Introduction

Chapter 1

Luminescence is the emission of optical radiation (infrared, visible, or ultraviolet light) by matter This phenomenon is to be distinguished from incandescence, which is the emission of radiation by a substance by virtue of its being at a high temperature (> 500^o C) (Black body radiation) Luminescence can occur in a wide variety of matter and under many different circumstances. Thus, atoms, organic, inorganic, or organometallic molecules; polymers; organic or inorganic crystals, and amorphous substances all emit luminescence under appropriate conditions.[1] The production of light in this manner is called Photoluminescence because activation of luminescence is provided by absorption of a photon.

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

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

Electroluminescence is the efficient generation of light in a non metallic solid or gas by an applied electric field or plasmas.

Chemiluminescence is produced as a result of a chemical reaction usually involving an oxidation-reduction process. The most common mechanism for such an emission is the conversion of chemical energy, released in a highly exothermic reaction, into light energy

Cathodoluminescence is due to the emission of light during electron irradiation

Bioluminescence is the result of certain oxidation processes (usually enzymatic) in biological systems

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

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

Sonoluminescence is the emission of light due to the excitation by sound waves

Thermoluminescence (TL) or more specifically Thermally Stimulated Luminescence (TSL) is activated thermally after initial irradiation by some other means

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

Thus there are two different types of luminescence . fluorescence (the emission of light takes place with a characteristic time $t_c < 10^{-8}$ S), in which emission takes place from an exicted singlet state and the phosphorescence ($t_c > 10^{-8}$S), in which emission occurs from an excited triplet state From a practical view point the only clear way to distinguish 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 a strong temperature dependence

In photoluminescence, an excited singlet state can be directly produced by photon absorption. This excited state can then undergo what are called radiationless transitions In these processes, other electronic states are reached without the absorption or emission of a photon, and the transition basically involve the conversion of electronic energy into vibrational (i.e. thermal) energy. For most molecules, the energy differences between the excited state are much larger than the gap between the lowest excited state and the ground state, the lowest excited state is usually fomed with very high efficiency after optical excitation into any of the higher excited states Thus, with very few exceptions, fluorescence and phosphorescence take place from the lowest excited singlet and triplet states, respectively.

Lamps and Phosphors :

Since the birth of the incandescent lamps more than a century ago, several new lamps have been developed Many of them are discharge lamps with far higher efficacies (lumens per watt) than the incandescent lamps. Different lamps have different possibility with regard to wattage, efficacy size, performance and colour temperature. **[2]**

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

Fluorescent powder is used in discharge lamps to convert the ultraviolet radiation into useful visible radiation. The powder increases the luminous flux and also changes the colour rendition index of the lamp

Quantum of powder used in a lamp depends on the type of lamp. For example in popular 4 ft. fluorescent lamp, 4 - 5 gm of powder is used, where as in 125W high pressure mercury vapour lamp it is in the range of 0 5 gm. In some cases, these powders are also used to reduce glare produced by the lamp. **[3]**

The most popular powder used in our country is cool day light halo phosphate powder This phosphor is being used by the industry since its introductionin the 1940's. The quality of the phosphor has improved substantially since it was introduced. (**Fig. 1 A.**) This powder is manufactured to give colour temperature of 6500° K and fairly good CRI (in the range of 70). Lamp manufacturer look forward to a

