Chapter -1

General Introduction
1.1 Introduction

In the recent years, much attention has been focused on oxide-based luminescent materials due to their commercial applications in color television, fluorescent tube, X-ray phosphors, and scintillators [1, 2]. Recently various phosphor materials have been actively investigated to improve their luminescent properties and to meet the development of different display and luminescence devices. Inorganic compounds doped with rare earth ions form an important class of phosphors as they possess a few interesting characteristics such as excellent chemical stability, high luminescence efficiency, and flexible emission colors with different activators [3,4]. There is growing interest in the development of new full colour emitting phosphor materials that combine thermal and chemical stability in air with high emission quantum yield at room-temperature.

The search for blue phosphors is of particular importance because of the limited number of stable blue luminescent materials available. Danielson et al. [5] have reported a novel blue luminescent material Sr$_2$CeO$_4$ prepared by combinatorial material synthesis technique, which exhibits the emission peak at 485 nm. Subsequently, several studies of this luminescent materials were conducted, and some synthetic routes have been developed to prepare the Sr$_2$CeO$_4$ powders and films, including traditional solid-state reaction [6-8], chemical co-precipitations [9-11], Pechini’s method [12], microwave annealing [13], ultrasonic spray pyrolysis [14], and pulsed laser depositions [15].

Sr$_2$CeO$_4$ consists of infinite edge-sharing CeO$_6$ octahedra chains separated by Sr atoms. The luminescence originates from a ligand-to-metal Ce$^{4+}$ charge transfer (CT). In CT transitions an electron is transferred from a ligand to 4f$^n$ shell of a rare earth (RE) ion. Some states that arise as a result of such transition are stable and can relax to the ground state with a photon emission. This phosphor exhibits blue-white luminescence efficiently under excitation with UV light, cathode ray or X-ray. Sr$_2$CeO$_4$ also acts as a sensitizer to transfer the absorbed energy to the dopants (activators) such as rare earth ions [16, 17]. The broad emission band is suitable for the doping of rare earth ions in pursuing new luminescent materials and some research work has been carried out by traditional solid-state reaction [18, 19], namely the metal oxides are used as precursors and the reaction reagents have to be calcinate at very high temperature for a long time.
Sr$_2$CeO$_4$ phosphor has been widely studied because of its importance in the realization of a new generation of optoelectronic and displaying devices [20].

Furthermore, luminescent properties were found to greatly depend on particle size, size distribution and particle morphology. This relationship is of current interest, and may lead to new fabrication processes to yield high-quality luminescent materials. Therefore, it is interesting to develop a synthetic route to yield Sr$_2$CeO$_4$ particles with smaller size and uniform morphology, since they have higher packing density and larger percentage of the active sites than bulk material. In light of the foregoing, the purpose of this thesis was drawn. Thus the main aim of the present study is the synthesis, characterization and photoluminescence properties of pure and rare earths (Dy, La and Eu) doped Sr$_2$CeO$_4$ phosphors of 0.01, 0.1, 0.2, 0.5 and 1.0% molar concentrations.

1.2 Luminescence

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 materials and a bright light is produced. Luminescence is a collective term for different phenomena where a substance emits light without being strongly heated. 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’. The materials exhibiting this phenomenon are known as ‘Luminescent materials’ or ‘Phosphors’ meaning ‘light bearer’ in Greek. The term phosphor was coined in 17th century by an Italian alchemist named Vincentinus Casciarolo of Bologona [21, 22].

The phenomenon of luminescence can be classified into various categories depending on the mode of excitation.

1. Photoluminescence, when the excitation is by electromagnetic radiation/photons.
2. Cathodoluminescence, when the excitation is by energetic electrons or cathode rays.
3. Electroluminescence is light emission triggered by electric influences.
4. Radioluminescence, when the excitation is by high-energy X-rays or $\gamma$ rays.
5. Sonoluminescence, when the excitation is by ultrasonic waves.
6. Triboluminescence can occur when a material is mechanical treated.
7. Chemiluminescence is light emitted during chemical reactions.
8. Bioluminescence is the form of chemiluminescence from living organisms.

