Chapter 1

Introduction

1.1. Introduction

1.1.1 Luminescence

Generation of light can be classified in two ways, one is incandescence and the other is luminescence. Incandescence is the light glow by the heating of the object/materials and a bright light is produced eg., electric bulbs. Luminescence is a collective term for different phenomena where a substance emits light without being strongly heated, i.e., the emission is not simply thermal radiation. This definition is also reflected by the term "cold light". The word luminescence was first used by a German physicist, in 1888, Eilhardt Wiedemann, in latin 'Lumen' means 'light' [1]. The materials exhibiting this phenomenon are known as 'Luminescent materials' or 'Phosphors' meaning 'light bearer' in Greek. The term phosphor was coined in 17^{th} century by an Italian alchemist named Vincentinus Casciarolo of Bologona [2]. The phenomenon of luminescence can be classified into various categories depending on the mode of excitation (the prefix before the term luminescence is the mode of excitation in most of the cases).

- Photoluminescence, when the excitation is by electromagnetic radiation/photons, is a less specific term, which embraces both fluorescence and phosphorescence;
- Cathodoluminescence, when the excitation is by energetic electrons or cathode rays;
- Electroluminescence is light emission triggered by electric influences;
- Radioluminescence, when the excitation is by high-energy X-rays or γ rays;
- Sonoluminescence, when the excitation is by ultrasonic waves;
- Triboluminescence can occur when a material is mechanical treated, e.g. fractured or polished;
- Chemiluminescence is light emitted during chemical reactions;
- Bioluminescence is the form chemiluminescence from living organisms;
- Thermoluminescence, also known as thermally stimulated luminescence, is the luminescence activated thermally after initial irradiation by other means such as α, β, γ, UV or X-rays. It is not to be confused with thermal radiation: the thermal excitation only triggers the release of stored energy.

Each process mentioned above has its own significance and advantage in the field of science and technology. Emphasis in the present work has been given to study the photoluminescence (PL) of phosphors that exhibit strong emission in the visible region. However, before going into the detail it is important to know the procedure leading to luminescence and its various characteristics.

1.1.2 Photoluminescence

As has been defined earlier, luminescence occurs when some form of energy excites solids and this energy is released in the form of photons. When this solid is excited by short-wavelength light (usually UV radiation), the phenomenon is known as photoluminescence.

Photoluminescence can be classified as either intrinsic or extrinsic luminescence.

1. Intrinsic luminescence: As the name implies, intrinsic luminescence refers to a situation in which the luminescence comes from within a pure material or crystal. It may be grouped into three categories:

a.) Band-to-Band Luminescence:

This kind of luminescence occurs due to the recombination of an electron in the conduction band with a hole in the valence band, producing a band-to-band transition. This type of luminescence process can only be observed in very pure materials at relatively high temperatures, but is transformed into exciton luminescence at low temperatures. Examples of such materials are Si, Ge and some IIIb–Vb compounds such as GaAs [3].

b.) Exciton Luminescence:

An exciton is a bound electron-hole pair in which an excited electron is interacting with a hole. As the exciton moves through the crystal, is carries some energy and the electron and hole recombine to produce luminescence. There are two kinds of excitons. The Wannier exciton is composed of an electron in the conduction band and a hole in the valence band bound together by the coulomb interaction and is found primarily in IIIb–Vb and IIb–VIb inorganic semiconductors. The Frenkel exciton exists when the expanse of the electron and hole wavefunctions is smaller than the lattice constant and can be found in organic molecular crystals such as anthracene, inorganic complex salts such as tungstates and vanadates, and in uranyl salts [3].

c.) Cross-Luminescence:

Cross-luminescence is produced when an electron in the valence band recombines with a hole created in the outermost core band. This kind of luminescence is typically observed in alkali and alkaline-earth halides and double halides.

2. Extrinsic Luminescence:

Extrinsic luminescence refers to luminescence caused by intentionally incorporating impurities or defects into a phosphor. In ionic crystals and semiconductors, it may be unlocalized or localized. It is unlocalized when the free electrons in the conduction band and free holes in the valence band of the host lattice also participate in the luminescence. On the other hand, the localized type occurs when the excitation and emission process of the luminescence are constrained within a localized luminescent center.

1.1.3 Thermoluminescence (TL) or Thermally Stimulated Luminescence (TSL)

Thermoluminescence (TL) or more specifically Thermally Stimulated Luminescence (TSL) is activated thermally after initial irradiation given to a phosphor by some other means. (α-rays, β-rays, γ-rays, UV-rays and X-rays). Thermally stimulated luminescence is (TSL) the phenomenon of emission of light from a solid which has been previously exposed to ionizing radiation under conditions of increasing temperature. Unlike other luminescence process such as Electroluminescence, Chemiluminescence, here heat is not an exciting agent, but it acts only as a stimulant. Hence it is better known as thermally stimulated luminescence (TSL) **[4]**. Excitation is achieved by any conventional sources like ionizing radiation, α-rays, β-rays, γ-rays and UV-rays and X-rays. TSL is exhibited by a host of materials, glasses, ceramics, plastics and some organic solids. By far insulating solids doped with suitable chemical impurities, termed as activator, are the most sensitive TL materials. The band theory of solids is normally used to explain this phenomenon. When a solid is irradiated, electrons and holes are produced. The defects in the solid results in the presence of localized energy levels within the forbidden gap. On irradiation, electron 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 valance band). From here they may get re-trapped again or

may recombine with trapped holes/electrons. The site of recombination is called recombination center. If this recombination is radiative, then center is called luminescence center. The intensity of emitted light versus the temperature known as a glow curve. A glow curve may exhibit one or many peaks depending upon the number of electron/hole traps with different trap depths, present in the lattice. These peaks may or 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 presents. Therefore each TSL peak correspond to the release for an electron (or hole) from a particular trap level within the band gap of the material. The nature of the TL glow peaks gives information about the luminescent centers present in the material. It may be mentioned that TSL is highly sensitive to structural imperfections in crystals. Apart from being a tool for the study of defects in solids, TSL has also found widespread use in radiation dosimetry, archeological dating of pottery, ceramics, minerals etc; and meteorite research.

The TL from the material is very sensitive to;

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

1.2 General characteristics of luminescence

The process of luminescence can be illustrated in figure-1

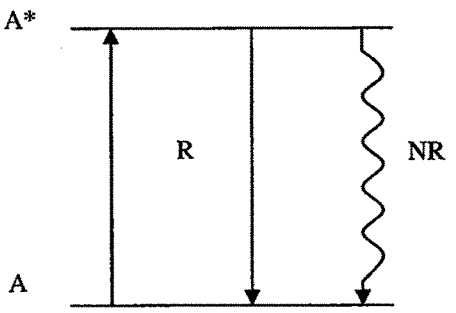

Figure-1 Energy level Scheme of the luminescent ion A. The * indicates the excited state, R the radiative return and NR the nonradiative return to the ground state.

The figure-1 depicts two types of return to the ground state, one radiative and the other non-radiative. The former is the one through which the luminescence process occurs. The other has no role in luminescence yet it occurs with the radiative emission due to the phonons which are converted to lattice vibrations that transport energy in the form of heat. An efficient luminescent material is one in which radiative transitions dominate over the non-radiative ones. Though practically in the luminescent materials the situation is more complex than depicted in figure above, the exciting radiation is not absorbed by the activator but elsewhere [5]. Depending on the duration of the emission, luminescence has further sub classification:

(a) fluorescence: On removal of excitation an exponential afterglow is observed independent of the excitation intensity and of temperature, with lifetime less than 10^{-8} seconds.

(b) phosphorescence: On removal of excitation there exists another phenomenon of afterglow (decay is more slow with complex kinetics), often dependant on intensity of excitation and strongly temperature-dependent, with life time of more than 10^{-8} seconds. 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. Since thermal activation of the metastable activator or trap is prerequisite to emission.

1.2.1 Model for a Luminescence Process to take place.

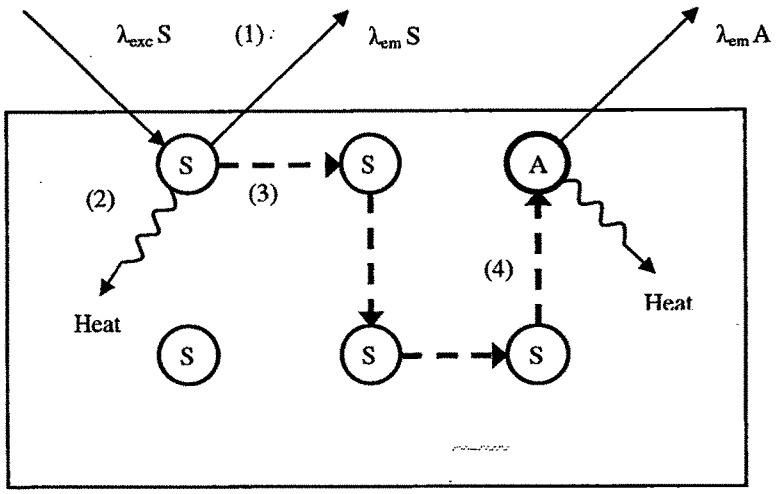

Figure-2 Schematic representation of the possible luminescence processes of a crystal system with donor D and acceptor A ions. Following excitation D may: (1) emit radiatively, (2) decay nonradiatively, (3) transfer energy to another D ion, or (4) transfer energy to an A ion in the last case, energy transfer to A is followed by either radiative or nonradiative decay.

In the host lattice the ion which absorbs the radiation is referred to as the donor, and the ion which excitation energy is transferred is the acceptor. From the schematic presented in Figure, four different processes following excitation of D can be distinguished: (1) D may luminesce, (2) D may decay nonradiatively producing heat, (3) D may transfer energy to another D type ion, or (4) D may transfer energy to an A type ion. If energy transfer to A is followed by nonradiative decay, A is referred to as a killer site, because it acts to quench luminescence. Commonly the nature of the transfer mechanism is inferred by examining how the luminescence decay of an ensemble of "equivalent" ions within a host lattice depends on their concentration and temperature. Figure-2 shows a schematic of the possible luminescence processes which can occur when ion within a larger ensemble is excited **[6]**.