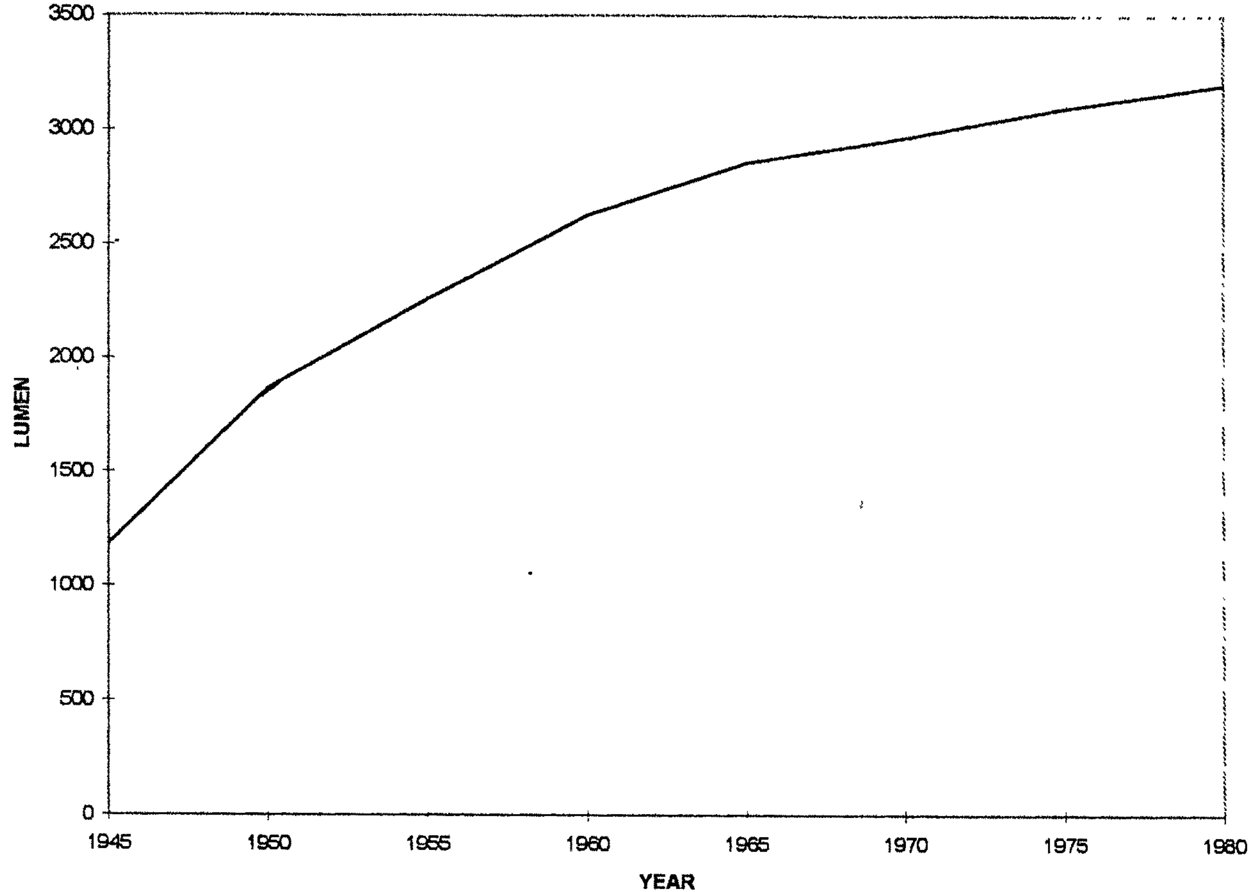

Fig 1A:- Lumen output progress of 40W fluorescent lamps coated with halophosphate phosphors technology wherein minimum quantity of powder is used without sacrificing the light output and visual appearance of the lamps Average particle size and particle size distribution play major role in coating process Fine powders give more silky finish to the lamps and narrow particle size distribution gives uniformity of the coating along the full length. Fine particle size powders are in the range of 4 - 5 microns and coarser powders are above 10 microns Lamp manufacturer prefer finer powders because these powders need not be milled and have more coverage per gram of powder used

Another important parameter is the fluorescence yield which is indirectly measured as the luminous flux or light out put. Finer powders tend to give better light out put. The trend is now changing with better technology adopted by powder manufacturers. Lamp manufacturer have to declare the colour temp and also sometimes CRI. Therefore, these two parameters also form an integral part of powder specification. Powder which give lower luminious flux or lower colour rendition are comparatively cheaper Another quality parameter of a discharge lamp is to maintain light level with time. This lumen maintenance is decided by fluorescent powder alongwith many other parameters like purity, manufacturing process etc. A bad powder will give poor lumen maintenance