9. 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.

All types of luminescence shown in Figure-1.1 and each process mentioned above have its own significance and advantage in the field of science and technology. Schematic illustration of (a)Photoluminescence, (b) Electroluminescence, (c) Cathodoluminescence shown in Figure-1.2. 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 detail it is important to know the procedure leading to luminescence and its various characteristics.

1.2.1 General Characteristics of Luminescence:

The process of luminescence can be illustrated in Figure-1.3. The figure depicts two types of return to the ground state, one radiative and the other one 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 photons 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-1.3, the exciting radiation is not absorbed by the activator [23-25]. Depending on the duration of the emission, luminescence has further sub classification:

(a) **Fluorescence**: On removal of excitation, there exists an exponential afterglow, 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 lifetime of more than $10^{-8}$ seconds.
Figure-1.1  Types of Luminescence
Figure-1.2 Schematic illustration of (a) Photoluminescence (b) Electroluminescence (c) Cathodoluminescence

Figure-1.3 Energy level Scheme of the luminescent ion A. The * indicates the excited state, R the radiative return and NR the non-radiative return to the ground state.
**Figure-1.4** Schematic diagram of (a) fluorescence and (b) Phosphorescence.

\[
T_f = t_1 + t_2 \\
T_p = t_3 + t_4 + t_5
\]

**Figure-1.5**: Schematic representation of the possible luminescence processes of a crystal system with donor S and acceptor A ions. Following excitation S may: (1) emit radiatively, (2) decay non-radiatively, (3) energy transfer to another ion S, or (4) transfer of energy to an ion A. In the last case, energy transfer to A is followed by either radiative or non-radiative decay.
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. Schematic diagram of fluorescence and phosphorescence shown in Figure-1.4

1.2.2. Model for a Luminescence Process
In the host lattice, the ion which absorbs the radiation is referred as the donor and the ion which transferred excitation energy is the acceptor. From the schematic representation in Figure-1.5, four different processes following excitation of S can be distinguished: (1) S may luminescence, (2) S may decay non-radiatively producing heat, (3) S may transfer energy to another S type ion, or (4) S may transfer energy to an A type ion. If energy transfer to A is followed by non radiative 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-1.5 shows a schematic of the possible luminescence processes which can occur when ion within a larger ensemble is excited [26].

1.2.3. Production and Decay process of excited states
Production and decay processes of excited states are described using an energy state diagram called Jablonski diagram shown in Figure-1.6. The ground state $S_0$ and lowest singlet and triplet states, $S_1$ and $T_1$ are composed of multiple vibration 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 $S_2$ or $S_3$ are produced. The higher vibrate states of $S_1$ relaxed to the lowest vibrate 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 non-radiative internal conversion (IC) processes. Triplet’s states are usually produced via an inter system 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 transition 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 $S_0$ transition 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.
1.2.4. Configurational Coordinate Model
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-1.7.
In this model a luminescent ion and the ions at its nearest neighbor 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.

1.2.5. Quenching of luminescence
There are dominant effects that reduce the efficiency of the phosphor. For example, the
killers and concentration quenching

**Killers:**
Killers are defects caused by incidental impurities and inherent lattice defects that
reduce the luminescence intensity of a phosphor [27]. The atoms and molecules
adsorbed at the surface of the phosphor may reduce luminescence by producing a non-
luminescent layer when they react with ambient vacuum species. Killers can affect the
luminescence of phosphors in two different ways. They give rise to deep levels in the
forbidden band which act as non-radiative recombination centres for free electrons in
the conduction band and holes in the valence band, or the excitation energy absorbed by
luminescent centres is transferred to killers without emitting radiation. An iso-electronic
trap is caused when an element belonging to the same column of the periodic table as
that of the constituent atom of the semiconductor.It can attract an electron or a hole
because of the difference in electron affinity thereby becoming a killer [28].
Figure-1.6 The Jablonski diagram, which explains the photophysical processes in molecular systems. (1) photo absorption; (2) vibrational relaxation; (3) internal conversion; (4) intersystem crossing; (5) radiative transition; and (6) non-radiative transition.