1.2.2 Production and Decay process of Excited states

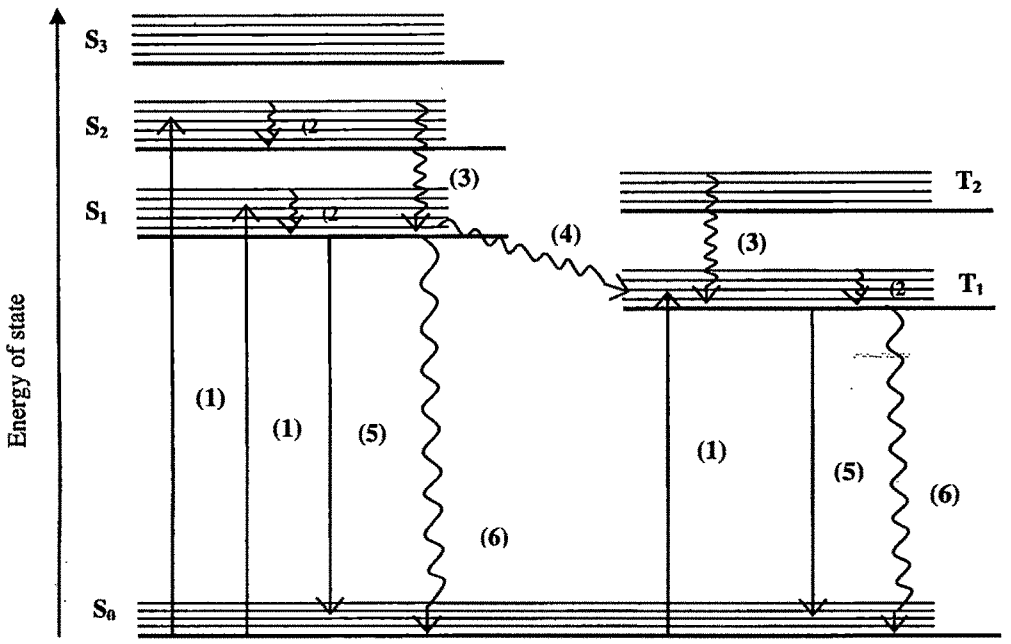

Figure-3 The Jablonski diagram, which explains the photophysical processes in molecular systems. (1) photoabsorption; (2) vibrational relaxation; (3) internal conversion; (4) intersystem crossing; (5) radiative transition; and (6) nonradiative transition.

Production and decay processes of excited states are described using an energy state diagram called Jablonski diagram shown in figure-3. The ground state S_0 and lowest singlet and triplet states, S_1 and T_1 are composed of multiple vibrational states due to the presence of vibronic motions of atoms that make up a molecule. When energy larger than the HOMO-LUMO energy difference is introduced into a molecule, either a higher vibronic state within S_1 states, or higher singlet excited states S_2 and S_3 are produced. The higher vibronic states of S_1 relax to the lowest vibronic state of S_1 within a time scale of picoseconds. The higher energy singlet states such as S_2 and S_3 relax to the S_1 state via nonradiative internal conversion (IC) processes. Triplets states are usually produced via an intersystem crossing (ISC) processes from $S_1 \rightarrow T_1$. Thus, radiative transitions take place as the electronic transition from the lowest excited states of S_1 or T_1 to the ground state S_0. the radiative transition from S_1 to S_0 is classified as a spin-

allowed transitions and hence the time scale of the transition is of the order of a few nanoseconds. On the other hand the time scale T_1 to S_0 tranisiton is much longer ranging form micro- to milliseconds because the process is spin-forbidden. Thus, an emission spectrum looks like the mirror image of the absorption spectrum of the molecule [1].

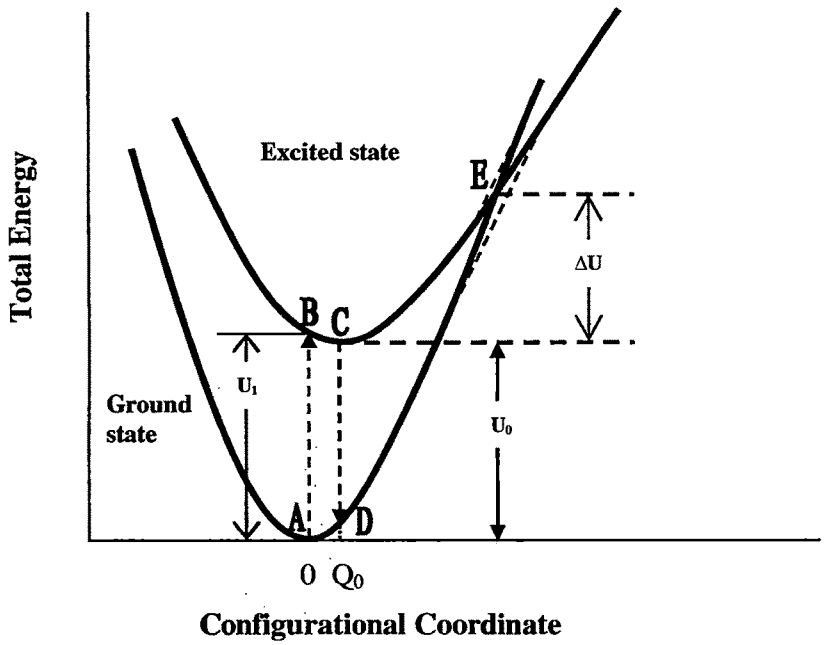

Figure-4 Configurational Coordinate diagram (Energy Levels of transitions taking place).

The Configurational coordinate model is often used to explain optical properties, particularly the effect of lattice vibrations, of a localized center and have been shown in figure-4. In this model a luminescent ion and the ions at its nearest neighbour sites are selected for simplicity. In most cases, one can regard these ions as an isolated molecule by neglecting the effects of other distinct ions. In this way, the huge number of actual vibrational modes of the lattice can be approximated by a small number or a combination of specific normal coordinates. This normal coordinates are called the configurational coordinates. The Configurational coordinate model explains optical properties of a localized center on the basis of potential curves, each of which represents the total energy of the molecule in its ground or excited state as function of the Configurational

coordinate. Here the total energy means the sum of the electron energy and ion energy [1].

1.3 Phosphor configuration

Phosphors, the term coined after the element phosphorous which glowed when in contact with air, basically, consists of an inert imperfect host crystal lattice to which some impurity ions called dopants, are intentionally added. Their history dates back to more than 100 years when a French chemist Théodore Sidot, (in 1886) accidentally prepared a prototype of ZnS-type phosphor [**1, 7**]. Since then the research and development of phosphors has undergone a many fold changes with invention and different application of these. Crystal lattice consists of periodic configuration of atoms. There are different kinds of crystals and are classified according to their symmetries, which specify invariant properties for translational and rotational operations. These crystals have closely spaced discrete energy levels, which merge into bands. Based on availability of electrons these bands form different electronic states called electronic energy band that also obey the symmetries of crystals [**1, 8**]. In these energy bands, the states with lower energies are occupied by electrons originating from bound electrons of atoms and called valence bands. The energy bands having higher energies are not occupied by electrons and are called conduction bands. The materials like rock-salt, zinc-blende etc. that exhibit crystal symmetries, usually, have no electronic state between the top of valence band and the bottom of conduction band. This vacant region between the valence band and conduction band is called forbidden gap or bandgap. Any deviation in a crystal from a perfect periodic lattice or structure is called imperfection. The common imperfections are chemical impurities, vacant lattice sites and interstitial atoms (atoms not in regular lattice positions). A point imperfection is localized at a point in the structure, in contrast, with a line or plane of imperfection. Many important physical properties of solids are controlled as much by imperfections as by the parent atom of the host lattice. The conductivity of some semiconductors is entirely due to the imperfections. A small concentration of point defects may drastically modify the electrical or the optical properties of a solid to make it useful in many industrial applications, such as solid-state electronic circuit element, phosphors for fluorescent lamp, television, solid-state laser and long persistent dark vision display devices.

Luminescence of crystals is connected with the presence of impurities. The colour of many crystals arises from imperfection. The chemical and physical properties of the solid are usually controlled by imperfections.

The point defects in solids can be classified as native defects and impurity defects. In a stoichiometric lattice, the common types of native defects are:

(a) Frenkel defects – in which either a cation or anion leaves the site and goes into an interstitial position creating a vacancy and interstitial pair.

(b) Schottky defects – in which a cation and an anion vacancy appear together.

(c) Anti Structure – in which a cation and an anion interchange.

In nonstochiometric lattice, the native defects do not have to appear in pairs but some mechanism for preserving charge balance must exist **[8, 9]**.