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

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

Interestingly, the triband phosphor system performing near the physical limits leaves no scope for further improvement in the luminous efficiency. Hence new directions in the research are being focused on the design of in-expensive phosphor system without compromising the performance and effectively harnessing the influence of impurities to achieve the ultimate efficiency. The search does not seem to be elusive Equally important are alternate discharge mechanisms (eg Xe discharge) paving way for higher lumen and more importantly, the concept of quantum-cutters underlying generating more than one visible photon for one UV **[4]**

New Phosphor blends

Because of an increasing awareness of the need for efficient, i.e energy-saving, lamps and the development of rare-earth-activated phosphors, new multicomponent systems have been introduced and are currently receiving an increasing emphasis in the lighting industry.

To illustrate the performance that is possible with optimum phosphor systems, **Fig. 1 B** shows the maximum candela (lumens), or light output, that can be obtained from

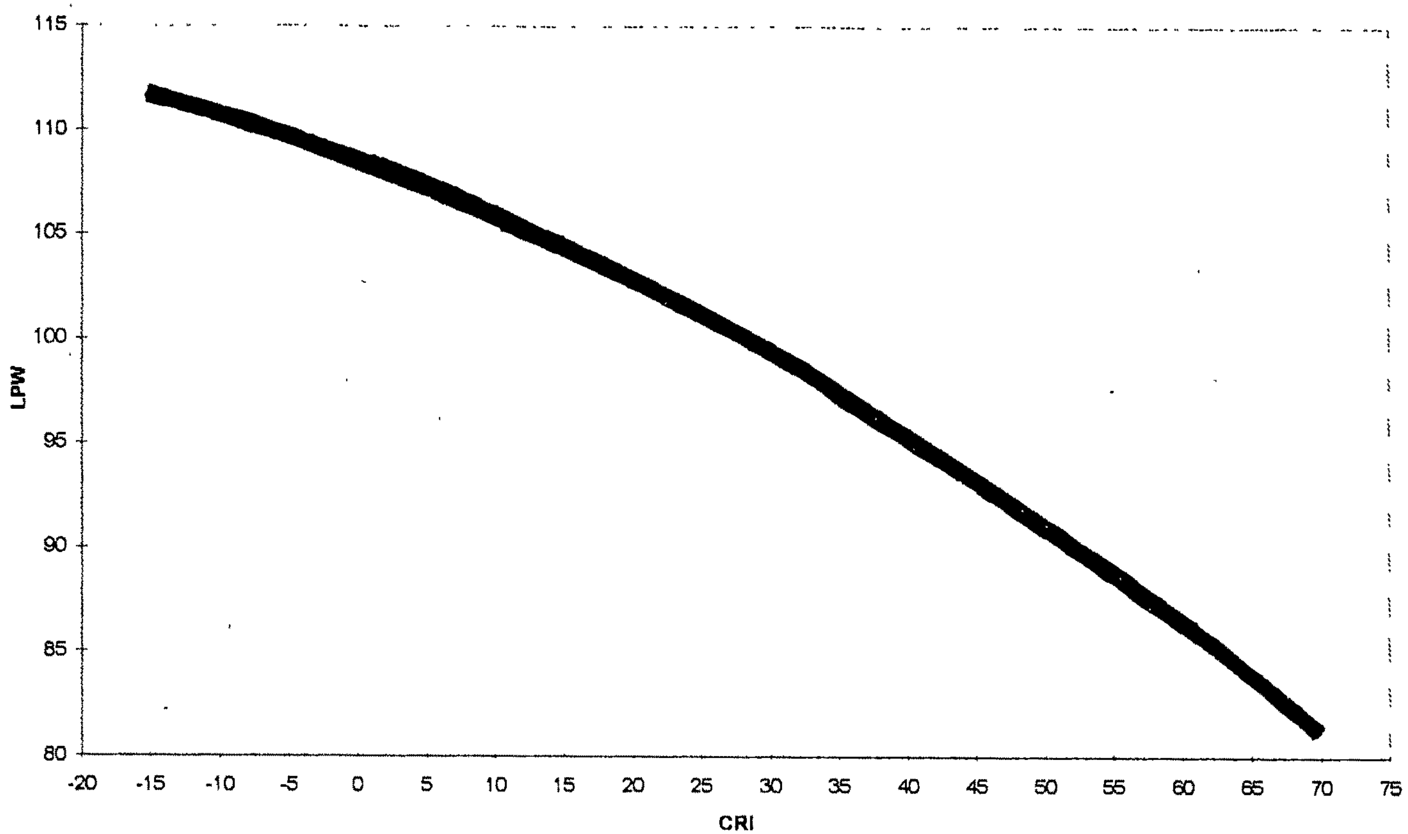

Fig 1B:- Light output(**LPW**) versus Colour Rendition Index(**CRI**) for simulated flourescent lamps with optimum phosphor spectra.

fluorescent lamps The numbers are calculated using simulated spectral-power distributions (SPDs). They include the visible mercury lines and assume the efficiency standard phosphor coatings The x axis is the general colour rendition index (CRI) which measures the average displacement of eight test colours on a uniform chromaticity diagram from their appearance under a standard incandescent source or daylight A CRI of 100 means that there are no colour distortions. The ability of a lamp not to distort colours is important to varying degrees in different applications.

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

Better colour rendition is desired in residential lighting and certain commercial applications where good colour reproduction is important An optimum SPD having very good colour rendition is achieved [5 , 6] using three narrow bands peaking near the wavelengths 610, 540, and 450 nm To utilize this principle, three-component phosphor blends have been developed