Figure-1.7: Configurational Coordinate diagram
**Concentration quenching:**
An increase in the concentration of activators and co-activators to obtain brighter phosphors may result in a reduction of light output due to concentration quenching. The primary cause of this quenching process is clustering of impurity ions in sol-gel glass pores at high doping levels. Non-radiative dipole-dipole interactions between ions, a process known as cross-relaxation, decrease the fluorescence intensity of certain susceptible transitions in ions. Moreover, this process has been found to be strongly concentration dependant. A lot of defects such as color center, OH- and other kinds of defects may trap energy and then form the quenching centers.

**1.3 Photoluminescence**
Photoluminescence (PL) refers to the luminescence stimulated by the excitation of solid material (phosphor) by light of another wavelength, typically ultraviolet (UV), visible or infrared light. PL analysis is non-destructive and the technique requires very little sample manipulation or environmental control. The fundamental limitation of PL analysis is its reliance on radiative events. The materials with poor radiative efficiencies, such as low quality indirect semiconductors, are difficult to study via ordinary PL. Similarly, the identification of impurity and defect states depends on their optical activity [29]. The most prevalent use of photoluminescent phosphors is in fluorescent lamps and it is divided into two major types, namely intrinsic photoluminescence and extrinsic photoluminescence. Intrinsic photoluminescence is displayed by materials, which contain no impurity atoms. Extrinsic photoluminescence results from intentionally incorporated impurities, in most cases metallic impurities or intrinsic defects [30].

**1.3.1. Intrinsic Photoluminescence**
There are three kinds of intrinsic photoluminescence, namely band-to-band, excitons and cross-luminescence. Band-to-band results from the recombination of an electron in the conduction band with a hole in the valence band and can only be observed in a very pure crystals at relatively high temperatures. An exciton is a composite particle resulting from the coupling of an electron and a hole; it then travels in a crystal and produces luminescence by releasing its energy at luminescent centers. Cross-luminescence is produced by the recombination of an electron in the valence band with a hole in the outermost core band. It can only take place when the energy difference between the top
of the valence band and that of the outermost core band is smaller than the band-gap energy; otherwise, an Auger process occurs.

1.3.2. Extrinsic Photoluminescence
Most of the observed types of luminescence that have practical applications belong to this category. Extrinsic luminescence is classified into two types, namely localized and delocalized luminescence. In a delocalized luminescence the excited electrons and holes of the host lattice participate in the luminescence process, while in a case of the localized luminescence the excitation and emission processes are confined in a localized luminescence center, the host lattice does not contribute to luminescence process.

1.3.3. Sensitized Photoluminescence
By definition, sensitized photoluminescence refers to a process whereby an impurity species (activator or acceptor) having no appreciable light absorption ability in a given spectral domain, is made to emit radiation upon excitation as a result of absorption by and transfer from another impurity species (sensitizer, or donor). This is shown in Figure 1.8.

**Sensitization mechanism**
The general steps of a sensitization mechanism are usually described as shown in Figure 1.9. First of all, the donor is excited either by optical or electrical pumping action (1). Then, energy from the excited donor (D*) is transferred to the acceptor (A) via a non-radiative process (2) which can be modeled using Foster-Dexter theory. Finally, the acceptor relaxes into a lower energy state by emitting a photon (3). The same process can reinitiate upon excitation of the donor.

1.4 Rare earth elements
The history of the rare earth elements (also called lanthanides) started almost 220 years ago in 1788 when Geijer reported on a black stone found close to the Swedish town of Ytterby. The stone was called Yttria. Later on Klaproth found a stone he named Ceria (1803). After decades of careful analysis, for example by Gadolin, both materials turned out to contain a number of different but chemically very similar elements, which made it hard to isolate them. It took about 100 years until all lanthanides were obtained in a pure form. From the mineral Ceria the light lanthanides lanthanum, cerium, didymium, samarium, europium and gadolinium were separated. Didymium was later on found to be a mixture of praseodymium and neodymium.
**Figure 1.8** Principle of sensitized photoluminescence, the activator is made to emit light after being excited via an energy transfer from the photo excited donor (D).

