two photons, which inevitably has a lower probability and the mechanism is thus much less efficient. Second harmonic generation (SHG) (d), under nonlinear optics (although mechanisms (a)–(c) are also nonlinear in character). Here, the interaction of two photons in the SHG material does not proceed by way of any excited energy state.

❖ Finally, the mechanism of up-conversion represented by (e) is sometimes called hot-band absorption. An electron in a vibrationally excited level of the ground state of a species is preferentially excited. Emission then proceeds back to a lower vibrational level within the ground state, and up-conversion by only a few units of thermal energy is observed.

1.3   Features of Rare Earth (RE) Ions & Luminescence:

1.3.1 Properties of the Rare Earth ions:

➢ The rare earths are silver, silvery-white, or gray metals.

➢ The rare earth metals have a high luster, but tarnish readily in air.

➢ The rare earth metals have high electrical conductivity.

➢ The rare earths share many common properties. This makes them difficult to separate or even distinguish from each other.

➢ There are very small differences in solubility and complex formation between the rare earths.

➢ The rare earth metals naturally occur together in minerals (e.g., monazite is a mixed rare earth phosphate).

➢ Rare earths are found with non-metals, usually in the 3+ oxidation state. There is little tendency to vary the valence. (Europium also has a valence of 2+ and cerium also a valence of 4+.)

In display application of luminescence mostly inorganic solids doped with rare earth impurities are used. It is necessary to understand the mechanism of these display materials. Basically, there are four important parameters, viz. excitation type and spectrum, relaxation to emitting state and the decay time, and emission intensity and emission spectrum. RE spectra were observed extremely sharp (line-spectra). The above-mentioned four factors vary from one-host materials to another. The characteristic properties of the RE ions are attributable to the presence in the ion of a deep-lying $4f$ shell, which is not entirely filled. The electrons of this shell are screened by those in the outer shells (except for La^{3+} and Lu^{3+}), and as a result they give rise to number of discrete energy levels. Since the presence of crystal lattice scarcely affects the position of these levels, there is a resemblance between the energy level diagram of a free ion and that of the incorporated ion. In case of the latter, usually the terms are shifted to lower wave numbers. Some empirical laws have been formulated regarding the magnitude of this effect. In spite of the resemblance of the energy levels of free RE ions and the RE ions in solids, there is an important difference in the emission properties. In solids, the emission of RE ions is observed at different spectral position than the absorption. The difference between the absorption and emission wavelength is described as 'Stokes Shift'. The shift for the transition within $4f$ shell results from the fact that the absorption and emission takes place between different levels. Usually, absorption corresponds to the transition from ground state to higher excited states. Electron in the higher excited state then loses energy to lattice till the states lying just below the previous excited states are available. When the difference between the adjacent states is large, then the energy corresponding to this transition cannot be transferred to lattice and it is given out in the form of emission. The emission thus corresponds to the transition from the intermediate state to the ground state. RE ions are usually trivalent. Ions corresponding to configurations $4f^{0}$(La^{3+}), $4f^{7}$(Gd^{3+}) and $4f^{14}$(Lu^{3+}) are stable. The RE element next to these three tends to exchange electron and acquire this stable configuration. For understanding the luminescent properties of rare earth ions, it is necessary to know their key energy levels. The energy level may be divided into three categories, those corresponding to $4f^{n}$ configuration, $4f^{n-15d}$ configuration, and those corresponding to charge transfer involving the neighboring ions.

1.3.2 Discrete f–f Transition:

Except for Ce^{3+} and Yb^{3+}, number of discrete $4f$ energy levels is large. For Gd^{3+}, there are as many as 327 levels of $4f$ configuration. These levels further increase in number due to crystal field splitting. Most often the levels relevant to photoluminescence that can be excited by UV light and other levels are ignored. The transitions within $4f$ shells are strictly forbidden, because the parity does not change. The forbidden transitions are observed due to the fact that the interaction of RE ion with crystal field or with the lattice vibrations can mix state of different parities into $4f$ states. Coupling of $4f$ electrons with transient dipoles induced in the ligands by the radiation field leads to an amplification of the even parity multipolar transition amplitudes for transitions within $4f$ shell. These transitions are called as induced electric dipole transition. Quite often, the transition corresponding to selection rules ($\Delta S = 0$, $L \leq \pm\ 2$ and $J \leq \pm\ 2$) shows large variations in oscillator strengths depending upon the surround environment. These have been termed as the *hypersensitive transitions*. Table 2.1 lists the various hypersensitive transitions for different RE3+ ions. The transitions that are not allowed as electric dipole may take place as magnetic dipole. The magnetic dipole transitions obey the selection rules $\Delta L = 0$, $\Delta S =$
0, $\Delta I = 0$ and $\Delta J = 1$. Spin orbit coupling weakens the selection rule on ΔL and ΔS. Interaction of RE ions with lattice vibrations also can mix the state of different parities into $4f$ states. Vibronic transitions of RE ions are due to coupling of $4f^{n}$ state with the vibrational mode of the lattice.

1.3.3 Broad Energy Bands:

In addition to the discrete $4f$ levels there are other levels present. These are usually in the form of broad bands and play vital role in excitation. For Ce^{3+} and Eu^{2+}, these are vital for emission as well. The bands referred to fall into two groups. In the first group, one of the $4f$ electrons is raised to the higher $5d$ levels. Transitions from configuration $4f^{n}$ to $4f^{n-1}$ are allowed. The second group of bands corresponds to the promotion of an electron from one of the surrounding ions to $4f$ orbit of the central ion. This is referred to as the charge transfer state and written as $4f^{n}2p^{-1}$.

1.3.4 f–d Transition:

$4f^{n-1}5d$ levels may be understood as formed by the electron in the $5d$ orbital interacting with $4f^{n-1}$ core. As a consequence of this strong crystal field effect on the

$5d$ electron, $4f^{n-1}5d$ configurations of RE ions in solids are very different from those of free ions. The $4f^n \rightarrow 4f^{n-1}5d$ absorptions of most of the RE^{3+} and RE^{2+} ions exhibit two features. First, they consist of strong bands corresponding to the components of $5d$ orbital split in the crystal field. Consequently, their spectra are similar when ions are embedded in same type of host. Second, the structures of $5d$ bands can be fitted to energy differences in the ground multiples of the $4f^{n-1}$ configurations. For most of the trivalent RE ions, transitions from configuration $4f\,n$ to $4f\,n{-}15d$ correspond to wave numbers exceeding 50,000 cm^{-1}, and thus not accessible to UV excitation. In case of Ce and Tb, they are usually accessible to UV excitation the position of these bands shifts to higher wave numbers as one moves along the RE series from Ce to Gd. For Tb, the position is suddenly lowered and again the increasing trend is observed up to Yb^{3+}.

1.3.5 CT Bands:

CT bands will depend on the ligand. It has been observed that the energy will decrease with the electro negativity of the ligand ion. Tetravalent ions often show absorption in the visible region of the spectrum, which corresponds to the CT state. In case of Eu^{3+}, the CT band provides strong excitation. No other RE ion is as much investigated for the CT bands as Eu^{3+}.