1.4 Doping

Few materials have band gaps where the width corresponds to the visible spectrum. However, materials with a relatively wide band gap can be made to luminesce in the visible. This is possible by the addition of different atoms or imperfections into the crystal. The additional atoms, called dopants have a different electron orbital structure compared to the host crystal lattice. Therefore, in regions of the crystal around the dopant atom, additional energy levels become available. That is, within the forbidden band gap of the material, energy levels can exist that can accommodate electrons or holes. These levels can be close to the conduction band, in which case the dopant is called a donor, or close to the valence band, in which case it is called an acceptor. Transitions between these levels can give rise to visible luminescence in which case the dopant is known as an activator. In most cases, the activator is present in extremely small concentrations, ranging from as much as 1 dopant atom in 5000 host atoms down to as little as 1 dopant atom in 5 billion host atoms. The phosphors in vacuum tube video display tubes are the phosphors formed due to doping of host material with activators. For example, ZnS doped with silver (Ag) or chlorine (Cl) produces blue light, ZnS doped with copper (Cu) or aluminum (Al) produces green light and Y_2O_3S doped with europium (Eu) produces red light. Transition

metals like Ag and Cu have partially-filled 3d outer shells which make transitions highly sensitive to the surrounding crystal field. The resulting luminescence spectrum is a broad, featureless shape, as can be seen spectrum in the figure for a green phosphor. On the other hand, rare earth metals like Europium have an unfilled 4f shell which is shielded from the surrounding crystal field by a filled $5s^2p^6$ outer shell [**1**]. Consequently the transitions which occur at rare earth metal impurities are sharp. Sometimes the excited electron can find other ways to dissipate its energy. Several non-radiative recombination mechanisms are possible. These are usually associated with defects in the crystal, or levels in the middle of the band gap, called deep levels, introduced by impurities called inhibitors. Still other defects in the crystal can result in shallow levels which are close to the edge of either the valence or conduction bands. Shallow levels in the band gap can trap the excited electrons. Certain characteristics of these shallow level prevent the electron from decaying immediately back into the valence band. Instead the decay may occur after a very long time. However a small amount of heat may dislodge the electron back into the conduction band from where it can readily decay back to the valence band. This is the mechanism behind the technique of thermoluminescence. Some materials can be dated by measuring how much light they produce when heated. This measures the remaining electrons trapped in the shallow levels and hence how long is has been since the original excitation promoted to the electrons.

1.4.1. Types of dopants

The dopant and dopant concentration plays different roles in different host lattices depending upon their electronic configuration, solubility and structure of the host lattices. Furthermore, dopants have been classified into various categories on the basis of their function in host lattices [**1, 10**].

Activator: When an electron from dopant ion jumps to the excited state after absorption of excitation energy and emits the energy in the form of radiation while returning to ground state, it is known as activator (A) or luminescent center. For example, rare-earth (Eu^{2+}) and transition metal ions (Cu^{+}) in crystal lattice of alkaline earth aluminates, and sulfides, respectively act as activators.

Sensitizer: In case of two dopants in a crystal lattice, one is known as sensitizer (S) and another is A. The 'S' absorbs most of the energy and transfers it to the

'A' for the process of emission as seen in figure-5 below. The metal ions, for example, forming sensitizer → activator pairs are $Ce^{3+} \rightarrow Tb^{3+}$ and $Eu^{2+} \rightarrow Mn^{2+}$.

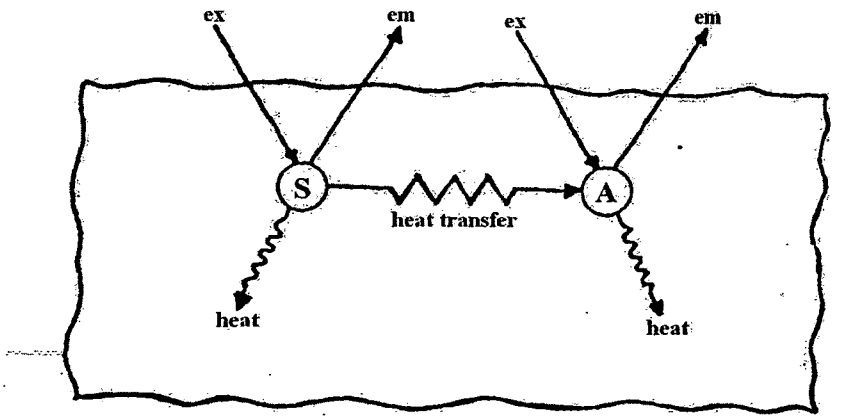

Figure-5 The type of dopants explained in detail in the figure.

Co-activator: The dopant ion that does not luminescence but help in the process of luminescence by acting as charge compensator or by creating hole/electron-traps is known as co-activator. For example, Al^{3+}, Cl-, F- in ZnS lattice.

Quenchers or Killers: The dopant ion that is responsible for decrease or complete disappearance of luminescence is known as quencher. When energy is transferred from an emitting center in a nonradiative manner with evolution of heat it causes quenching of luminescence. For example, Fe, Co and Ni in ZnS act as nonradiative centers thus called quenchers.

1.5 Phosphor Research Past and Present

Research and Technology in phosphors requires a unique combination of interdisciplinary methods and techniques. Synthesis and preparation of inorganic phosphors are based on physical and inorganic chemistry. Luminescence mechanism are interpreted and elucidated on the basis of solid-state physics. The research and development of major applications of phosphors belongs to the field of illuminating engineering, electronics and image engineering. Research on phosphors has a long history. A Prototype phosphor the ZnS-type phosphor for TV tube was first prepared by Theodore Sidot a young French chemist in 1886. This marked the beginning of scientific research, and synthesis of phosphors [**1,**

7, 11]. In early 20th century Leonard and co-workers in Germany performed active and extensive research on the phosphors. They prepared various kinds of phosphors based on alkaline earth chalcogenides and investigated their luminescence properties. Early lamp phosphors were natural fluorescing minerals, e.g. Willemite, Mn-activated Zinc orthosilicate, that were grinded to a powder and empirically blended together so as to obtain an approximately white field from fluorescent lamp. P.W. Pohl and co-workers in Germany investigated Ti^{+} activated alkali halide phosphors in details in the late 1920s and 1930s. A major turning point follows the development in 1940s with synthesis of Sb-Mn co-activated halophosphate phosphors. In a single material blue emission from the Sb^{3+} activator and the orange emission from Mn^{2+} co-activator can be adjusted such that they can produce white field corresponding to wide range of color temperature **[12]**. In 1960 efficient rare earth activated phosphors were developed for use in color TV (Tb^{3+}- green, Eu^{3+} -red and Dy^{3+} -yellow). In 1970 tricolor lamp was introduced. Blue emission from Eu^{2+}, red emission from Eu^{3+} and green emission from Ce^{3+}-Tb^{3+} pair was used in tricolor lamp. At present a combination of halophosphate and tri-band phosphor blend is used in many lamps as a compromise between performance, phosphor cost and the lamp making cost. In recent years the Plasma Display Panels (PDP) are replacing the conventional color televisions. In phosphor area today top priority is the replacement of the high performance, but very expensive rare earth activated phosphors with cheaper materials. The fluorescent lamp is widely used as energy efficient light source, which has gone through various essential stages of development such as gas filling krypton instead of argon and the use of highly efficient phosphor coating. Compact fluorescence lamps are now replacing GLS lamps and have 8 times life than that of GLS lamps and is 5 times more efficient. Fluorescent powder is used in discharge lamps to convert to ultraviolet radiation into useful visible radiation. The powder increases the luminous flux and also changes the color rendition index of the lamp. Quantum of powder used in a lamp depends on the type of lamp. For example in popular 4ft fluorescent lamp, 4-5 gm of powder is used if the phosphors grain size is 4-5 microns. The most popular powder used in India is cool daylight halo phosphate powder. This phosphor is being used by the industry since its introduction in the 1940's. This powder manufactured to give color temperature of 6500K and fairly good CRI (in the range of 70) **[12]**. Lamp

manufacturer look forward to a technology wherein minimum quantity of powder is used without sacrificing the visual appearance and light output of the lamps. Average particle size and particle size distribution plays a major role in coating process. Fine powder gives more silky finish to the lamps and narrow particle size distribution gives uniformity of the coating along the full length. Fine particle size powders are in the range of 4-5 microns and coarser powders are above 10 microns. Lamp manufacturer prefer fine powders because these powders need not be milled and have more area coverage per gram of powder used. Another important parameter is the fluorescence yield, which is indirectly measured as the light output or luminous flux . Finer powders tend to give better light output. The trend is now changing with better technology adopted by powder manufacturer have to declare the color temperature and also sometimes CRI [5]. Therefore, these two parameters also form an integral part of powder specification. Powder which give lower color rendition are comparatively cheaper or lower luminous flux. Another quality parameter of a discharge lamp is to maintain light level with time. This lumen maintenance is decided by fluorescent powder along with many other parameters like purity, manufacturing process etc. A bad powder will give poor lumen maintenance. 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 color rendition index (~90), in particular the high wall load-factor enabled this phosphor system to be applied in compact fluorescent lamps where stability against high-load of UV is the stringent requirement for the successful lamp performance. Interestingly, the triband phosphor system performing near the physical limit leaves no scope for further improvement in the luminous efficiency. That's why new ways in the research are being focused on the design of in-expensive phosphor system without compromising the performance and effectively harnessing the influence of impurities to achieve the ultimate efficiency. The search does not seem to be elusive. Equally important are alternate discharge mechanism (e.g. Xe discharge) paving way for higher

lumen and more importantly, the concept of quantum-cutters underlying generating more than one visible photon for one UV.

The following are the devices which uses the phosphors:

1. Light sources represented by fluorescent lamps.
2. Display devices represented by CRT and PDP.
3. Detector systems represented by X-ray screens and scintillators.
4. Other simple applications such as luminous paints with long persistent phosphorescence.