**Figure 1.9** Sensitization mechanism of the acceptor (A) by excitation of the donor (D\(^*\)) is used to represent an excitation state.
The mineral Yttria was found to contain the elements terbium, erbium, ytterbium, holmium, thulium, dysprosium and lutetium. Despite their name, rare earth elements are relatively plentiful in the Earth’s crust, with cerium being the 25th most abundant element at 68 parts per million. However, because of their geochemical properties, rare earth elements are typically dispersed and not often found in concentrated and economically exploitable forms. The few economically exploitable deposits are known as rare earth minerals. It was the very scarcity of these minerals that led to the term rare earth. The first such mineral discovered was gadolinite, a compound of cerium, yttrium, iron, silicon and other elements. This mineral was extracted from a mine in the village of Ytterby in Sweden; several of the rare earth elements bear names derived from this location. The rare earth elements (REEs), which include the 15 lanthanide elements (Z = 57 through 71) and yttrium (Z = 39), are so called because most of them were originally isolated in the 18th and 19th centuries as oxides from rare minerals. Lanthanide elements with low atomic numbers are generally more abundant in the earth’s crust than those with high atomic numbers.

Rare earth Elements includes: 39-Yttrium(Y), 57-Lanthanum (La), 58-Cerium( Ce), 59-Praseodymium(Pr),60-Neodymium(Nd),61-Promethium(Pm), 62-Samarium(Sm), 63-Europium(Eu),64-Gadolinite(Gd),65-Terbiuim(Tb),66-Dysprosium(Dy),67-Holmium (Ho),68-Erbium(Er),69-Thulium (Tm),70-Ytterbium(Yb),71-Lutetium(Lu).

The lanthanide elements traditionally have been divided into two groups: the light rare earth elements (LREEs)—lanthanum through europium (Z = 57 through 63); and the heavy rare earth elements (HREEs)—gadolinium through lutetium (Z = 64 through 71). Although yttrium is the lightest REE, it is usually grouped with the HREEs to which it is chemically and physically similar. Rare earths are found with non-metals, usually in the 3+ oxidation state. There is little tendency to vary the valence. (Europium also has a valence of 2+ and cerium also a valence of 4+)

Rare earths are used in a variety of applications because of their magnetic and conducive properties such as:

- **Commercial applications**: Rare earth elements are used in items ranging from cell phones and computer hard drives to MRI machines. In addition, they are necessary in
the production of many green technologies, including electric and hybrid vehicle motors, wind turbines, and energy efficient fluorescent light bulbs.

- **Military applications:** Rare earths also play a critical role in sophisticated military applications including guidance and control systems; advanced optics technologies; radar and radiation detection equipment; and advanced communications systems. Some of the defense related weapons and equipment that contain rare earths are: Predator unmanned aerial vehicles, Tomahawk cruise missiles, Zumwalt-class destroyers, night vision goggles, smart bombs, and sonar transducers.

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

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

1.6 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. 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$^{2+}$ activated alkali halide phosphors in details in the late 1920s and 1930s. A major turning point follows the development in 1940s with synthesis of Sb-Mn co-activated halophosphate phosphors. In a single material blue emission from the Sb$^{3+}$ activator and the orange emission from Mn$^{2+}$ co-activator can be adjusted such that they can produce white field corresponding to wide range of color temperature. Homboltz and co-workers at Radio Corporation of America (RCA) also investigated many phosphors for application in TV tubes. Their achievements are compiled in Leverenz’s book. Data on the emission spectra in the book remains useful even today.