1.3.6 Excitation by Energy Transfer

Apart from the *f–d* allowed transitions and the CT bands, strong excitation can often be achieved by the energy transfer. A RE ion or other species may absorb the energy and transfer to another RE ion which may lose the energy radiatively. When the energy transfer results in the increase in RE emission it is termed as the sensitization. The RE ion from which the emission results is called as the activator and the one which absorbs energy as the sensitizer. An unwanted feature of the energy transfer is the reduction in emission. Indeed, there are many more examples of energy transfers resulting into reduction of the desired emission than the one in which sensitization has been achieved. The concentration quenching of RE emission most often takes place through the energy transfer. One may expect that the RE luminescence will increase with increase in the concentration of luminescent ions. In practice, this is valid only up to certain limiting concentration above which a RE ion in excited state loses energy to a nearby ion in the ground state. The excitation energy, thus hops from one

ion to the other and ultimately it may reach a killer site (e.g., an impurity ion which absorbs the energy and dissipates it nonradiatively). The concentration quenching may take place through cross-relaxation also. In this process, the excitation ion comes to a less excited state. When the transition from this less excited state to the ground state is nonradiative, luminescence is completely quenched. Otherwise one observes emission at the longer wavelengths taking place at the cost of the short wavelength emission. Since the interaction with lattice will be temperature dependent, it is quite understandable that the position, splitting, and lifetimes of various levels can be temperature dependent. It is quite common to find that at lower temperatures the host lattice offers conditions conductive for luminescence while at high temperatures, the nonradiative processes become dominant. This has been termed as thermal quenching. For many applications it assumes prime importance. It determines the operating temperature of the device based on the luminescent materials. In some cases (e.g. Y_2O_3: Eu), increase in luminescence efficiency at which high temperatures has been observed. This occurs due to the thermal quenching of the processes which compete with the desired emission.

1.4   Rare Earths elements energy levels and transitions:

Fig.1.4a Periodic table of elements

Rare earth	Excited state	Ground state
Ce	$^5D_{3/2}$	$^2F_{7/2}$, $^2F_{5/2}$
Pr	$^3H_5$, $^3F_2$	$^3H_4$
Nd	$^4G_{5/2}$, $^2G_{7/2}$, $^4G_{7/2}$	$^4I_{9/2}$
Pm	$^5G_{12}$, $^5G_3$	$^5I_4$
Sm	$^4H_{7/2}$, $^6F_{1/2}$, $^6F_{3/2}$	$^6H_{5/2}$
Eu	$^7F_2$	$^7F_1$, $^7F_0$
Gd	$^8S_{7/2}$	$^6P_{7/2}$, $^6P_{5/2}$
Tb	$^7F_5$	$^7F_6$
Dy	$^6F_{11/2}$, $^6H_{13/2}$, $^6H_{11/2}$	$^6H_{15/2}$
Ho	$^5G_6$, $^3H_6$	$^5I_8$
Er	$^2H_{11/2}$, $^4G_{11/2}$	$^4I_{15/2}$
Tm	$^3F_4$, $^3H_4$, $^3H_5$	$^3H_6$

Table 1.4b Energy levels of RE elements

There are 14 rare earth elements and they lie between lanthanum (^{57}La) and hafnium (^{72}Hf).Their atomic configurations consist of partially filled 4f shells. It is important to note that ions with either filled 4f levels such as Lu^{3+} or ions that have no 4f electrons such as La^{3+}, will have no electronic energy levels to induce excitation in/or near the visible region. The azimuthal quantum number (l) of 4f *orbitals* is 3, which gives $2l + 1 = 7$ orbital state (7 orbital orientations) and allows 14 electrons to stay. In the non excited state, these electrons will be distributed in such a way that they will have the maximum combined spin angular momentum (S). According to Hund's rule, the spin angular momentum S is added to the orbital angular momentum L to give the total angular momentum J. For the lowest ground state, $J = L - S$, when the number of 4f electrons is less or equal to 7, and $J = L + S$, when the number of 4f electrons is larger than 7.

1.4.1 Electronic Transitions:

An electronic state is indicated by notation $^{2S+1}L_J$, where L represents the letters S, P, D, F, G, H, I, K, L, M, N… corresponding to the resultant orbital quantum number of 4f electrons $L = 0, 1, 2, 3, 4, 5, 6, 7, 8$ respectively. An electronic state is actually

expressed as an intermediate coupling state and can be described as a mixed state of several $^{2S+1}L_J$ states and a spin–orbit interaction. This mixing due to spin–orbit is actually small for the levels near the ground states, and it is larger for the states that are neighbors with the same J numbers. The effect of the mixing is very large in the optical transition probabilities, although it is relatively small on the energy levels. Rare earth ions (doubly or triply charged) can be present in ionic solids. For the case of the triply charged, all $5d$ and $6s$ orbitals are empty and the $4f$ is partially occupied. The optically active $4f$ electrons are shielded from the crystalline electric field by the outer $5s$ and $5p$ shells. The resulting effect is that the neighboring ligands have very little affection on the $4f$ electrons. The energy levels of the $4f$ electrons are very similar to the free ion levels characterized by the L, S, and J values with allowance made for some term mixing and this is because of the weak interaction with the lattice environment. The spectral lines (either of emission or absorption) are sharp and the energy positions are not (usually) crystalline host dependent. For the case of divalent rare earth ions, the energy separation between the $4f^n$ and $4f^{n-1}5d$ configurations will be large and the transitions between these two may be observed by normal spectroscopy. These transitions are dipole-allowed and are about 106 times stronger than the very frequently observed $4f \rightarrow 4f$ transitions in trivalent (rare-earth) ions. The emission and excitation spectra of the divalent europium ion are mainly composed of two types of electronic transitions: a strong $4f \rightarrow 5d$ transition with a high energy and a weak $4f \rightarrow 4f$ transition at low energies. The gross feature of the spectra of this type of rare earth ions is considered to arise from the T_{2g} and E_g components of the $5d$ electron in the cubic crystalline field. The strongest lines were actually assigned to pure electronic transitions from $4f^n$ to $4f^{n-1}5d$ which was assumed to be caused by the interaction between the $4f^{n-1}$ core and the $5d$ electron, the $4f^{n-1}5d$ level being spaced with the energy gaps in the $4f^{n-1}$ ground multiplets.

Optical absorption of $4f$ electrons transitions is strongly forbidden by the parity selection rule. However, this rule can be relaxed. When an ion occupies a crystalline site there are uneven components of the crystal field. These components mix a small amount of opposite parity wave functions into the $4f$ wave functions, and this causes intra-configurational $4f$ transitions to gain some intensity. The allowed optical inter-configurational transitions for rare earth ions are divided into two types: $4f\,n \rightarrow 4f^{n+1}L^{-1}$, L = ligand (charge-transfer transitions) and $4f^n \rightarrow 4f^{n-1}5d$ transitions. And both are allowed and have broad absorption band. The first type of charge transfer is

found in rare earth elements that like to be reduced and is commonly observed in tetravalent rare earth ions. The second (5d transition) on the other hand is found for the ones which like to be oxidized and is commonly observed in divalent rare earth ions.