1.5.1 New Phosphor Blends

Because of an increase awareness of the need for efficient, i.e. energy saving, lamps and the development of rare-earth-activated phosphors, new multi-component systems have been introduced and are currently receiving an increasing emphasis in the lighting industry. Color rendition index (CRI) which measures the average displacement of eight test colors on a uniform chromaticity diagram from their appearance under a standard incandescent source or daylight. A CRI of 100 means that there are no color distortions **[1, 5]**. The ability of a lamp not to distort colors is important to varying degrees in different applications. Optimum SPDs giving white light with a color temperature of 4200K consist of two bands peaking near 575nm and 450nm, respectively. Similar results are obtained for other white colors. When the two bands are very narrow, maximum luminous efficiency is obtained but color rendition is very poor. As the bands broaden, color rendition is improved at the expense of luminous efficiency. Better color rendition is desired in residential lighting and certain commercial applications where good color reproduction is important. An optimum SPD having very good color rendition is achieved using three narrow bands peaking near the wavelengths 610, 540 and 450nm. 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 $Y_2O_3:Eu^{3+}$, is essential to optimum efficiency and very good color rendition. However, some flexibility is possible in the choice of green and blue phosphor emissions. For example, a broad green emission provided by a strontium halo phosphate phosphor can be used with little loss in

luminous efficiency. Phosphor blends also used to achieve an infinite variety of SPDs for most important applications, reprographic recording, including plant growth, special color effects, etc. Optimum phosphor blends with the narrow red emission provide 40-50% more light output than deluxe phosphor blends previously used for applications requiring good color rendition, which contained the broad red-emitting phosphor Strontium Orthophosphate activated with Tin (II). Still other phosphor systems are used to obtain very high color rendition for color-critical applications. A CRI of 95 or higher can be obtained with phosphors or pigments that absorb some of the radiant power from the visible mercury lines in the blue violate region of the spectrum [1]. In many of the applications inorganic solids doped with rare earth impurities are used. To understand the how the rare earth impurities make various applications possible, it is important to know the luminescent characteristics of these material. Most probably there are four parameters, viz excitation type and spectrum, emission intensity and the emission spectrum, relaxation to emitting state and decay time, which determine the utility of rare earth doped phosphors. All these parameters are further depend on the temperature and the concentration. This dependence is equally important in context of the utility of the phosphors in various photoluminescence (PL) applications.

1.6 Nanotechnology and Nanophosphor research

Nano-, a prefix denoting a factor of 10^{-9} has its origin in the Greek *nanos*, meaning dwarf. The term is often associated with the time interval of a nanosecond, a billionth of a second, and the length scale of a nanometer, a billionth of a meter or 10Å. In its broadest terms, nanoscience and nanotechnology congers up visions of making, imaging, manipulating and utilizing things really small. Feynman's prescient nanoworld "on the head of a pin" inspires scientists and technologists to venture into this uncharted nano-terrain to do something big with something small. It excites investors and corporations, governments and policy makers to gamble on nanoscience breakthroughs and create new nanotechnologies. While early theoretical concepts and experimental results for nano-size materials and devices appeared five decades ago, it is rather recent scientific developments that have inspired a

resurgence of activity in the field. The stimulus for this growth can be traced to new and improved ways of making and assembling, positioning and connecting, imaging and measuring the properties of nanomaterials with controlled size and shape, composition and surface structure, charge and functionality, for use in the macroscopic real world.

1.6.1 Large and Small Nanomaterials

It was not so long ago in the world of molecules and materials that 1nm (1nm = 10Å) was considered large in chemistry while 1μm (1μm = 1000nm = 10,000 Å) was considered small in engineering physics. Matter residing in the "fuzzy interface" between these large and small extremes of length scales emerged as the science of nanoscale materials and has grown into one of the most exciting and vibrant fields of endeavor, showing all the signs of having a revolutionary impact on materials as we know them today. In our time, "nano" has left the science reservation and entered the industrial technology consciousness and public and political perception. Indeed, bulk materials can be remodeled through bottom-up synthetic chemistry and top-down engineering physics strategies as nanomaterials in two main ways, the first by reducing one or more of their physical dimensions to the nanoscale and the second by providing them with nanoscale porosity. When talking about finely divided and porous forms of nanostructured matter, it is found that "nanomaterials characteristically exhibits physical and chemical properties different from the bulk as a consequence of having at least one spatial dimension in the size range of 1–1000nm". [13]

1.6.2 Classification of nanomaterials

The classification of the nanomaterials should be as simple as possible. For this reason seven main material categories were defined in order to give a good overview of the different nanomaterials in the roadmaps. The seven main material categories are defined as:

1) Carbon based nanomaterials
2) Nanocomposites
3) Metals & alloys
4) Biological nanomaterials
5) Nano-polymers
6) Nano-glasses

7) Nano-ceramics

The usage of the term Nanophosphor is not old with revolutionary papers from the group of Bhargava et al [**14**] appearing with limitations of size domain (2-5nm). To have a thorough understanding of the physics and to develop applications based on nanophosphor that come under the category of 'doped nanocrystals (DNC)' and the 'quantum dots' efforts world over are being given. [**15-18**]. Over the years many nanophosphors have been synthesized using different techniques. Synthesis techniques for nanomaterials, in general, can be divided into two broad categories as chemical methods and physical methods. Under chemical methods different routes, viz., colloidal, capping, cluster formation, sol–gel, electrochemical, etc., are being followed. Physical methods mostly used are molecular beam epitaxy, ionised cluster beam, liquid metal ion source, consolidation, sputtering and gas aggregation of monomers. Sputtering is again achieved by either using high-energy ions or laser ablation. Again aggregation can be brought about by one of the ways, from oven sources, laser vaporization or laser pyrolysis. In all these techniques, the size has to be restricted to 3-5nm, i.e., less than twice of Bohr radii of exciton as quantum confinement regime is limited to the size. A recent review by Harish chander [**17**] in the field of nanophosphor gives a idea and an understanding of how this field has emerged through a period of time starting from early 1980 onwards. Graphical representation of the top down and the bottom up approach has been shown in figure-6 for the synthesis of nanophosphors.

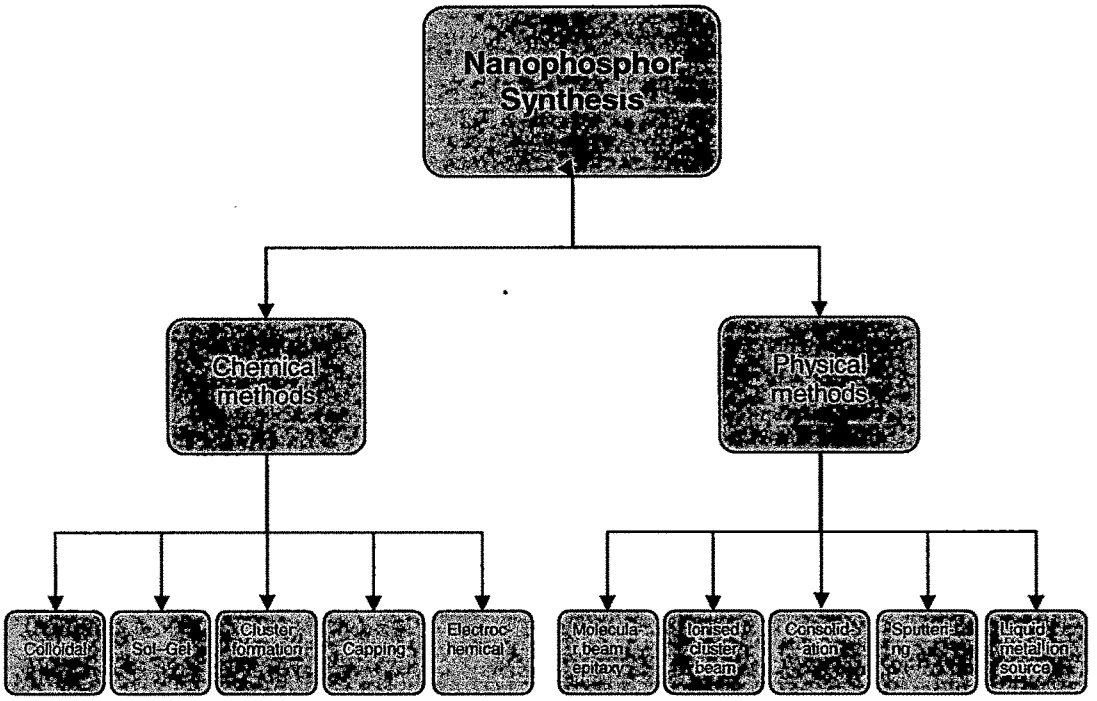

Figure-6 Graphical representation of the typical synthesis followed for nanophosphors with both top-down and bottom up approach.

1.7 Nanocrystals and their effect on the luminescence properties and the size dependent properties of the Phosphors

The optical properties of the solids have been an area of interest for the past few centuries, but for the past few decades they have been an area of high interest for those working with nanocrystals. The optical properties can give an insight to the mechanism and the nature of the material formed. These properties have led to the discovery of various inorganic hosts having different technological applications. The concentration of these have mainly been on the metallic nanocrystals [**19**] and semiconductors (mainly the Doped nanocrystals (DNC)), which shows the quantum confined effect. The applications of these have metallic nanocrystals have been from various optical data storage, solar energy conversion, sensors, as catalysts because of their high surface to volume ratio and due to their different shapes [**19**]. There is a no dearth of information available on the DNC but there is still much to be done in the field of insulators such as phosphor either doped or undoped. Though for the past decade it has also seen a dramatic rise in the number of papers and information available [**20-29**]. The optical properties for nanocrystals have an important feature that all of these

show a difference in the wavelength appearing for a bulk with the nanocrystals, the observation of this has been correlated to the 'blue shift' or the increase of the band width of the nanocrystal. For the particles of nanosize dimension, it is believed that the surface of the particles has major influence on the luminescence properties due to the large surface to volume ratio [**30**]. The resolution of images on a cathode ray tube display is related closely to the particle size of phosphors. In general smaller particles are favourable for higher resolution. Phosphor in the micrometer size (4-8micrometer) regime, used extensively in the conventional color television set, is not suitable for high-definition television (HDTV). Applications of the nanometer phosphors for displays has gathered great interest, since Bhargava et al. reported the optical properties of ZnS:Mn nanocrystal with high quantum efficiency in 1994 [**14, 31**].

1.7.1 Phosphor preparation Techniques

Almost all phosphor materials are synthesized or manufactured by a high temperature solid-state reaction or by a sol-gel process. During synthesis, a host matrix is formed from high-purity starting chemicals and the impurities, also known as activators and coactivators, are diffused into the crystal lattice in the required quantities. The activators are mostly responsible for the luminescence. In some cases, coactivators play an important role in diffusing the activators effectively into the crystal lattice and sometimes participate in keeping crystal neutrality through charge compensation. The synthesis sequence varies depending on the type of phosphor being prepared.