Results based mainly on simulations using different phosphor SPDs indicate that narrow red emission near 610 nm, which is available from Y_2O_3:Eu(III), is essential to optimum efficiency and very good colour rendition However, some flexibility is possible in the choice of green and blue phosphor emissions. For example, a broad green emission provided by a strontium halophosphate phosphor can be used with little loss in luminous efficiency [7] Optimum phosphor blends with the narrow red emission provide 40-50% more light output than deluxe phosphor blends previously used for applications requiring good colour rendition, which contained the broad red-emitting phosphor Strontium Orthophosphate activated with Tin(II).

Still other phosphor systems are used to obtain very high colour rendition for colour-critical applications. A CRI of 95 or higher can be obtained with phosphors or pigments that absorb some of the radiant power from the visible mercury lines in the blue-violet region of the spectrum. Phosphor blends can be used to achieve an infinite variety of SPDs for special applications, including plant growth, reprographic recording, special colour effects, etc.

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

Quantum Efficiency :

Absolute quantum efficiency of a phosphor is defined as the ratio of the number of photons/sec emitted to that of the number of UV photons/sec absorbed by it The measurement of quantum efficiency (Q) is often described as tedious and time consuming, which involves the determination of the spectral energy distribution of the source, the spectral response of the photodetector, and the spectral and spatial distribution of fluorescence. Importance of the knowledge of Q on the development of inorganic phosphors can only be gauged from the conscientious effort put in by a large number of workers in the last fifty and odd years, for a reliable method of its measurement Williams made a thorough review of the different techniques employed for its measurement. A signal contribution was made to the measurement of Q using direct optical methods for inorganic powder phosphors. **[8]** Employing a thermopile detector having flat radiant spectral response over the wavelengths from UV through visible to infrared, and with the aid of light collecting optics and noise eliminating electronics, they success to a great extent was achieved in evaluating the absolute Q of inorganic phosphors to an accuracy of ± 15%