1.4.2 Stark Splitting:

As mentioned above, 4f electrons of rare earth are shielded from crystal environment by 5s and 5p shells. However, in a crystal field, the J degeneracy of spin–orbit state $^{2S+1}L_J$ can be shifted and split. This is called Stark splitting. In other words, this effect is the splitting of the spectral line into several components in the presence of an electric field. This effect is the analogous to the Zeeman Effect in a magnetic field, but in this case the splitting is not symmetric. This splitting only occurs when the ion is polarized by the electric field resulting in a dipole moment. This dipole moment only depends upon magnitude (M_J), not direction, so the energy levels will be split into $J + 1$ or $J + 1/2$ levels. This splitting is usually much less than the separation of the spin–orbit levels. Because of this, the main features of the energy levels diagrams remain almost unchanged for the rare earth ions in different host materials. On the other hand, the crystal-field splitting will vary for different host, and it will show the different symmetries and strengths of the crystal fields.

1.4.3 Multiphonon Process:

Most 4f emitting levels are separated from the next lower level in a distance of at least 2×10^3 cm^{-1}. Excited states of this kind release their energy via either of two competitive ways: light emission or by phonon emission. The rate of phonon emission is dependent on the number of phonons emitted at the same time to bridge the energy gap. The probability of multiple phonon transitions is given by the relation: $w \propto \exp^{-kE}/ h\nu_{max}$ where w is the phonon transition rate, E is the energy gap closest to the lower level and $h\nu_{max}$ is the maximum energy of phonons (coupled to the emitting states). When E increases the phonon emission rate decreases rapidly; therefore, the competitive light emission process (radiative) becomes the dominant one. On the contrary, if the phonon energy is large or E is small, the phonon transition probability can be very high, and the radiative transition of the upper excited level can be seriously quenched.

1.4.4 Crystal Field Splitting:

Wave functions of $5d$ of rare earth such as Eu^{2+} and $3d$ electrons of transition ions such as Mn^{2+} are quite extended. They will strongly interact with ligand ions in crystals. As a result, the resultant orbital states of d electrons will be split. The splitting is usually much larger than the splitting by L–S coupling. Crystal-field splitting depends on several factors:

(1) Number of electrons in the d orbitals.

(2) Oxidation state of the crystal (a high oxidation state will lead to a high-energy splitting).

(3) The arrangement of the ligands around the crystal.

(4) The nature of the ligands.

The most common type of complex is the octahedral. In this case, six ligands form an octahedral field around the metal ion and the ligands point directly into the d-orbitals and cause high-energy splitting. The second most common type of complex is the tetrahedral, for this case four ligands form a tetrahedral field around the metal ion, for this case the electrons are not oriented directly against the orbitals; therefore, the energy splitting level is lower than the previous case. The physics of this phenomenon is the following: as we know the transition metals have ions with partially filled orbitals (five of them) and they are degenerate. When a ligand approaches the metal ion, the electrons from the ligand are at different distances to the d-orbitals, and the electrons in the d-orbitals and the ones in the ligand have an acting repulsive force, because the d-orbitals are repulsed unequally by the ligand, and obviously the d-orbitals will split into energy. In some cases, there are more than one d-electron and in these cases we observe a strong crystal field.

1.4.5 Energy Transfer:

The process in which the excitation of a certain ion migrates to another ion is called energy transfer. It is very important to understand this effect in order to develop efficient luminescent materials. The luminescent materials had several types of energy transfer.

1) **Resonant energy transfer between ions of same energy level**- for this case, the excitation energy of a certain ionmigrates to another one of the same species that is in the ground state. This type of transfer is also divided into

three categories: First, multipolar interaction, and this is both transitions are of electric dipole character; the second is the exchange interaction, and this is when the donor and the acceptor are both located so close that their electronic wave functions overlap and the transfer is due to a quantum mechanical interaction; and lastly, the phonon-assisted energy transfer, which occurs when there is a difference E between the transition energies of the donor and the acceptor, and is compensated by either a phonon emission or absorption.

2) **Spectral diffusion-** in this case, the excited ion can give its energy to other ions that are at different sites and/or lattice environment, due to the fact that the doping ions stay at a slightly different lattice environment. This will translate to a shift in the emission spectrum to longer wavelengths and an increment on the width of the emission peak.

3) **Energy donation**- in this case, the energy transfer can occur between different ions, one of them is called a donor and the other an acceptor. An ion at an excited higher energy level can transfer most of its energy to other ions. The other ions stay at a lower energy levels and release the differential energy in the form of phonons.

4) **Sensitizer's transfer**- a donor that usually has a strong absorption of external radiation and transfers it very efficiently to an acceptor is called a sensitizer; the caused emission is greatly enhanced. This process is also known as sensitization of the luminescence.

5) **Quenching centers transfer**- in this case, the acceptor kills the emission of the active center or the donating ions, and these ions neither emit at the required wavelength nor emit at all. Mostly, the phosphors that exhibit this type of luminescence are activated by sensitizers or co-activators (i.e. Mn2+).

It is important to determine the optimum concentration of dopant to be used, in order to obtain efficient luminescence with a minimum energy loss. For display application, the purity of color is the most important issue. For many ions emissions can be from different upper excited states. The way to keep this emission from the upper states from occurring, and to purify the luminescence is to quench the emission via cross relaxation. In this process, the excited ions from the upper states prefer to release part of their energy to the neighboring ions at the ground state, and then move to the lowest metastable state. Then these ions will return to the ground state and release the remaining energy at the desire wavelength. In order to be able to do this, the doping

concentration should be sufficiently high, but it is important to note that in a heavily doped system the average distance between the ions becomes smaller, and therefore the excited ions can move around in the host causing resonant energy transfer. Such transfer gives more chance to send the excitation to a quenching center, which will release the energy through a non radiative process. This phenomenon is called concentration quenching, as we briefly described earlier. A compromise concentration should then be determined and this will give an efficient sensitization (efficient upper-state quenching) and a maximization of the number of activators to participate in the luminescence process. However, the concentration should not lead to any concentration quenching. These centers also can produce an undesired afterglow. The sensitization is used to enhance the energy excitation efficiency. In rare earth phosphors, when UV or VUV radiations populate optically a 5d state, radiative and/or non radiative channels are available for energy relaxation in the solid state. Energy transfer to the emitting 4f level occurs through lattice phonon relaxation and intra-system energy crossing when the energies match. The efficiency of the latter process depends upon the magnitude of the square overlap integrals between absorption and emission. Following the well-known configuration coordinate model, coordinate displacement between the equilibrium positions of the ground and 5d excited states, called the Franck–Condon shift, can be adjusted in phosphor design by choosing suitable host anionic groupings in order to fix the emission frequency or to increase the phosphor efficiency. It is worthwhile considering that the variation of the energy of the lowest 4f–5d level versus the number of f-electrons in the shell follows the variation of 3+/4+ redox potential along the lanthanide series. It is related to the ability of the trivalent rare earth ion to lose one electron, and consequently to the stabilization energy of the 4+ state. In large band gap materials, the energy levels of the impurity center are sparsely distributed between the valence and conduction bands.