A. Solid-state reaction. The formation of a phosphor host and doping process by solid solution is critical and is highly dependent on the reaction on the reaction temperature and conditions. Since the purity of starting chemicals is very important to the synthesis of phosphors, the starting chemicals are typically 99.9-99.999% in purity. It is important to minimize the concentration of specific contaminants such as Fe, Co, and Ni, which can seriously degrade phosphor performance. Required amounts of starting ingredients are mixed in the presence of an appropriate flux (if necessary) and fired at high temperatures (900-1500°C) in air or in a controlled atmosphere (N_2, C, CO, or N_2 with 2-5% of H_2). The

calcinations conditions such as firing temperatures, duration of firing, firing atmosphere, and rate of heating and cooling for a particular phosphor are optimized empirically. The phosphor particle size and shape are also related to the morphology of starting chemicals and flux. The presence of flux materials of low melting compounds such as alkali halides helps to complete the doping process at lower temperatures. The general preparation procedure of solid-state reaction is well described in the literature [**1**].

B. Combustion synthesis. Combustion synthesis has been proposed to prepare oxide-based phosphors of smaller size particles. This method involves a highly exothermic reaction between an organic fuel and metal salts (oxidizers) in an aqueous solution. The reaction is initiated at low temperatures (around 500^0C) and proceeds to completion in a few minutes. The peak reaction temperatures depends on the fuel and oxidizer molar ratio (f/o).

C. Sol-gel technique. The sols are dispersions of colloidal particles in a liquid from which a gel can be formed. The gel is an interconnected, rigid network, having submicrometer pores and a polymeric chain whose average length is of the order of microns. Sol-gel processes are classified by the way the gels are dried: they are known as a sol-gel if they undergo normal dying above room temperature, as aerogels if dried at room temperature, and as xerogels if processed in vacuum. The particle size of the finished product is a function of the initial concentration of the starting sols, the gelation and drying process, calcination temperatures, and rates of cooling. The sol-gel process has many advantages over conventional methods (high-temperature solid-state reaction) in the synthesis of fine powders, particularly phosphor materials. Since all the starting materials are mixed at the molecular level in the sol solution, a high degree of homogeneity is achievable. Doping of impurities (activators/coactivators) through solutions is straight forward, easy, and effective. The pores in properly dried gels are often extremely small and the components of a homogenous gel are intimately mixed. The surface area of powders produced from sol-gel is very high, allowing lower processing temperatures. It is known that phosphor materials are extremely sensitive to impurities, even at ppb levels.

The above-described low-temperature process minimizes the potential for cross contamination. The selection of a precursor is crucial in the sol-gel process.

D. Coprecipitation method. The coprecipitation method is being employed to prepare submicron size and spherical-shaped phosphors for various display applications. In the coprecipitation method, solutions of salts containing the phosphor constituents are precipitated by adding suitable hydroxides, such as an ammonia solution or an oxalate. After filtering and drying, the precipitates are fired as required at designated temperatures. Since the starting precipitate is made of very small particles, coprecipitates generally need low firing temperatures to synthesize the required phosphors. For example, small and spherical-shaped $(Y,Gd)BO_3:Eu^{3+}$ can be synthesized by the coprecipitation method [1].

E. Hydrothermal technique. In the hydrothermal method, oxide- and silicate-based phosphors can be synthesized at low temperatures and under high pressure. In this method, the reaction is carried out in either an open or a closed system. In the open system, the solid is in direct contact with the reacting gases, which also serve as the pressure medium. In the seeded hydrothermal method, the presence of a polymeric stabilizer enhances the nucleation and crystallization processes of oxide particles under hydrothermal conditions [1].

F. Spray pyrolysis. In recent years, spray pyrolysis has become another method to prepare submicron and spherical-shaped phosphors. Here, an ultrasonic spray generator is used to generate fine droplets of suitable precursors to the phosphor to be prepared. Every phosphor particle is of high phase purity as each particle arises from one droplet in which constituents are mixed homogeneously. The preparative conditions, concentration of precursors, nature of additives, and flow rate control the size and morphology of phosphor particles. The droplets are dried, decomposed, and crystallized in the dispersed phase when passing through a reactor at a high temperature for a short time (seconds). The disadvantage with this process is the hollowness of particles, which causes reduction in the brightness and the lifetime of the phosphor [1]. Hollow phosphors are less stable thermally and mechanically.

1.8 Sol-Gel

Material science on a whole has attracted physicists, chemists and metallurgists equally, with research work carried out now being interdisciplinary. To give an idea of how the material science on a whole is developing and who all can benefit and how it has shaped, a graphical representation has been presented in figure-7, which is self explanatory.

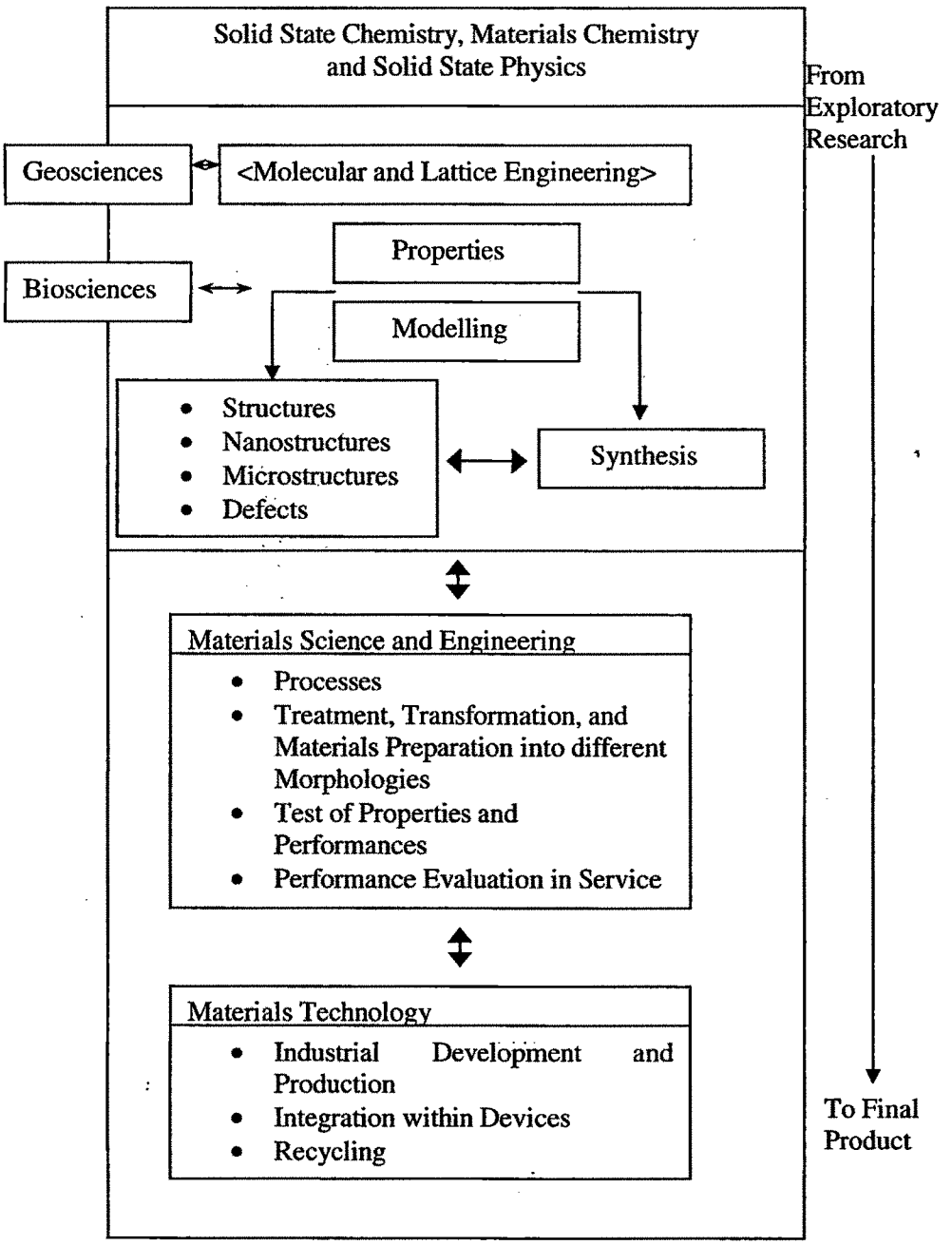

Figure-7 Multidisciplinary approach of Material Sciences.

Synthesis of phosphor is the core area of research till date and the different types of synthesis techniques involved in preparation of compounds have added dimensions to the very routine solid state reaction. Study shows that now alternate methods of synthesis are being tried to yield better results with better luminescent properties as well as good efficiency. Research and development in this field has gained momentum off late, almost daily new challenges are being thrown and greater heights are being achieved. Among the many synthesis techniques available the sol-gel is a very efficient one to produce phosphors with good optical properties. The aim of this research work was to examine the changes, if any, in the synthesis technique applied to see the changes in the optical properties of the phosphor thus synthesized.

Sol-gel science has been known to man for a long period of time but the practical applicability of this science especially in synthesis of the phosphor is relatively new. This has caught a pace and is seducing researchers to work with this. The rapid development of sol-gel techniques during the past two decades has led to fast progress in the deliberate synthesis of porous materials. The sol-gel process, which was discovered over 150 years ago, was originally a method for the production of ceramic materials. However, it was not until the 1960's that sol-gel research emerged as a major field of study **[32]**. These techniques complement a broad range of conventional procedures used for the preparation of amorphous solids or glasses, such as precipitation or impregnation methods followed by high-temperature treatments. The figure-8 gives an idea of the sol-gel technologies and their products. Sol-gel methods represent an attractive and easy-to-tailor alternative to conventional synthesis methods, such as ceramic firing, impregnation, precipitation/peptization or ion exchange on supported oxides. A broad range of porous materials-such as metal oxides, mixed oxides, crack-free or nonshrinking monoliths, fibers, membranes, and highly ordered crystalline materials with pores of uniform size is accessible through sol-gel processes **[33]**. For the preparation of polynary porous mixed oxides or glasses, the sol-gel process represents an attractive alternative to conventional synthesis methods **[34]**. In recent years, much attention has focused on the novel combination of organic species with inorganic minerals and networks because of the exciting range of properties demonstrated by these hybrid materials and the potential they offer to mimic the vast array of structures on display in Nature.