After World War II, the advances in the optical spectroscopy of solids, especially those of transition metal ions help to evolve research on phosphor and solid state luminescence. In 1960 efficient rare earth activated phosphors were developed for use in color TV (Tb$^{3+}$- green, Eu$^{3+}$- red and Dy$^{3+}$ - yellow). In 1970 tricolor lamp was introduced. Blue emission from Eu$^{2+}$, red emission from Eu$^{3+}$ and green emission from Ce$^{3+}$ - Tb$^{3+}$ pair was used in tricolor lamp. At present a combination of halophosphate and troposphere blend is used in many lamps as a compromise between performance, phosphor cost and the lamp making cost. In phosphor area today top priority is the replacement of the high performance, but very expensive rare earth activated phosphors with cheaper materials. This essentially means replacing the rare earth ions with transition metal ions or post transition ions.

The advent of trichromatic fluorescent lamps is the corner stone in the lighting industry. The introduction of rare-earth phosphor systems for lamp applications has revolutionized the industry for it addressed to the major issues concerning the lamp performance viz; higher lumen output (90-100 lumens/W). Higher wall load factor and
better color rendition index (Ra=90), in particular the high wall load –factor enabled this phosphor system to be applied in compact fluorescent lamps where stability against high-load of UV is the stringent requirement for the successful lamp performance. Interestingly, the triband phosphor system performing near the physical limit leaves no scope for further improvement in the luminous efficiency. That’s why new ways in the research are being focused on the design of in-expensive phosphor system without compromising the performance and effectively harnessing the influence of impurities to achieve the ultimate efficiency. The search does not seem to be elusive. Equally important are alternate discharge mechanism (e.g. Xe – discharge) paving way for higher lumen and more importantly, the concept of quantum – cutters underlying generating more than one visible photon for one UV.

1.7 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. This enlists the maximum candela (lumens) or light output, which can be obtained from the fluorescent lamps. The numbers are calculated using simulated spectral-powder distributions (SPDs). They include the visible mercury lines and assume the efficiency of standard phosphor coatings. The X-axis is the general color rendition index (CRI) which measures the average displacement of eight test colors on a uniform chromaticity diagram from their appearance under a standard incandescent source or daylight. A CRI of 100 lumens per watt is that there are no color distortions. The ability of a lamp not to distort colors is important to varying degrees in different applications. Optimum SPDs giving white light with a color temperature of 4200 K consist of two bands peaking near 575 nm and 450 nm, respectively. Similar results are obtained for other white colors. When the two bands are very narrow, maximum luminous efficiency is obtained but color rendition is very poor. As the bands broaden, color rendition is improved at the expense of luminous efficiency.

Better color rendition is desired in residential lighting and certain commercial applications where good color reproduction is important. An optimum SPD having very good color rendition is achieved using three narrow bands peaking near the wavelengths
610, 540 and 450 nm. To utilize this principle, three component phosphor blends have been developed [31, 32].

Results based mainly on simulations using different phosphor SPDs indicate that narrow red emission near 610 nm, which is available from Y$_2$O$_3$: 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$^{2+}$. 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 violet region of the spectrum.

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

1.8 Rare earth ions and luminescence properties:
The electronics configurations of trivalent rare-earth ions in the ground states are shown in Table-1.1. The lanthanides from Ce$^{3+}$ to Lu$^{3+}$ have one to fourteen 4f electrons added to their inner shell configuration, which is equivalent to Xe. The ions with no 4f electrons i.e. Sc$^{3+}$, Y$^{3+}$, La$^{3+}$ and Lu$^{3+}$, have no electronic energy levels that can induce excitation and luminescence process in or near the visible region. In contrast the ions
from Ce$^{3+}$ to Yb$^{3+}$, which have partially field 4f orbital, have energy levels characteristic of each ion and show a variety of luminescence properties around the visible region. Many of these ions can be used as luminescent ions in phosphors, mostly by replacing Y$^{3+}$, Gd$^{3+}$, La$^{3+}$ and Lu$^{3+}$ in various compound crystals. The azimuthal quantum number \((l)\) of 4f orbital is 3, giving rise to \((2l+1)\) orbital, each of which can accommodate two electrons. In the ground state, electrons are distributed so as to provide the maximum combined spin angular momentum \((S)\). The spin angular momentum \(S\) is further combined with the orbital momentum \((L)\) to give the total angular momentum \((J)\) as follows.