1.5 Introduction to Thermoluminescence:

1.5.1 Historical Background of Luminescence Phenomenon:

Historically, Thermoluminescence (TL), or more appropriately Thermally Stimulated Luminescence (TSL) may be said to have its beginning in 1663 with Robert Boyle reported to the Royal Society of London on 28 October, 1663 his observation (Sir

Robert Boyle, Experiments and Considerations Touching Colours, 1664): "Eleventhly, I also brought it some kind of glimmering light by taking it (natural diamond) into bed with me and holding it a good while upon a warm part of my naked body." Not much later Elsholtz (1676) observed similar effect in fluorspar (Encyclopedia Britannica). In 1705, Oldenberg described the phenomenon of thermoluminescence in the mineral, fluorite. However, experimental and radiation induced TSL under its modern name in a wide variety of natural and synthetic materials was probably first reported by Wiedemann and Schmidt (1895) of Germany in an article entitled "On Luminescence" in a then widely read and highly regarded scientific journal. Wiedemann and Schmidt were probably the first to report the TSL of at least two of the modern materials widely used, viz. fluorite and CaF_2: Mn. They also spoke of the possibilities of TSL of glasses and borates. But the real boost can be said to have been given in the late 1940s and early 1950s by the pioneering work of Farrington Daniels and his group at the University of Wisconsin (USA).

Farrington Daniels and his group first suggested the use of TSL as a technique in radiation dosimetry through studies on LiF as a TSL material. Lithium fluoride was used to measure radiation dose after an atomic bomb test. Soon the idea of using TSL in dosimetry caught on and many groups started working in the field of thermoluminescent dosimetry (TLD). It became evident that in LiF the desirable properties of the material were the result of the interplay between the complex defects present within the material resulting from the presence of the Mg and Ti. This realization emerged from the work of Cameron and colleagues and this work led eventually to the patenting of TLD-100 by the Harshaw Chemical Company in 1963. In the last few decades there has been tremendous research in this field. Thermoluminescence (TL), as an experimental technique, finds application in diverse scientific disciplines such as radiation dosimetry, archaeology, geology, medicine, solid state physics, biology and organic chemistry. In the last four decades, many new and dosimetrically useful TLD materials were reported: $Li_2BV_4O_7$:Mn, CaF_2:Dy, $CaSO_4$:Dy and $CaSO_4$:Tm BeO; Al_2O_3:Mg,Y and Al_2O_3:Si,Ti, CaF_2:Tm, LiF:Mg,Cu,P; $Li_2B_4O_7$:Cu and MgB_4O_7:Dy or Tm, Al_2O_3:C. Subsequently, a large number of laboratories have also been successful in preparing LiF: Mg, Cu, P; BeO; $CaSO_4$: Dy or Tm and some other TLD phosphors as reported by Akselord et al. The presence of rare-earth ions in the natural fluorite (CaF_2) as efficient emission centers, led to the development and study of rare earth doped phosphors such as CaF_2:Dy,

CaF_2:Tm, $CaSO_4$:Dy, $CaSO_4$:Tm and Mg_2SiO_4:Tb. These phosphors have proved to be more sensitive in comparison to LiF: Mg, Ti phosphor.

The late nineteenth-early twentieth century was dominated by studies on natural minerals. Natural CaF_2 was used by Marie Curie to detect radiations from radium source. X-ray induced TSL studies on $CaSO_4$:Mn were carried out by Wiedemann and Schmidt but its use as a possible TSL dosimeter was demonstrated by Akiyama et al.. Despaired with unpredictable properties of LiF, Daniels group turned their attention to the next material, Al_2O_3 in the form of sapphire was high grade optical material, but due to lack of sensitivity, lost its credibility. In 1957, two new materials BeO and CaF_2: Mn made their appearance. CaF_2: Mn had major impact in this field due to its excellent sensitivity and simple glow curve structure. It is the first TLD material in this field and still never went back seat any time.

Another remarkable newcomer was LiF: Mg, Cu, P but remained unnoticed until the group at Solid Dosimetric and Detector Laboratory in Beijing reported the manufacture of a LiF: Mg, Cu, P TLD material, known as GR-200, in 1986. This is reported as an ultra-sensitive material with sensitivity as high as 50 times that of TLD-100. This is followed by even more sensitive material, Al_2O_3:C. These two materials are now dominating the field of TLD material research. At the 12th International Conference on Solid State Dosimetry, it was reported that LiF:Mg,Cu,Na,Si has a similar glow curve shape to that of LiF:Mg,Cu,P but the relative TSL sensitivity is about 2 times that of LiF:Mg,Cu,P. General processes involved in TSL had been developed by Randall and Wilkins; Garlick and Gibson gave a theoretical basis to this phenomenon.

The TSL phenomenon has a very high sensitivity of detecting the presence of defect centers which are responsible for the TL process. It was estimated that the technique is capable of detecting as few as 10^9 defects levels in the material. TSL is one of a family of processes collectively known as thermally stimulated phenomenon. Other members of the family are thermally stimulated conductivity (TSC), thermally stimulated capacitance (TSCap), thermally stimulated polarization (TSPC) and depolarization currents (TSDC), including ionic thermo currents (ITC), deep level transient spectroscopy (DLTS), thermo- gravimetry (TG), and several more. Each of these phenomena may be described by two fundamental stages: Stage I, the perturbation of the system from equilibrium into a metastable state; and stage II, the thermally stimulated relaxation of the system back to equilibrium. In each of the

above techniques, one monitors the non-isothermal change of a particular property of the material (e.g., luminescence, conductivity, capacitance, etc.) as the system returns to equilibrium during stage II.

In the case of TSL, stage I necessitates the absorption of energy, normally from ionizing radiation, in order to perturb the material into a non-equilibrium state. Energy storage occurs through the processes of electron-hole pair production, exciton creation, and/or direct displacement damage, followed by charge localization (trapping) at defects within the host lattice of the irradiated material.

During stage II, the stored energy is released as the temperature of the sample is increased, and a fraction of the released energy appears in the form of luminescence. The luminescence originates from electron-hole recombination or vacancy-interstitial recombination. In either case, electrons undergo de-excitation from metastable excited states to the ground state, thereby restoring equilibrium. The simplest manner in which this can be achieved is via electron– hole recombination of thermally freed charges. The recombination process results in the emission   of phonons (non-radiative recombination) or photons (radiative recombination). It is the latter that are monitored when recording the TL emission. Thus, we have the thermally stimulated return of the system from its metastable state to equilibrium, with a portion of the excess energy being liberated as light.