Low temperature routes to inorganic oxides have attracted considerable interest, in part because of the opportunity provided for combining the oxides with thermally labile organic compounds. The oxides and their hybrids have a plethora of uses, including the development of next generation passive (e.g. semi-structural) and active (e.g. electronic) materials, catalysis and catalyst supports, ceramics, sensor applications and active glasses. The most common approach has involved the preparation of sol-gel hybrids, including the combination of inorganic oxides (particularly silica) with polymers and the formation of organicallymodified silica (ormosils) from alkylalkoxysilanes. All of these methods use the well-established hydrolytic route to the oxide, involving the hydrolysis and condensation reactions of alkoxide (or other) precursors, usually in a solvent system carefully chosen to avoid the common problem of premature phase separation [**32**]. Sol-Gel processing with metal alkoxides as precursors has been extensively studied for the preparation of ceramics and glasses. Many ceramic and glass fibers have also been prepared successfully by sol-gel processing, in which gel fibers can be directly drawn from the viscous sol and can be converted to ceramic or glass fibers after firing [**35**].

The sol-gel process is a solution process, characterized by hydrolysis of precursors followed by polycondensation with formation of an oxide gel, which can be converted to an oxide by removal of all liquid components. Through separation of the mechanism of the sol-gel process into multiple steps (hydrolysis and prehydrolysis; acid-, base-, or fluoride-catalyzed polycondensation for gelation; drying; aging; and calcination), each step can be controlled by directed parameter variation to affect the final microstructure in such a way that selectivity and functional activity, such as catalytic properties, are improved. Amorphous oxides are formed by sol-gel processes in a polycondensation reaction under kinetically controlled reaction conditions. The choice of reagents, additives, and reaction and drying conditions allows for the control of pore structure and porosity, composition, surface polarity, surface acidity, and crystallinity. Meso- and macroporous structures are essential to guarantee the required mass transport for catalytic reactions [**36**]. In the preparation of mixed oxides, it is of utmost importance to avoid the formation of oxide domains of individual elements. Only a homogeneous distribution of all types of metal atoms of which the mixed oxide is composed can guarantee materials properties different from those of a purely

physical mixture of individual oxides. This property, simply termed mixed oxide or homogeneous mixed oxide, is strongly affected by the initial reaction conditions during gel formation. Similarly important for the properties of amorphous micro- or mesoporous structure can be the nature of the inorganic oxide precursor. Many physical or chemical properties of metal oxides are modified by the presence of second or third metal centers. As documented below, there are already such large varieties of sol-gel processing that mixed oxides of any composition are synthetically accessible. Gel formation is observed when the reaction volume is filled with small particles, which tend to aggregate. Polycondensation under acidic conditions results in the preferential formation of linear polycondensates. This linear chain formation continues until the whole reaction volume is filled with linear oxide chains. Cross-linking starts upon growth at inner chain positions and accelerates with the diffusional limitation of continuing terminal chain growth. For the formation of mixed oxides, differences in rates of hydrolysis and polycondensation as well as electronegativity of the central atoms greatly affect the chance for the formation of the desired mixed oxides. For the formation of mixed oxide sols, acid-catalyzed hydrolysis is essential because base catalysis results in precipitation and inhomogeneous sols, depending on the differences in the metal centers' electronegativity [**37**]. Under basic gelation conditions, the attacking reagent is the hydroxide ion, which attacks directly at the metal ion to accelerate hydrolysis as well as polycondensation. This results in accelerated hydrolysis and condensation of the more electropositive ions, which in turn leads to immediate oxide domain formation and thus undesired phase separation (formation of nanoparticles). Under basic gel conditions, sequential formation of pure particulate oxides will dominate the process. Ethylene glycol, an often-used network-forming agent, is partly oxidized by acid to oxalic acid, which polycondenses with further equivalents of ethylene glycol. The polymeric species complexes, through chelation, a large variety of different metal ions. Ethylene glycol has been used in sol-gel processes to form micro-, meso-, or macroporous materials through the formation of a primary organic network. The removal of the organic backbone requires a pyrolysis step. Depending on the conditions chosen, xerogels [**38**] or aerogels can be obtained. The morphological properties of the porous materials formed can be controlled by (a) the synthesis parameters, (b) dilution of the

reactive components, or (c) control of the growth mechanism of the particles or clusters through the choice of reactants (precursors), the pH of the solution, catalyst type, gelation temperature, and calcination protocol [**34, 39**].

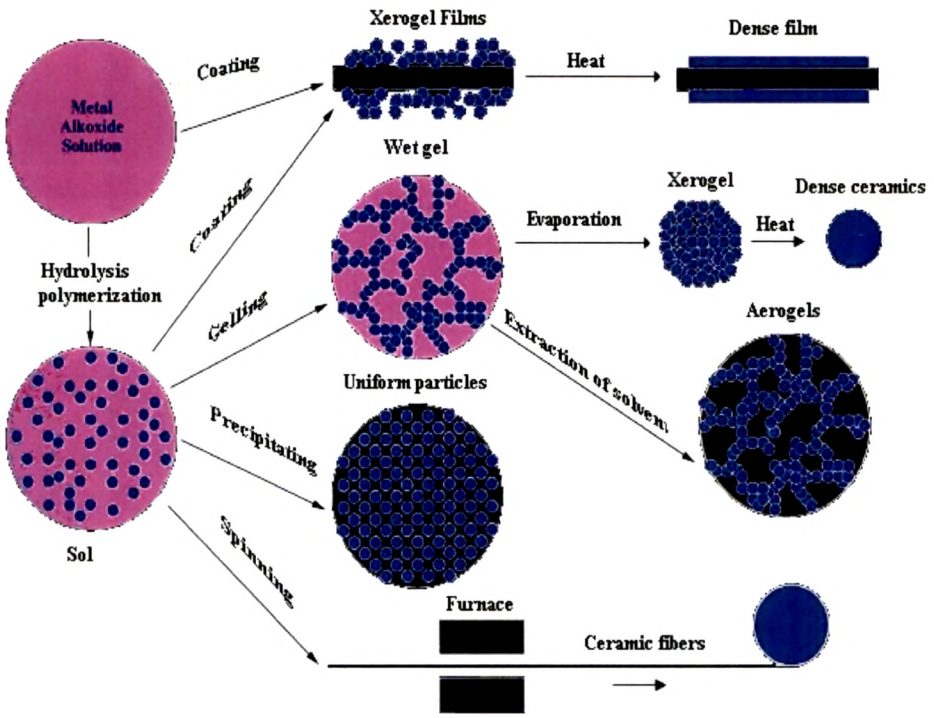

Figure-8 Sol-Gel technologies and their products.

1.8.1 Preparation of Nanophosphor by sol-gel

A simple and economical method for making high-quality luminescent material is desirable. Optimum phosphor characteristics are achieved with a particle size of 1μm with the applicability of phosphors for field emission and vacuum fluorescent display devices which have critical dependence on their particle sizes, the quantum efficiency of the luminescence of these materials increases as the size of the crystals decreases. Optimum performance in these devices can be achieved by employing ultra fine phosphor particles. **[40, 41]**. The phosphors prepared by traditional high-temperature solid state reaction are very large, these must be ground or milled to achieve a finer powder. The efficiency of the phosphors decreases significantly during grinding or milling, and the grain morphology is changed. The synthesis of fine phosphors by the sol-gel method is possible. The composition is easy to control, and a high degree of homogeneity is possible. YAG phosphors doped with activators are mainly synthesized by solid-state reaction techniques which require high sintering temperatures (above 1600°C), long reaction times (10 - 20h) and extensive ball milling, which generally introduces additional impurities and defects. **[16, 42]**. Compared to solid-state reactions, this mild synthesis method usually results in the formation of mixed oxides of improved homogeneity. The solution-based sol-gel method is one of the most important techniques for the synthesis of various materials as it possesses a number of advantages like low cost, requires only mild reaction conditions, low-temperature processing, easy coating of large surfaces, and possible formation of porous films and homogeneous multicomponent oxide films and provides homogeneous gels with most elements of the periodic table that are capable of solid oxide formation functional coating films [28]. Furthermore, the high versatility of the sol–gel process allows easy reach of various compositions and variation of the nature and the concentration of the doping ion. **[43-45]** Materials prepared by sol–gel chemistry are also usually obtained at temperatures much lower than those required for classical solid-state chemistry. This is very interesting from an economical point of view but also for reaching new compositions **[44]**. In fact, now sol-gel is fast developing itself as a synthesis technique extensively used for the preparation of nanophosphors. **[47-**

51]. Efforts are being made to develop various kinds of luminescent film via a sol–gel method in the past decade. Representative examples are $Y_3Al_5O_{12}$:Tb [52] and Y_2SiO_5:Tb [53] films for cathodoluminescence,$Y_3Al_5O_{12}$:Eu [54] films for FEDs, Y_2O_3:Eu [55] and Zn_2SiO_4:Mn [56] films for photoluminescence. In most of the above cases, the sol-gel precursors used are metal alkoxides and/or organometallic compounds, which suffer from the disadvantages of high cost, toxicity, and difficulty in controlling the experimental processes. The sol-gel synthesis process using alkoxides as raw materials has been demonstrated to produce powders with high sinterability [45]. However, stringent operation conditions and complicated handling procedures are required in the synthesis due to the high sensitivity of alkoxides to moisture. Furthermore, the high cost of alkoxides and toxicity of the alkoxide precursors used in the conventional sol-gel process is unfavorable for industrial production. An alternative approach to forming thin films is a Pechini-type sol-gel process, which mainly employs inorganic salts as precursors, citric acid as the chelate ligand, and polyethylene glycol (PEG) as the cross-linking agent [57-59]. Nitrate salts have been recommended for sol-gel synthesis to avoid the problems associated with the use of alkoxides [60]. Complicated handling procedures, such as refluxing of alkoxides, are exempt from this developed sol-gel synthesis, while the resulting powders still retain good sinterability. The effects of the calcination and sintering temperatures on the microstructures of the ceramics are extensively explored [61].