\[
J = L - S, \text{ when the number of 4f electrons is less than 7}
\]

\[
J = L + S, \text{ when the number of 4f electrons is larger than 7.}
\]

An electronic state is indicated by notation $^{2s+1}L_J$ where \(L\) represents S, P, D, F, G, H, I, K, L, M... Corresponding to \(L = 0,1,2,3,4,5,6,7,8,9,\ldots\), Respectively. More accurately, an actual electronic state is exposed as an intermediate coupling state, which can be described as a mixed state of $^{2s+1}L_J$ states combine by spin orbit interaction. For qualitative discussion, however, the principal \(L\) State can be taken to represent the actual state. The mixing due to spin-orbit interaction is small for the levels near ground states. While the considerable for excited states that have been neighboring state with similar \(J\) numbers. The effect of mixing is relatively small on the energy levels, but can be large on their optical transition probabilities.

The 4f electronic energy levels of lanthanide’s ions are characteristic of each ion. The environment does not affect the levels much, because 4f electrons are shielded from external electronic fields by the outer 5s$^2$, 5p$^6$ electrons. This feature is in strong contrast with transition metal ions, whose 3d electrons, located in an outer orbit, are heavily affected by the environmental or crystal electrical field. The characteristic energy levels of the 4f electrons of trivalent lanthanide ions have been precisely investigated by Dieke and co-workers. The energy levels may be divided into three categories, those corresponding to 4f$^n$ configuration, 4f$^{n-1}$5d configuration and those corresponding to charge transfer involving the neighboring ions.

(i). Discrete f-f transitions:

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

In the second order, therefore, the electric dipole transition becomes parity allowed. Transitions corresponding to the even values of J (0 →0 excluded) increase in their oscillator strengths due to this effect. The transitions, which are not allowed as electric dipole, may take place as magnetic dipole. The magnetic dipole transition obey the selection rules ΔL = 0, ΔS = 0, Δl = 0 and ΔJ = 0 (0 →0 excluded) Spin orbit coupling weakens the selection rule on ΔL and ΔS. Interaction of rare earth ions with lattice vibrations also can mix the state of different parities into 4f states. Vibronic transitions of rare earth ions are due to coupling of 4f^n state with the vibrational mode of the lattice. In first order, coupling occurs only with IR vibrations to break the parity selection rule of the purely electronic f → f transitions. The exhaustive calculations on f → f transitions are Racah, Judd and Offelt carried out vibronic transition probabilities.

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

(iii). Charge transfer bands:
Charge transfer bands were first observed and interpreted by Jorgenson for trivalent Sm, Eu, Tm and Yb. These were later studied for various rare earth ions. Jorgenson also gave the theory for calculating the position of CT bands. Obviously this will depend on
the ligand. It has been observed that the energy will decrease with the electron negativity of the legend ion. In case of Eu³⁺, the CT band provides strong excitation. After this brief discussion of the general features which is necessary for understanding the peculiarities of the luminescence process, the characteristic features of luminescence of La, Eu and Dy which are relevant to the present work will be reviewed.

1.9 Characteristic feature of La, Eu and Dy Luminescence:

(i). Luminescence of Ce³⁺:
This ion has single 4f electron electrons outside the closed shells in its lowest energy state. Spin orbit coupling causes a splitting of a ground state into a \(^2\)F\(_{5/2}\) and \(^2\)F\(_{7/2}\) state approximately 2000 cm\(^{-1}\) higher in energy. The 5d \(\rightarrow\) 4f transition being parity and spin allowed has large transition probabilities. Since the 5d electron orbital is much more strongly affected by the neighboring ions, the 4f \(\rightarrow\) 5d absorption transition is strong broad band. The emission is similarly broad with two peaks corresponding to the \(^2\)F\(_{5/2}\) and \(^2\)F\(_{7/2}\) terminal states. The decay time of the Ce³⁺ emission is \(10^{-7}\) to \(10^{-8}\) sec, the shortest in observed lanthanide ions. Due to this short decay times \(\text{Y}_{2}\text{SiO}_{3}:\text{Ce}³⁺\) and \(\text{YAlO}_3:\text{Ce}³⁺\) are used for flying spot scanner or beam index CRT tubes. Excited Ce³⁺ ions can also acts as sanitizers and transfer their energy to other suitable rare earth ion, e.g. Tb³⁺ in such host as \(\text{CeMgAl}_{11}\text{O}_{19}\), LaPO₄.