1.5.2 Theory of Thermally Stimulated Luminescence:

Basic Phenomenon: The phenomenon underlying the TSL process is usually explained on the basis of band structure of electronic transition in an insulating material exhibiting TSL. The figure 1.5.1 shows the simplest process one can visualize that can occur in the phosphor during and after exposure of ionizing radiation. TL is usually observed by heating a sample at a constant rate to some temperature (e.g. 500°C) and recording the luminescence emitted as function of temperature. The TL signal is characterized by a so-called "glow curve", with distinct peaks occurring at different temperatures, which relate to the electron traps present in the sample. Defects in the lattice structure are responsible for these traps. A typical defect may be created by the dislocation of a negative ion, providing a negative ion vacancy that acts as an electron trap. Once trapped, an electron will eventually be evicted by thermal vibrations of the lattice. As the temperature is raised these vibrations get stronger, and the probability of eviction increases so rapidly that within

a narrow temperature range trapped electrons are quickly liberated. Some electrons then give rise to radiative recombinations with trapped "holes", resulting in emission of light (TL). Although a TL glow curve may look like a smooth continuum, it is composed of a number of overlapping peaks derived from the thermal release of electrons from traps of different stabilities.
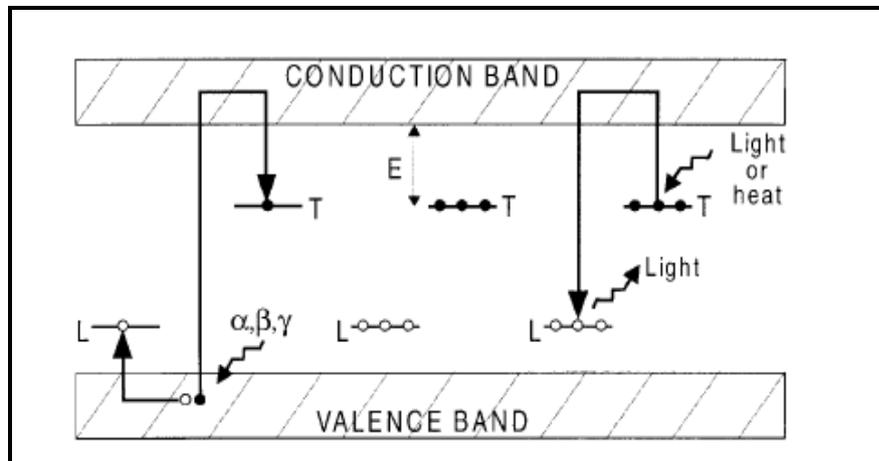
Fig. 1.5.1 Energy-level representation of TL process showing schematic of ionization, storage, and eviction (T = Electron Trap, and L = Luminescence Center)

The TL process can be summarized as follows:

(i)   Ionization is due to exposure to nuclear radiation with trapping of electrons and holes at defects T and L, respectively.

(ii)   Storage of radiation energy during time; if leakage is negligible the lifetime of the electrons in the traps needs to be much longer than the storage time of the sample. This lifetime is dependent on the energy depth E of the trap below the conduction band.

(iii)   By heating the sample, electrons are evicted from the electron traps and some of these reach luminescence centers (L); if so, light (i.e. TL) is emitted as a result of the process of recombination into these centers.

Dynamics of De-trapping (Trap-emptying Process): Release of the charge carrier, i.e., the trapped electron or the hole from its trapped position is the most important step in the emission of TL. The release of the charge carrier can be achieved in two ways:

- Optical stimulation
- Thermal stimulation

In optical stimulation, an optical photon of energy greater than the binding energy of the charge carrier can knock it out from its trap by direct hit. In contrast to this the thermal stimulation process consists of multiple hits. The energy required for the release of the charge carrier is called the thermal activation energy. It is observed that thermal activation energy is always smaller than the optical activation energy. This arises due to the change in the configuration co-ordinates of the trap in the excited state than in the normal state.

How does an electron trapped at a depth of 1 eV get free at a temperature barely 100-200 ^{o}C?

This question is important because the average thermal energy available at 200°C is = 3/2k (273+200) = 0.04 eV only, which is much smaller compared to 1eV (the activation energy). The Maxwell-Boltzmann distribution for a system in equilibrium at temperature T tells that the fraction of the particles having thermal energy of 1eV above the ground level is $N/No = e^{-E/kT}$. For E=1eV and sample temperature, T=200°C, this fraction would be about 10^{-13}.

It is only this fraction which is capable of escaping from the trap. This, however, is an incredibly small fraction to make an impact on the total population of the charge carriers in the traps. Yet the traps get emptied in 'no time' when the sample temperature is raised quickly to the peak temperature of the glow curve.

How does this happen?

Two factors are reasonable for this:

The few energetic electrons (E≥1 eV) make an attempt to escape into the conduction band at an incredibly fast rate. The attempt frequency is as high as 10^{13} second (vibrational frequency) this is called 'frequency factor' or more precisely 'attempt to escape frequency'. How does an electron or a hole make an attempt? –It is by jumping and knocking around randomly. Some knocks may push it backward from the 'mouth' of the trap. Probability for escaping from the traps is given as

$$p = s \exp\left(\frac{-E}{kT}\right)$$

Where, s=frequency factor. If s=10^{13} and N/N0=10^{-13}, then P=1 per second. This means, 100 % probability for escaping from the traps. Apparently, only an insignificant fraction, i.e., 10^{-13}, is able to escape at any point of time when the glow peak is being emitted.

The second factor which helps to empty the traps quickly is the rapidness with which thermal equilibrium (Maxwell-Boltzmann distribution) is re-established after the charge carriers with E≥1eV (i.e. 10^{-13} fraction) have escaped. To visualize the rapidness with which equilibrium is re-established, we need to remember that the particles in equilibrium at room temperature have a velocity of 2000 ms^{-1}, which is approximately equivalent to 2×10^{13} lattice distances. This means that in 1 second 2×10^{13} knocks are exchanged by a single particle. Due to such a high frequency of collisions, the equilibrium is re-established quickly. Thus once again we have particles with energy E≥1eV. The process of re-establishing equilibrium and escaping (de-trapping) thus sustains (the phonon relaxation time is 10^{-13} second).

Mathematical Description:

First Order Kinetics:

The most simplified mathematical model which describes the above process was first given by Randall and Wilkins.

Consider a material containing defects which give rise to a single electron trap level, having trap depth or activation energy E containing n electrons at time t and at temperature T (in kelvin). The energy distribution of electrons within the trap will be described by Boltzmann distribution and hence the probability p of release of an electron from the trap is given by the Arrhenius equation,

$$p = s \exp\left(\frac{-E}{kT}\right) \qquad (1)$$

where, k is Boltzmann's constant and s is a frequency factor or attempt to escape factor having value in the order of the lattice vibration frequency, namely 10^{12} - 10^{14} s^{-1}. The rate of release electrons from the trap is

$$-\left(\frac{dn}{dt}\right) = ns \exp\left(\frac{-E}{kT}\right) \qquad (2)$$

Randall and Wilkins [18] assumed that all electrons released from traps undergo TSL transitions, i.e., there is no re-trapping. This leads to the concept that the rate of release is proportional to the trapped charge concentration, and thus termed a "first-order" reaction. The intensity of the TSL glow, I(t) depends on the rate of release of electrons from traps and their rate of arrival at luminescence centers,

$$I(t) = -C\left(\frac{dn}{dt}\right) = Cns\exp\left(\frac{-E}{kT}\right) \qquad (3)$$

Where C is a constant related to luminescence efficiency.