1.8.2 Advantages of Sol-Gel

Advantages of the sol-gel approach include in particular its variability, tolerance to precursor variation, and the small scale of the samples needed for primary screening:

1. Because of the tolerance to the chemical nature of the precursors, most elements of the periodic table capable of forming stable solid oxides can be used.
2. Using complex agents and parameter optimization, a large variety of homogeneous gels, a prerequisite for mixed oxide formation, have already been generated. There appears to be no limit, so any mixed oxide today can be formed by the sol-gel approach.

3. This technique offers a wide range of parameters to control or vary the morphology of the final materials.

In contrast to conventional synthesis procedures, the common operations of additional heating, filtration, adjustment of pH, and other procedures are not required for gelation in sol-gel processing, which suits the use of pipetting robots. The use of metal salts instead of alkoxides or carboxylates represents an important extension of the sol-gel procedures because highly diverse materials libraries can now be prepared readily. In general, because they are converted at mild temperatures during calcination to oxides under release of nitrous gases, nitrates as opposed to halides represent the most attractive metal salts **[34]**. The active precursor results in a low sintering temperature and minimizes the potential for cross contamination. Many researchers have synthesized phosphors by sol-gel processing, but most of the starting materials used were esters or alcohols, which evaporate easily and pollute the environment **[61-65]**. Among the various synthesis methods, the sol-gel method is quite common for processing of nanostructured materials. The sol-gel method offers a molecular-level mixing of the precursors, which is capable of improving chemical homogeneity of the resulting powders to a significant extent **[66, 67]**. Regardless of the method of preparation, two primary goals are usually associated with nanocrystalline preparation: (1) small diameters (<100nm) and (2) narrow particle size distribution. Small diameters are preferred because above 100nm, the properties tend to approach those of bulk materials. Narrow particle distributions are preferred for potential application purposes. The sol-gel method is an example of a controlled precipitation reaction in which the particles do not precipitate but are dispersed in solution as colloids. Since the atomic structure of nanocrystalline ceramics differs from structures of bulk materials, the structure-dependent properties are expected to be different from the properties of the bulk. When electrons are confined in a small domain, such as a nanoparticle, the system is commonly referred to as quantum confinement **[14, 15, 19]**. Quantum confinement changes the overlap of the wave functions of the activator (impurity) atoms with those of host atoms. As a result, there are more efficient interactions between the activator and host atoms.

1.9 Overview of Lanthanide Luminescence as a Probe of Nanocrystalline Structure

The lanthanides have a well-documented history in studies of luminescence primarily for the fact that the f-f transitions produce narrow lines. Since the 4f electrons of the lanthanides are shielded from perturbations with the lattice by the outer 5s and 5p electrons, the 4f orbitals retain their hydrogenic character, resulting in sharp transitions between the 4f levels [2]. Current work on lanthanide luminescence is diverse in scope due to both fundamental interest and potential applications. Consider a case of an Eu^{3+} ion doped in $NaGdTiO_4$, at around 27C the values of the nonradiative rate exceeds that of radiative (figure-9), so that the nonradiative process dominates and the emission occurs mainly from the $^5D_0$ level. In compounds where higher phonon energy is available (eg, borates, silicates), the $^5D_1$ emission of Eu^{3+} is usually hardly detectable. Ions like Tb^{3+} and Eu^{3+} may emit from higher excited states: Eu^{3+} not only from red ($^5D_0$), but also from $^5D_1$ (green) and $^5D_2$ (blue), however, this depends critically on the host lattice. In Y_2O_3 for example all these emissions are observed, but not in borates or silicates [5].

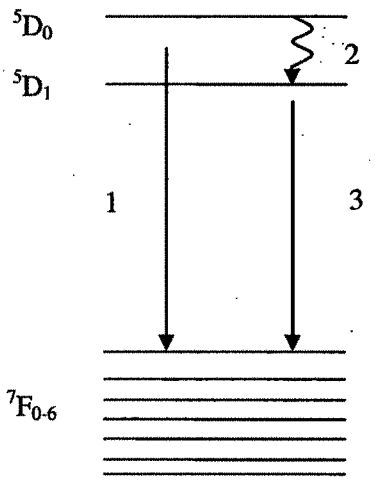

Figure-9 Energy level scheme of Eu^{3+}. The $^5D_1$ level can decay radiatively to the ^7F_J levels (arrow 1), or nonradiatively to the $^5D_0$ level (arrow 2). The latter is followed by $^5D_0 \rightarrow {}^7F_J$ emission (arrow 3). The amount of $^5D_1$ emission is determined by the rate ratio of processes 1 and 2.

Charge transfer excitation of Eu^{3+} also plays an important role in the applications, as it is also used in a three colour luminescent lamps, eg. $Y_2O_3:Eu^{3+}$ whose excitation in the charge transfer state at 254nm results in efficient red emission ($^5D_0 \rightarrow {}^7F_2$) within the $4f^6$ configuration. Figure-10 shows the relevant configurational coordinate diagram. The useful properties are based on a fast radiationless process, the transition from charge transfer state to the excited levels of the $4f^6$ configuration.

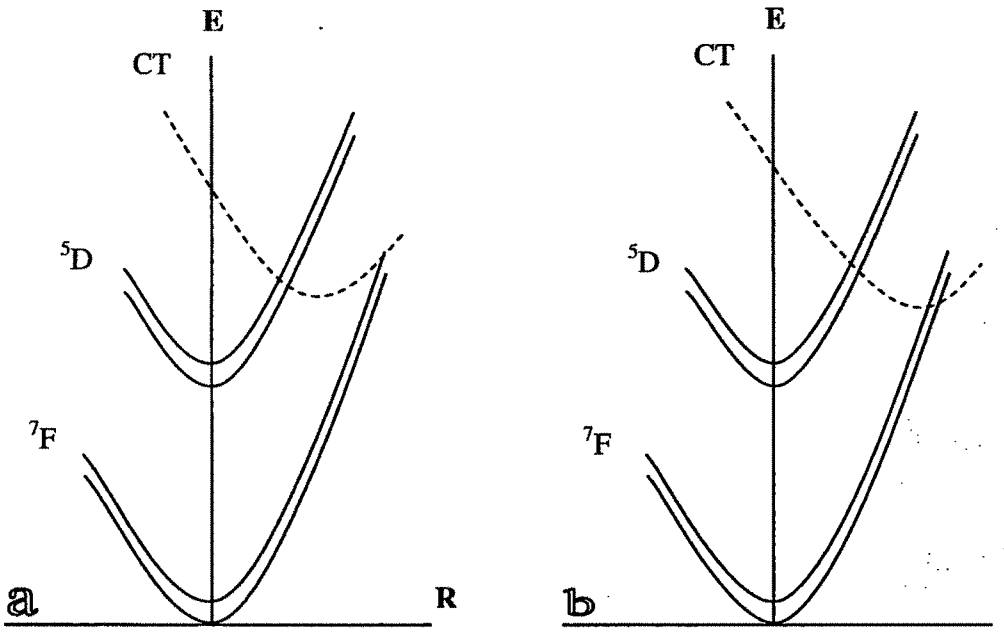

Figure-10 The role of the charge transfer state (CT) in the quenching of the luminescence of the Eu^{3+} ion. Only a few parabolas of the $_4f^6$ configuration have been drawn. In (a), the situation for $Y_2O_3:Eu^{3+}$ is depicted: the CT state feeds the emitting ^5D levels. In (b), the CT state has a larger offset. As a consequence the CT state populates, at least partly, the ground state levels, so that the luminescence is strongly reduced.

In addition to the technologically important applications, lanthanides serve as a probe of their local chemical environment. As mentioned in the foregoing paragraph, the 4f transitions are sharp and the 4f orbitals are sensitive to their local crystal field. Consequently, the J-multiplet levels are split and the splitting pattern is dependent on the strength of the crystal field and local site symmetry. Therefore, the luminescent spectra consist of lines that are characteristic of the local chemical environment. A study of the optical spectroscopy of lanthanide

ions in bulk materials has contributed to a better understanding of the crystallinity, structure, phase distributions and defect chemistry in these materials [2]. These types of measurements have been demonstrated previously in a variety of bulk materials. A specific lanthanide ion of interest is Eu^{3+}, which has been studied in several different hosts, but most commonly in Y_2O_3 due to its use as a commercially viable red phosphor. Eu^{3+}:Y_2O_3 has been used commercially for cathode ray tube displays, scintillators, and other display technologies due to high radiant efficiency and temperature stability [1].

1.10 Applications of phosphors

The phosphors with short decay times find applications as essential components in fluorescent lamps, television picture tubes, flat-panel displays, plasma display panels etc. [1]. Table-1 lists their applications in devices. However, phosphors with delayed emission are also extremely useful as sources of light energy (lamps) at the time of sudden power failure or intentional blackouts. These have great potential for luminous paints, watches [17, 50], display industries [1, 7], exit signage and emergency escape route guidance systems. The interest in these phosphors has grown due to increasing number of applications in radiation detectors [5], sensors for structural damage [1, 5] and temperature detection [1]. Considering its innumerable applications, the present work was concentrated on the synthesis, characterization and studies on luminescence properties of multicolour emitting phosphors.