By making best use of the flat quantum response available from a silicon photodiode (SPD), a simple method of the measurement of Q is developed with the use of a drift free current measuring electrometer amplifier. [9] Using the relationship $E = hc/\lambda$ and 1 watt = 10^7 erg/sec; one can calculate the number of photons/sec for every watt of radiant power at any given wavelength. Table gives the calculated value of the number of photons/sec for several wavelengths. From the spectral response characteristic curve of a typical photodiode (Type No. S-1337-1010 BQ; Hamamatsu make) one can also calculate the current generated by it for every photon of wavelength λ (from 250 nm to 1100 nm) striking its photosensitive surface/sec From this calculation, it emerges that the SPD has practically flat quantum response, i.e the current generated by it by a photon of any wavelength in the spectral range from 400 nm to 700 nm striking its surface is approximately the same Hence, a working relationship interconnecting the Q of a phosphor and the current generated by the photodiode for UV and visible radiation can be worked out A MgO powder of known reflectivity for UV radiation is used as a standard for determining the actual number of UV quanta/sec striking the phosphor surface The reproducibility achieved using this method is close to ± 5%.

Thermally stimulated luminescence

Thermally stimulated luminescence is the phenomenon of emission of light from a solid which has been previously exposed to ionising radiation under conditions of increasing temperature Unlike other luminescence processes such as electro-luminescence, cathodo-luminescence, chemiluminescence etc., here heat is not an exciting agent, but it acts only as a stimulant. Hence it is better known as thermally stimulated luminescence (TSL). Excitation is achieved by any conventional sources like ionising radiation, ultraviolet rays, light, mechanical vibrations, stress etc. TSL is exhibited by a host of minerals, inorganic crystals, glasses, ceramics, plastics and some organic solids. By far insulating solids doped with suitable chemical impurities, termed as activators, are the most sensitive TSL materials. The band theory of solids is normally used to explain this phenomenon. When a solid is irradiated, electrons and holes are produced. The defects in the solid result in the presence of localised energy levels within the forbidden gap. On irradiation, electrons and holes can be trapped at these defect sites. When the solid is heated, these trapped electrons/ holes get enough thermal energy to escape from the trap to the conduction band (or valence band) From here, they may get retrapped again or may recombine with trapped holes/electrons. The site of recombination is called recombination centre. If this recombination is radiative, then the centre is called luminescent centre Alternatively a trapped hole can be released by heating which can recombine with a trapped electron resulting in luminescence. These features are shown diagrammatically in **Fig. 1 C.** It is not required that all charge recombinations should result in luminescence They can be non-radiative too The plot of intensity of emitted light versus the temperature is known as a glow curve. A glow curve may exhibit one or many peaks depending upon the numbers of electron/hold traps with different trap depths, present in the lattice. These peaks may or may not be well separated. The position, shape and intensity of the glow peaks therefore are characteristic of the specific material and the impurities and defects present. Therefore each TSL peak corresponds to the release of an electron (or hole) from a particular trap level within the band gap of the material. The spectral nature of the glow peaks gives information about the luminescent centres. It may be mentioned that TSL is highly sensitive to structural imperfections in crystals Defect densities as low as $10^7/cm^3$ also can give measurable TSL if radiative recombination is unity whereas techniques like EPR and OAS are sensitive only for relatively higher defect concentrations such as $10^{12}/cm^3$.**[10]** The first step towards understanding the mechanism for the TSL glow peaks is the identification of the trapping centres and the recombination centres for the observed light emission. Hence TSL studies together with EPR and OAS investigations of irradiated and annealed samples can lead to the mechanisms responsible for the TSL