 If we define rate of heating as

$$\beta = \frac{dT}{dt} \qquad (4)$$

Equation (2) becomes,

$$\left(\frac{dn}{dT}\right) = -\left(\frac{1}{\beta}\right)ns\exp\left(\frac{-E}{kT}\right) \qquad (5)$$

On integration, we get

$$\ln\left(\frac{n}{n_0}\right) = -\int\left(\frac{1}{\beta}\right)s\exp\left(\frac{-E}{kT}\right)dT \qquad (6)$$

Where n_0 is the number of electrons present in the trap at time t_0 and temperature T_0. Finally, substituting for n in equation (3),

$$I(T) = n_0 s\exp\left\{\frac{-E}{kT}\right\}\exp\left\{\frac{-s}{\beta}\int_{T_0}^{T}\exp\left(\frac{-E}{kT}\right)dT\right\} \qquad (7)$$

This is the expression for the glow intensity I from electrons trap at a single trapping level E. It is a Randall and Wilkins expression for first order (monomolecular) kinetics. The plot of I against T is termed as glow curve. The glow curve has a characteristics asymmetric shape being wider on the low temperature side than on the high temperature side. The condition of maximum intensity can be found by differentiating equation (7) with respect to T and equating the derivative to zero (i.e., $(dI/dT)_{T=Tm} = 0$) which yields,

$$\frac{\beta E}{kT_m^2} = s\exp\left(\frac{-E}{kT_m}\right) \qquad (8)$$

where T_m is glow peak temperature. From eqns. (1) and (8), it is concluded that greater the value of E and the value of s, the greater is the thermal stability of the trapped electrons and hence the higher is the temperature of the glow peak.

35

Second Order Kinetics:

A modification of this view was presented by Garlick and Gibson, who used this same one-trap, one-recombination center model but who included the concept of significant re-trapping of the released charges. This leads to the rate of the reaction being proportional to the square of the trapped charge concentration, and thus, we have a "second-order" reaction. Here we have,

$$\frac{dn}{dt} = -n^2 s' \exp\left(\frac{-E}{kT}\right) \qquad (9)$$

Where $s' = s/N$, and N is the total concentration of available electron traps. This leads to the Garlick-Gibson equation for TSL under second-order kinetics:

$$I(T) = \frac{n_0^2 s' \exp\left[-\frac{E}{kT}\right]}{\left[1 + \frac{n_0 s'}{\beta} \int_{T_0}^{T} \exp\left(\frac{-E}{kT}\right) dT\right]^2} \qquad (10)$$

The main feature of this equation is that the glow is nearly symmetric, with the high temperature half of the curve slightly broader than the low temperature half. This can be understood from the consideration of the fact that in the second order reaction, significant concentrations of released electrons are re-trapped before they recombine in this way giving rise to a delay in the TSL and spreading out of the emission over a wider temperature range.

General Order Kinetics:

The Randall-Wilkins and Garlick-Gibson forms of TSL equation have been derived with the use of specific assumptions concerning the relative values of the re-trapping and recombination probabilities. However, when these simplifying assumptions do not hold, the TSL peak will fit neither first- nor the second order kinetics. May and Partridge gave the following empirical expression for general order TSL kinetics:

$$I(t) = -\frac{dn}{dt} = n^b s' \exp\left(\frac{-E}{kT}\right) \qquad (11)$$

where s' has the dimension of $m^{3(b-1)}s^{-1}$ and b is defined as the general-order parameter and is not necessarily 1 or 2. Integration of the above equation for $b \neq 1$ yields,

$$I(T) = s''n_0 \exp\left(\frac{-E}{kT}\right) \times \left[1 + (b-1)\frac{s''}{\beta}\int_{T_0}^{T} \exp\left(\frac{-E}{kT}\right)dT\right]^{-b/(b-1)} \quad (12)$$

Where $s'' = s'n_0^{b-1}$ with units s^{-1}. The above equation includes the second-order case (b=2) and reduces to equation (7) when b → 1. It should be noted that the dimensions of s' is $m^{3(b-1)}s^{-1}$ which means that the dimension changes with the order of kinetics b. Thus, it is difficult to interpret s' physically.

The theoretical mechanism discussed above is related only to electrons trapped at a single trapping level. In real phosphors many different trapping levels will be present, each one due to a particular lattice defect or complex of defects. Each trapping level will give rise to an associated glow peak maximum, which may or may not be resolved during readout. The area and peak height of each glow peak depends on number of associated electron traps present. This in turn depends on the number of lattice defects and, for real phosphors, on the type and amount of impurity atoms present, as well as on the thermal history and treatment of the material.

Determination of TSL Parameters:

During the process of TSL, part of energy, absorbed by the phosphor crystals, is re-emitted during subsequent heating in the form of light. The plot of the TSL intensity (light output) as a function of rising temperature (at a constant rate of increase in temperature i.e. $\beta = dT/dt =$ constant) exhibits one or more peaks and is called a glow curve.The glow curve provides a useful tool for studying the traps and trapping parameters (such as trap depth E, kinetic order b and frequency factors, etc.). Number of methods based on different models that explain the TSL behavior of different phosphor systems, have been developed for determination of trapping parameters utilizing the glow curve technique. Based on these models different expressions have been derived for calculation of electron or hole trap depths from conduction or valence band respectively, using different experimental methods such as shape of the glow curve, glow peak maxima and change in the maximum peak temperature and different heating rate and isothermal decay method

The values of trap depths for the same material by different methods are found to be somewhat different and also discrepancies in the results are observed when the same material is used by different workers for the calculation of trapping parameters. These discrepancies are because of different approximations and models used by different workers, different levels of impurities present in the sample and various experimental conditions employed. However, the study of trapping parameters gives definite information regarding the order of kinetics, trap (energy) distribution and frequency factor.

These methods can broadly be divided in the following categories:

Empirical method, Initial rise method, Variable heating rate, Isothermal decay method, Peak shape methods and Numerical curve fitting method.

All these methods require reliable temperature control and separation of glow peaks is a necessity in most of the glow curves as these methods mainly use peak resolution technique. However, in complex glow curves it may not be that easy.

The isothermal decay method, for determination of thermal activation energy, is the only method, which is not affected by temperature and emission spectra and allows estimation of the order of kinetics b for general order case. For the first-order kinetics, the TSL will decay exponentially with time and a plot of $\ln(I/I_0)$ vs. t will give a straight line of slope $m = s \exp(-E/kT)$. If the decay is monitored at several different temperatures a plot of $\ln(m)$ vs. $1/T$ will give a straight line of slope E/k from which E can be calculated. The intercept will give $\ln(s)$. The general order feature of the isothermal decay of TSL can be demonstrated if a plot of $I^{(1-b)/b}$ vs. t yields a straight line. Since the value of b is not known before hand, a straight line will only be obtained when correct value of b is inserted. The initial rise method is a widely used method for calculating trapping parameters (E & s) and is independent of order of kinetics. However, it is affected by satellite peaks and by thermal quenching.

1.5.3 Applications of Thermoluminescence:

The applications of the phenomenon of TSL to the measurement of dose have progressed a great deal since the initial work by Daniels et al. Several thermoluminescent phosphors are now used routinely in many dosimetric applications for environmental monitoring, personnel dosimetry and medical applications. For dosimetric applications, it is always desirable to use TLD phosphors in various physical forms, as routine measurements with loose powder are quite cumbersome

38

due to associated weighing of individual powder samples. A large number of dosimetric phosphors are now available in various physical forms such as single crystals, extruded ribbons (chips) in different thickness (0.15 to 0.8 mm), microrods, and sintered pellets and as thin substrates for beta and charged particle dosimetry. However, among the large number of thermoluminescent materials investigated and described in the literature, only a few have been found to be attractive for dosimetry purposes, especially for applications in connection with personnel and environmental dosimetry.