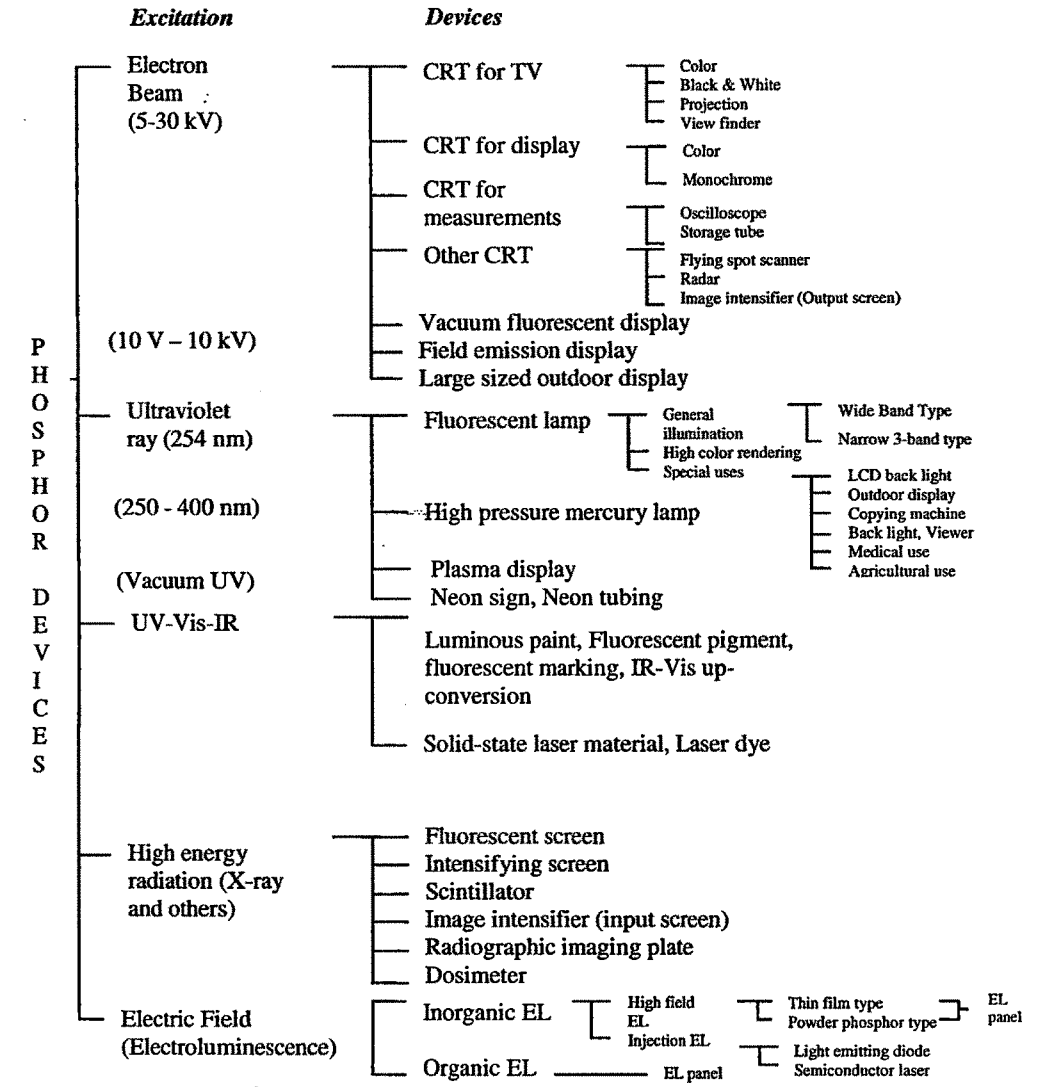

Table -1 Phosphor Devices and their Applications

1.10.1 Phosphor Demand and status

The current world market place for phosphors is about $450m annually with an expectation to grow in the 8-10% range. And, they have to compete with and against several display technologies and applications such as liquid crystal, plasma, LEDs, OLEDs, automotive and field emission, which in turn require a growing range of phosphor types to satisfy new and existing uses. These include cathodic, electroluminescent, plasma, LED, colour conversion, micro display, xenon activated, and image panel application. In an atmosphere of heightened

awareness, new compounds, materials properties, formats and processes are being examined covering doping activation, particle sizes, particle coatings and even nano-dots, all to provide more efficient and more stable phosphors with improved aging and half-life characteristics. These will all affect the supply, demand, pricing and new business opportunities as the market volumes and values continue to grow [**68**].

1.11 About the Present Work

In the last two decades considerable interest has been directed towards the synthesis and characterization of economical and efficient rare earth doped phosphors using different hosts has been developed for various applications. The red [$^5D_0 \rightarrow {}^7F_2$] and orange emission [$^5D_0 \rightarrow {}^7F_1$] of Eu^{3+} and green emission of Tb^{3+} [$^5D_4 \rightarrow {}^7F_5$], is usually used in these phosphors. These phosphors find applications in fluorescent lamps, color TV screen, cathode ray tubes, Plasma Display Panels, discharge lamps etc. These phosphors are not commercially synthesized in India, and are imported. Also no systematic efforts were made towards studying the use of indigenous chemicals for the synthesis of these phosphors. In this direction the Display Materials Laboratory at Applied Physics Department, The M. S. University of Baroda, India is working since more than a decade with a number of publications on various applications of the synthesized phosphor [**69-75**].

With the work by Danielson et al appeared in science, [**76**] of the discovery of a new phosphor material (Sr_2CeO_4) by combinatorial synthesis, since then a number of publications have appeared for the same. But the synthesis techniques used were either very sophisticated costly or the standard solid state reactions. There were absolutely less or very less reports on the comparisons of the optical properties of the different synthesis techniques. The optical properties are dependent on the synthesis techniques, thus to have an idea on the effect of different techniques on the Sr_2CeO_4 was our idea to explore. Sol-Gel techniques have been explored for oxide based materials and have been extensively used in the oxide based synthesis. Our interest was further to give a special emphasis to sol-gel in this study and to explore the possibility and fabrication of the same for

the synthesis of the phosphor. The rare earth based phosphors find their use in the almost all the display devices.

The focus in this study of nanocrystalline materials is the use of the trivalent rare earth doped ions (Eu^{3+}, Sm^{3+}, Dy^{3+} etc) to probe the structure of the nanocrystalline systems and also to study the charge transfer process through which the emission is occurring radiatively. The rare earth incorporation also induces a colour change and this can be tuned to suit our needs. Recent studies of nanocrystalline ceramics have shown that tremendous changes in properties can be achieved compared to analogous materials with micrometer-scale structure. Since the particle size of these materials is between molecular and bulk, nanocrystals have hybrid properties that are not well understood. Gaining a deeper understanding into the structural changes that can occur when the particle size is reduced may be helpful for developing specific applications using nanocrystalline materials.

The work presented in this thesis consists of the experimental results of the phosphors synthesized using different routes in the laboratory. By considering the application potential of Sr_2CeO_4 doped with different concentrations of Eu^{3+}, Sm^{3+}, Dy^{3+} the present work was under taken for this thesis. Since the CFL's are the present day energy saving lamps which are widely used globally therefore it is considered the present phosphor synthesis will help the local industry to use the indigenously developed materials. By considering the application potential of the following phosphors are studied for their PL and TL characteristics. Sr_2CeO_4 was syntheiszed with different routes of solid state, sol-gel and combustion routes.

Sr. No.	Sample Name	Doping concentration (mol%)
1	Sr_2CeO_4	0
2	Sr_2CeO_4 :Eu^{3+}	0.5
3	Sr_2CeO_4 :Eu^{3+}	1
4	Sr_2CeO_4 :Eu^{3+}	1.5
5	Sr_2CeO_4 :Eu^{3+}	2
6	Sr_2CeO_4 :Eu^{3+}	4
7	Sr_2CeO_4 :Sm^{3+}	0.03125
8	Sr_2CeO_4 :Sm^{3+}	0.125
9	Sr_2CeO_4 :Sm^{3+}	0.25
10	Sr_2CeO_4 :Sm^{3+}	0.5
11	Sr_2CeO_4 :Sm^{3+}	1
12	Sr_2CeO_4 :Sm^{3+}	1.5
13	Sr_2CeO_4 :Sm^{3+}	2
14	Sr_2CeO_4 :Dy^{3+}	0.5
15	Sr_2CeO_4 :Dy^{3+}	1
16	Sr_2CeO_4 :Dy^{3+}	1.5
17	Sr_2CeO_4 :Tb^{3+}	0.5
18	Sr_2CeO_4 :Tb^{3+}	1
19	Sr_2CeO_4 :Tb^{3+}	1.5

Table-2 Doped phosphors synthesized by the Sol-gel technique with their concentrations

The synthesized phosphors i.e. Sr_2CeO_4 were prepared using sol-gel as well as high temperature solid state reaction and combustion method and also with different rare earths Eu^{3+}, Sm^{3+} Dy^{3+} and Tb^{3+} at various concentrations. Few samples of combustion synthesized Sr_2CeO_4 with different fuels were prepared and then the fuel to metal ratio was varied. The various concentrations of the Sol-gel synthesized phosphor have been presented in table-2. The PL spectra were recorded at room temperature using the Shimadzu RF-5301 PC Spectrofluorophotometer. Thermoluminescence of the synthesized phosphors are also studied with beta radiations using Nucleonix TLD auto ranging reader system. The results are analyzed in the context of available theories and literature on the phosphor material. The main aim of the present research work is to synthesize an indigenous nano Sr_2CeO_4 phosphor for fluorescent/Compact Fluorescent Lamps. Commission Internationale de l'Eclairage (CIE) coordinates were also calculated by the equidistant wavelength method and have been elaborated and discussed. These values gives us an insight to the nature of colour

emission and tunablity of the phoshors. Phosphors having a small particle size and high efficiency would be most useful. These promising results suggest that the role of defect chemistry will be of major importance in understanding more clearly how the increased surface-to-volume ratio affects the structure and therefore the properties of nanocrystals.

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