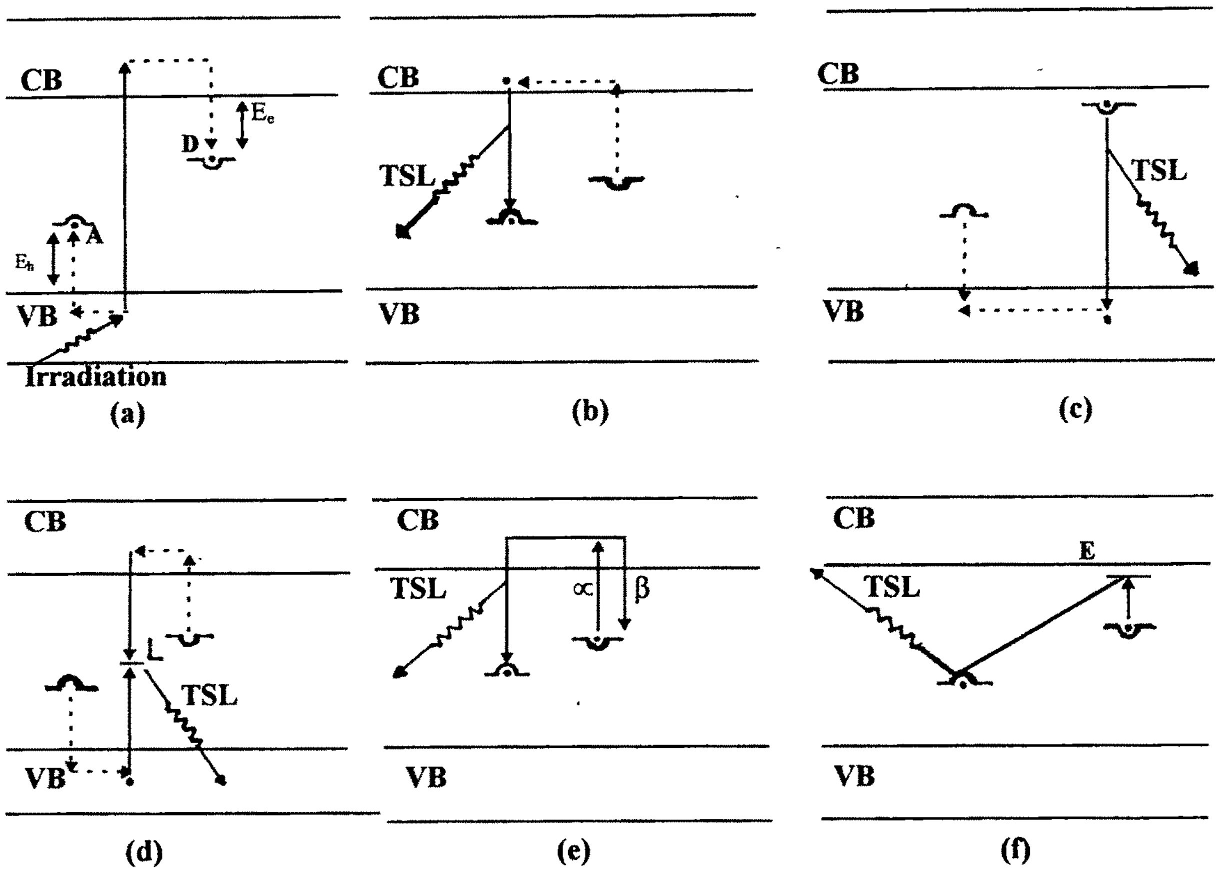

Fig 1C:- Processes involved in radiation induced electron/hole trapping and subsequent recombination on thermal stimulation with associated luminescence emission.

VB- Valence band, CB - Conduction band, E_h - Trap depth for hole, E_e - Trap depth for electron, L - Luminescent centre, A - Hole trap and D - Electron trap.

(a) On γ - irradiation, electrons and holes are produced and trapped at electron/hole traps.

(b) On thermal stimulation, trapped e is released and recombines at trapped hole site.

(c) e-h recombination at trapped electron site. (d) e-h recombination at luminescent centre site.

(e) Process of detrapping and retrapping(second order kinectis,α - detrapping probability and β- retrapping probability) ; (f) e-h recombination via an excited state 'E' and tunneling.