Applications of Thermoluminescence to Archaeology:

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

i)   It gives the exact date of kiln firings of the sample (the other methods mostly depend on the shape and style of the pottery and hence correlate with the civilization to which it belonged).

ii) TL dating is possible even beyond 30,000 years, but minimum age is 5 years with an accuracy of ±1 year.

iii) Authentication and detection of forgery can be quickly and easily done by using this method.

The TL/OSL dating is done from a quartz grain which is collected from pottery or brick by reading the TL-output. 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 sometime 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 onset 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 expressed 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, i.e.,

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

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

The accumulated dose absorbed by ceramic artifacts over their archeological or geological lifetime can be appreciable, and this dose lends itself to determination of its age using TSL. The materials of interest are ceramics containing luminescent materials – particularly quartz and feldspar that, when heated after irradiation exposure, emit TSL proportional to the time of their exposure. The radiation originates from cosmic rays and from gamma, beta and alpha irradiation from the local surroundings (due to traces of uranium, thorium and potassium). The "natural" signal is thus related to the age of the specimen by

$$\text{Age} = \text{Natural TSL} / (\text{TSL per unit dose}) \times (\text{natural dose rate})$$

Thus, age assessment consists of measurement of the natural TSL, calibrating the TSL signal from the material to determine the TSL per unit dose, and measurement of the natural dose rate in the location of the find. Strictly, the "age" being determined is the time since the TSL signal was last reset to zero. Thus, a "zeroing" event – such as high temperature heating (e.g., in the manufacture of pottery) or optical bleaching (e.g., during the deposition of sediments) – must have occurred in order for the method to be applicable. Otherwise, a TSL signal related to the geological age of the component mineral will be determined instead.

Application of TL in Biology and Biochemistry: Application of TL technique in the study of biological and biochemical systems is increasingly favoured in recent times and necessarily all the measurements are done in the LNT-RT range. 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 or 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 in the Z diagram 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 standardize 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 non-destructively 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 trails, 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 reduce 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.

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 start 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 it saturates. If one selects a material (e.g., quartz) with a negligible radioactivity in it, the accumulated TL mostly represents the environmental dose rate at a place from where the geological specimen was collected.

Accumulation of TL can be affected by natural light especially its ultraviolet component. In geology, the sunlight bleaching is considered to be the basis for dating the geological event. The exposure of sand grains to sunlight during their weathering and transport through wind and water results in bleaching of their geological TL. This bleaching is effective enough to reduce Thermoluminescence level to a negligible

value. These bleached sand particles, once embedded in a sand dune or beach, 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% or –5%.

Radiation Dosimetry:

In the present scientific world, ionizing radiations have been found very useful in 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 if possible the 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 to as dosimeters. Professionals 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 technique [TLD]
5. Optically stimulated luminescence technique [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 may 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. Some of the phosphors like LiF, $Li_2B_4O_7$, BeO, etc. which are nearly tissue equivalent score 4 definite points

over others like $CaSO_4$, CaF_2, Mg_2SiO_4, etc. which are however more sensitive. Many phosphors have been developed for TLDs.

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 in real practice. Later on they found that TLD technique is better for many reasons. And hence during last three to four decades they have developed and established the TLD technique. This has become popular now-a-days due to prominent applications of thermoluminescence dosimetry in radiation protection. The dosimeters have been widely used for in-phantom and in-vivo dosimetry in medical applications. Another area, where thermoluminescence dosimeters have found use is 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 scatter measurement around open top installations, area monitoring around radiation installations, etc. Rapid fading ratio of main TL low temperature peak of certain phosphors such as CaSO4: Dy has been used 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. Besides this, TL dosimetry also includes archaeological dating, i.e. dating of ancient potteries and ceramics, space dosimetry, dosimetry of non-ionizing radiations such as UV and microwave dosimetry. 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 application in agriculture. In this field their use is mainly concerned with high level photon dosimetry such as dose measurement in food preservation, radiation sterilization of seed, pest control, etc. Formally, the dose measurement in agriculture relied heavily on chemical dosimeters, e.g., the ferric

(Fe^{2+}, Fe^{3+}) system. TLDs constitute a less expensive method and are applicable in the dose range of 10^{-4} to 10^{8} rad.

TSL Dosimetry:

In TSL dosimetry the relationship between the TSL signal and the absorbed dose to be measured must be determined by an appropriate calibration. Thermoluminescent Dosimeters (TLDs) have found increasing application with the progress made in the development of solid thermoluminescent dosimeters and instrumentation for reading them. Many TLD based systems are now commercially available, and are widely used in routine personal dosimetry, environmental monitoring and clinical radiation dosimetry. The extreme sensitivity of TSL for detecting the presence of defects, as few as 10^{9} within a specimen, is beneficial for detecting low radiation levels which are encountered in personal and environmental monitoring.

Thermoluminescent Dosimeters (TLDs) are increasingly accepted for radiation dosimetry for the following reasons:

    a. The existence of nearly tissue equivalent thermoluminescent materials;

    b. Sufficiently high sensitivity and accuracy for both personal and environmental monitoring;

    c. Commercial availability as small sized solid detectors adaptable for both manual and automatic processing;

    d. Suitability for skin and extremity dosimetry;

    e. Availability of materials with excellent long-term stability under varying environmental conditions;

    f. Ease of processing;

    g. Reusability; and

    h. Linearity of response with dose and dose rate over a large range.

Environmental Dosimetry:

In recent years, regulatory authorities in many countries have become more acutely aware of the increasing concern demonstrated by the public with regard to the potential environmental impact of "man-made" radiation exposure, controlled releases of gaseous radio-nuclides from nuclear power stations during day-to-day operations, low-level waste disposal, nuclear fuels reprocessing, incidents of nuclear power station accidents and activities connected with nuclear power industry have led to widespread public concern about possible detrimental effects to the public.

1.6 About the present work:

In recent years, great effort has been devoted to the controllable synthesis of rare earth-doped nano particles driven primarily by the fact that doped nano crystalline phosphors yielded high luminescence efficiencies. With rapidly shrinking size, nano materials display novel shape and size-dependent properties for their extremely small size and relatively large specific surface areas. Based on these unique and fascinating properties, rare earth doped nano crystalline materials may play an important role in display devices, optical telecommunication, solid-state lasers, and so on. Therefore, the development of a facile synthetic method toward high quality rare earth nanocrystals with uniform size and shape is very important for the exploration of new research and application fields.