(ii). Luminescence of Eu³⁺:
A number of luminescence lines due to \(^5\)D\(_j\) \(\rightarrow\) \(^7\)F\(_j\) of Eu³⁺ in \(\text{Y}_2\text{O}_2\text{S}\).The emission in the vicinity of 600nm are due to the magnetic dipole transition \(^5\)D\(_0\) \(\rightarrow\) \(^7\)F\(_1\), which is insensitive to the site symmetry. The emission around 610- 630nm is due to electric dipole transition of \(^5\)D\(_0\) \(\rightarrow\) \(^7\)F\(_2\) induced by the lack of inversion symmetry at the Eu³⁺ site, and is much stronger than that of the transition to the \(^7\)F\(_1\) state. Luminescent Eu³⁺ ions in commercial red phosphor such as \(\text{YVO}_4\), \(\text{Y}_2\text{O}_3\) and \(\text{Y}_2\text{O}_2\text{S}\), occupy the sites that have no inversion symmetry. The strong emission due to the electric dipole transition is utilized for practical applications. If the Eu³⁺ site has inversion symmetry in electric dipole emission is weak, and the magnetic dipole transition becomes relatively stronger and dominates. The spectral luminous efficacy as sensed by the eye has its maximum at 555nm.In the red region, this sensitivity drops rapidly as one moves towards longer wavelengths. Therefore, red luminescence compared of narrow spectra appear brighter to the human eye than various broad red luminescence having same red chromaticity and emission energy.
(iii). **Luminescence of Dy\(^{3+}\):**

The luminescence lines of Dy\(^{3+}\) are in the 470 to 500 nm region to the \(^4F_{9/2} \rightarrow ^6H_{15/2}\) transition, and in the 570 to 600 nm region due to the \(^6F_{15/2} \rightarrow ^6F_{11/2}\) transition. The color of the luminescence is close to white. In Y(P,V)O\(_4\), the relative intensity of the latter decreases with increasing P concentration. This can be understood if one considers that the \(\Delta J=2\) transition probability decreases with a decrease in the polarity of the neighboring ions as in the case of the \(^5D_{0} \rightarrow ^7F_{2}\) transition of Eu\(^{3+}\).

1.10 Energy transfer and sensitization of luminescence:

The energy transfer processes are often used in practical phosphors in order to enhance the emission efficiency. The process is called as sensitization of luminescence. The donor is called as sensitizer. The emission intensity in Mn\(^{2+}\) activated silicate, phosphate and sulfide phosphors for sulfide phosphors for example is sensitized by Pb\(^{2+}\) and Ce\(^{3+}\).

In halo phosphate phosphors 3Ca\(_3\) (PO\(_4\))\(_2\) Ca (FCL)\(_2\): Sb\(^{3+}\), Mn\(^{3+}\), the Sb\(^{3+}\) plays a role of a sensitizer as well as activator. Ce\(^{3+}\) sensitizes the green emission of Tb\(^{3+}\) in many oxides, Phosphates and vanadates.

**Theory of energy transfer:**

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

\[
S^+ + A \rightarrow S + A^*
\]

Where the asterisk indicates the excited state.

The different mechanisms of the energy transfers are (1) Radiative transfer, (2) Resonance exchange, (3) Spin Coupling, (4) Non-resonance process and (5) Spatial resonance.
Radiative transfer:
In radiative energy transfer process real photons are emitted by the sensitized ion and are then absorbed by any activator ions within a photon travel distance. Because of this fact, this transfer process depends on the shape of the sample. Here both the oscillators are assumed to be of the same kind.