Apart from being a tool for the study of defects in solids, TSL has also found widespread use in radiation dosimetry, archaeological dating of pottery, ceramics, minerals etc , and meteorite research

Electronic energy levels of defects in solids

The energy levels of electrons in crystalline solids are determined by the interaction between the many atoms (typically $10^{22}/cm^3$) that constitute the crystal. When such huge number of atomic wave functions combine, the number of energy levels split from any given atomic level is large. There is only very small energy difference between the levels split from one atomic level. These energy levels essentially form an energy continuum (or band) There is an energy separation between 1s and 2s bands, 2s and 2p bands and so on But within a given band, discrete energy levels have extremely small separation in energy The energy levels of electrons in crystals can be determined by the existence of a potential function that is periodic in space. The interaction of electrons with each other and this periodic potential must be considered to derive the allowed energy levels for electrons in crystals The periodic function of the lattice coupled with the wave function of a free electron when solved quantum mechanically permits only specific values for electron energies in the solids **[11]** The allowed energy levels fall into a series of energy bands with the bands separated by regions of forbidden energy gaps Imperfections in a crystal gives rise to localised energy states, an electron associated with the imperfection having energy level that is forbidden in a perfect crystal Local deviations from the periodic potential of the perfect crystal give rise to localised energy states characterised by wave functions that decay exponentially in amplitude with distance from the imperfection site. When considered with respect to energy bands, these localised levels normally lie in the forbidden gap between the valence and the conduction bands. Prominent imperfections are impurities, vacancies, interstitial or complex imperfections formed by the aggregate of the simple imperfections Since the conditions of growth of real crystals is frequently under a thermodynamic environment favouring the existence of imperfections, such departures from the periodic potential of the perfect crystal are the rule. Localised levels can also be directly associated with the impurity itself and correspond to atomic levels of the impurity as altered by the dielectric constant and interaction of the crystal Such levels are additional levels which are not at all present in the chemically pure crystal.

Electron Paramagnetic Resonance (EPR)

Electron paramagnetic resonance is a branch of absorption spectroscopy in which electromagnetic radiation of microwave frequency induces transitions between the zeeman components of the electronic ground state of a paramagnetic ion or a system containing unpaired spins. The energy level splitting is created by a static magnetic field This phenomenon was discovered by Zavoisky in 1945. Since then it has found widespread application in solid state spectroscopic studies. Let us consider a single electron with only spin angular momentum, s = 1/2. The magnetic moment of the electron, $\mu = -g.\beta.s$. where g is the spectroscopic splitting factor, β is the Bohr magneton and s is the spin quantum number. s can have values +1/2 or -1/2. In a magnetic field H, the two fold spin degeneracy is lifted by the interaction of the magnetic moment, μ with H. The interaction energy is given by $E = -\mu.\ H = g.\beta.\ H.\ m_S$, where m_S is the projection of 's' along the field direction. Magnetic dipole transitions can be induced between these two energy levels by applying electromagnetic radiation with frequency such that $h\nu = g\ \beta.H$ This is the basic condition for resonance absorption, which is shown in **Fig. 1D.**

In paramagnetic systems with more than one unpaired electron (s > 1/2), multiplicity of levels result from the ligand field even in the ground state Wherever there are zero field splitting of the ground state multiplet, Zeeman components cease to be equally spaced and all transitions with $\Delta m_s = \pm 1$ do not occur at the same energy and 2s well separated lines are observed. This is known as the fine structure. In addition, interaction of the electron spin, of a paramagnetic ion with its nuclear spin, I result in further splitting of the energy levels in the presence of the magnetic field resulting in 2I + 1 lines This is known as hyperfine structure. If the electron spin interacts with spins of