Rare-earth-doped phosphors are known to emit at distinct and different wavelengths in the electromagnetic spectrum and have been widely used in color cathode ray tubes (CRT), tri-phosphor fluorescent lamps, X-ray intensifying screens and newly developed vacuum mercury-free lamps, as well as various types of displays such as plasma display panels, field emission displays and projection TVs. Recently, breakthroughs in inorganic light emitting diodes (LEDs) technology are significantly catalyzing the development of energy-efficient solid-state lighting (SSL) with long lifetime. Solid-state lighting technology has now already penetrated in a variety of specialty applications, in effect; LEDs have completely changed the "world of luminance", for example automobile brake lights, traffic signals, liquid crystal displays and mobile backlights, flashlights and all manner of architectural spotlights. Laser detection phosphors [LDP] are used to detect the presence of lasers in the infra-red region by converting the energy to visible. The rare earth phosphates have technological importance. Lanthanum phosphate ($LaPO_4$) possesses various properties of technological importance.

- Very low solubility in water.
- High thermal stability.
- High refractive index.

$LaPO_4$ has been found to be a suitable and effective deboning material for high-temperature oxide/oxide composites, however, the properties of lanthanide compounds depend strongly on their composition and morphology. $LaPO_4$ powder can be synthesized from direct solid–liquid reaction of lanthanum oxide and

phosphoric acid. Although it is a simple and effective synthesis route, the shape of the particles is hard to control and the morphology is heterogeneous. Other synthesis methods, such as sol–gel or template based methods are capable of controlling the size, morphology, and crystallization degree of nanoparticles. The experimental process, however, is quite complex.

In this thesis the effect of trivalent RE ions Ce-Tb, Tb-Ce, Eu-Tb and Ce-Eu-Tb with various concentrations of Tb, Ce, Eu doped in $LaPO_4$ is studied. These phosphors are synthesized using solid state reaction. The emission spectra of $LaPO_4$ sample doped with terbium and other combinations at different molar percentages were recorded with excitation wavelength of 254 nm at room temperature and their characterization like SEM, XRD, FTIR, EDAX and particle size analysis are discussed in this thesis. In $LaPO_4$ doped Ce^{3+}, Eu^{3+} and Tb^{3+} phosphor due to the little difference between ionic sizes of Eu^{3+} ion and La^{3+} ion, Eu^{3+} ions can occupy La^{3+} ion sites, which gives rise to a characteristic crystal splitting of the energy levels. The Ce^{3+} and Eu^{3+} ions sensitize the luminescence of Tb^{3+} ions and good PL intensity is obtained. The materials studied are very attractive luminescent properties for the generation of the three primary colors, due to the red, green and blue emissions of $LaPO_4:Eu^{3+}$, $LaPO_4:Tb^{3+}$ and $LaPO_4:Ce^{3+}$, respectively.

The most important rare earth phosphors are Y, Eu, and Tb, which are used to emit light at the wavelengths (and therefore colors) to which our eyes are most sensitive. These three elements are used in different combinations of phosphors to emit blue, red, and green light.The phosphors consisting of a rare earth phosphate (RE PO_4) (RE = La, Y, Eu, Tb, Gd) matrix doped with RE cations find important applications, especially in optoelectronic and biomedicine. For most of these applications, particles with uniform shape and narrow size distribution are highly desirable.

In this thesis the effect of trivalent RE ions Tb-Eu, Gd-Eu, Tb-Gd-Eu with various concentrations of Tb, Gd, Eu doped in $LaYPO_4$ is studied. These phosphors are synthesized using solid state reaction. The emission spectra of $LaYPO_4$ sample doped with Europium and other combinations at different molar percentages were recorded with excitation wavelength of 254 nm at room temperature and their characterization like PL, TL, SEM, XRD, FTIR, EDAX and particle size analysis are discussed in this thesis. The following phosphors are synthesized and studied for their PL and characterized using SEM, XRD, FTIR, EDAX and particle size analysis.

List of Prepared Phosphors (LaPO$_4$ base)

Sr. No.	Chemical formula of the Sample
1	Base compound LaPO$_4$
2	LaPO$_4$: Ce (0.5%)
3	LaPO$_4$: Eu (0.5%)
4	LaPO$_4$: Tb (0.5%)
5	LaPO$_4$: Ce (0.5%), Tb (0.1%)
6	LaPO$_4$: Ce (0.5%), Tb (0.5%)
7	LaPO$_4$: Ce (0.5%), Tb (1.0%)
8	LaPO$_4$: Ce (0.5%), Tb (1.5%)
9	LaPO$_4$: Ce (0.5%), Tb (2.0%)
10	LaPO$_4$: Tb (0.5%), Ce (0.1%)
11	LaPO$_4$: Tb (0.5%), Ce (0.5%)
12	LaPO$_4$: Tb (0.5%), Ce (1.0%)
13	LaPO$_4$: Tb (0.5%), Ce (1.5%)
14	LaPO$_4$: Tb (0.5%), Ce (2.0%)
15	LaPO$_4$: Eu (0.5%), Tb (0.1%)
16	LaPO$_4$: Eu (0.5%), Tb (0.5%)
17	LaPO$_4$: Eu (0.5%), Tb (1.0%)
18	LaPO$_4$: Eu (0.5%), Tb (1.5%)
19	LaPO$_4$: Eu (0.5%), Tb (2.0%)
20	LaPO$_4$: Eu (0.5%), Ce (1.0%), Tb (0.1%)
21	LaPO$_4$: Eu (0.5%), Ce (1.0%), Tb (0.5%)
22	LaPO$_4$: Eu (0.5%), Ce (1.0%), Tb (1.0%)
23	LaPO$_4$: Eu (0.5%), Ce (1.0%), Tb (1.5%)
24	LaPO$_4$: Eu (0.5%), Ce (1.0%), Tb (2.0%)

List of Prepared Phosphors (LaYPO$_4$ base)

Sr. No.	Chemical formula of the Sample
1	Base compound LaYPO$_4$
2	LaYPO$_4$: Ce (0.5 %)
3	LaYPO$_4$: Eu (0.5 %)
4	LaYPO$_4$: Gd (0.5 %)
5	LaYPO$_4$: Tb (0.5%)
6	LaYPO$_4$: Tb (0.5%), Eu (0.5%)
7	LaYPO$_4$: Tb (0.5%), Eu (1.0%)
8	LaYPO$_4$: Tb (0.5%), Eu (1.5%)
9	LaYPO$_4$: Tb (0.5%), Eu (2.0%)
10	LaYPO$_4$: Gd (0.5%), Eu (0.5%)
11	LaYPO$_4$: Gd (0.5%), Eu (1.0%)
12	LaYPO$_4$: Gd (0.5%), Eu (1.5%)
13	LaYPO$_4$: Gd (0.5%), Eu (2.0%)
14	LaYPO$_4$: Tb (0.5%), Gd (0.5%), Eu (0.5%)
15	LaYPO$_4$: Tb (0.5%), Gd (0.5%), Eu (1.0%)
16	LaYPO$_4$: Tb (0.5%), Gd (0.5%), Eu (1.5%)
17	LaYPO$_4$: Tb (0.5%), Gd (0.5%), Eu (2.0%)

The thesis consists of six chapters including conclusions. Chapters 1, 2 and 3 are the introduction, phosphor preparation and instrumentation. Chapters 4 and 5 are the results and discussions on the 41 prepared lanthanum phosphors and lanthanum yttrium phosphors. Each chapter is followed by references and cross references. Chapter 6 is the conclusions drawn from chapter 4 and 5 followed by brief suggestions for future work.

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