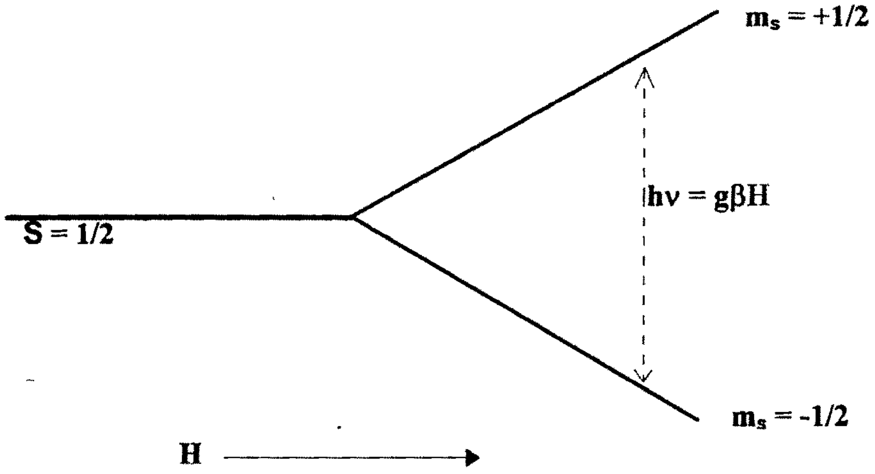

Fig. 1D :- The energy level splitting for s = 1/2 system in the presence of a magnetic field H and condition for resonant absorption of microwaves nuclei other than the one on which the electron is there, further splitting can occur resulting in what is known as superhyperfine structure in the EPR spectra.

The resonance line from the unpaired electrons in a sample is not infinitely sharp Broadening due to spin-lattice relaxation results from the interaction of the paramagnetic ions with thermal vibrations of the lattice. The spin system exchanges its energy with the latice. Spin-spin interaction results from the small magnetic fields that exist on the neighbouring paramegnetic ions. As a result of these fields, the total field at the ion is slightly altered and the energy levels are shifted and a distribution of energies result which produces the broadening. This effect can be reduced by diluting the salt with an isomorphous diamagnetic material.

EPR technique has found widespread application in physics and chemistry EPR studies give the magnitude of levels separated by a few cm^{-1} from ground state at room temperature itself. Precise information about the strength and symmetry of the crystal field around the paramagnetic ion can be obtained The anisotropy in the g values of the centres gives information about interaction of ground levels with higher excited levels. EPR studies of doped crystals showing phase transitions give information about the nature of the transitions. Hyperfine structure observed in the EPR spectra gives information about the nuclear spin and about the interaction of electron spin and nuclear magnetic moment Positions of paramagnetic ions in single crystals can be detected by EPR studies EPR is a very important tool in unravelling the nature of radiation induced defects like colour centres.

About the work:

The work presented in this thesis can be basically divided into two parts One that deals with the commercial lamp phosphors and another with the phosphors synthesised in the laboratory. The samples of the commercial lamp phosphors were obtained from prominent lamp manufacturers namely, Osram (

(Germany), Philips (Holland & India), G E (USA), Cona (Holland) and Solichem. The samples have been coded to mantain confidentiality. Few lamps were made out of the samples and their parameters studied. The synthesised phosphors i. e. $LaPO_{4\,[ASRI]}$. Ce,Tb were prepared using high temperature solid state synthesis method with different Cerium and / or Terbium concentration.

The thesis is divided into four chapters Chapter 1 gives an intrroduction of the theoratical basis of phenomenas and techniques, which are relevant to the work

Chapter 2 deals with the instrumental techniques used for characterisation as well as measurement of different parameters. It gives description of instruments like X- ray diffractometer, Spectrophotofluorometer,Quantum Efficiency measurement apparatus, Thermoluminescence set - up, EPR Spectrometer, Integrator (for lumen output measurement), Colorimeter (for x & y coordinate measurement), Particle size analyser, Radiation sources and furnace.

Chapter 3 is the study of commmercial lamp phosphors. Characterisation of the samples reveal that all of them are Calcium halophosphates doped with Antimony and Manganese A corelation has been attempted between the Quantum efficiency of the samples and the lumen output of the lamps made out of the same phosphor samples On the other hand, the colour rendering properties of the lamps have been corelated to the emission spectra of the phosphors. The TSL - EPR corelation gives an authentic idea of the radicals responsible for the TSL, while the TSL spectra suggests the luminescence centres. The significance of the particle size distribution has been also discussed

Chapter 4 contains the study of laboratory made lamp phosphor $LaPO_4$. Ce,Tb. This phosphor is used as the green component in trchromatic phosphor blends. Preparation and characterisation of the samples, Quantum

Efficiency and the excitation as well as emission spectra of the samples has been discussed. The TSL characteristics, TSL spectra and TSL - EPR corelation has been also given

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