1.11 Origin of Research Problem
Rare earth ions doped phosphors have been used in varied fields based on their electronic and optical characters arising from their 4f electrons. Among the rare earth elements, europium is a special element as dopant, because it exhibits the property of valence fluctuation, i.e., the valence state is divalent or trivalent. And it shows different characteristics luminescence due to the different valence [33-35]. The red light emission of Eu\(^{3+}\) is centered at near 612 nm, which is owing to intra-4f transition. While the emission of Eu\(^{2+}\) from the dipole allowed 5d–4f transition varies in a wide range from red to ultraviolet which depends on the crystal structure of host materials [36]. It is well-known that the optical properties of rare earth ions doped luminescent materials are greatly influenced by the matrix. It has been reported that Eu\(^{2+}\) ions or Eu\(^{3+}\) ions exhibit favourable luminescence behaviour in many matrixes [37, 38].

In the recent years considerable interest has been directed towards the synthesis and characterization of economical and efficient rare earth doped phosphors using different host. The red \(\left[^{5}D_0 \rightarrow ^{7}F_2\right]\) and orange emission \(\left[^{5}D_0 \rightarrow ^{7}F_1\right]\) of Eu\(^{3+}\) and green emission of Dy\(^{3+}\) 470 to 500nm region to the \(^{4}F_{9/2} \rightarrow ^{6}H_{15/2}\) transition, and in the 570to 600nm region due to the \(^{6}F_{15/2} \rightarrow ^{6}F_{11/2}\) transition is usually used in these phosphors. These phosphors find applications in fluorescent lamps, color TV screen, cathode ray tubes etc. These phosphors are not commercially synthesized in India, and are imported. Also no synthetic efforts were made towards studying the use of indigenous chemicals for the synthesis of these phosphors. The physical properties of Rare Earths used in the present investigation are enlisted in Table-1.I.

Optical properties were studied by recording the emission spectra of the powder samples. The spectra were recorded at room temperature using Shimadzu spectrofluorophotometer. The results are analyzed in the context of available theories and literature on the phosphor material. The main aim of the present research work is to develop indigenous blue and white phosphors for Lamps. An attempt is made in this direction.
**Table 1.I.** Electronic configurations of trivalent rare-earth ions in the ground state

<table>
<thead>
<tr>
<th>Atomic No.</th>
<th>Ions</th>
<th>Elements</th>
<th>4f electrons</th>
<th>S</th>
<th>L</th>
<th>J</th>
<th>$\Sigma s$</th>
<th>$\Sigma \ell$</th>
<th>$\Sigma (L+S)$</th>
</tr>
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<tbody>
<tr>
<td>21</td>
<td>Sc$^{3+}$</td>
<td>Ar</td>
<td></td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<tr>
<td>39</td>
<td>Y$^{3+}$</td>
<td>Kr</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<tr>
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<td>La$^{3+}$</td>
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<td></td>
<td>0</td>
<td>0</td>
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<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>58</td>
<td>Ce$^{3+}$</td>
<td>Xe</td>
<td>$\uparrow$</td>
<td>1/2</td>
<td>3</td>
<td>5/2</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>59</td>
<td>Pr$^{3+}$</td>
<td>Xe</td>
<td>$\uparrow$ $\uparrow$</td>
<td>1</td>
<td>5</td>
<td>4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>Nd$^{3+}$</td>
<td>Xe</td>
<td>$\uparrow$ $\uparrow$ $\uparrow$</td>
<td>3/2</td>
<td>6</td>
<td>9/2</td>
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<td></td>
<td></td>
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<tr>
<td>61</td>
<td>Pm$^{3+}$</td>
<td>Xe</td>
<td>$\uparrow$ $\uparrow$ $\uparrow$ $\uparrow$</td>
<td>2</td>
<td>6</td>
<td>4</td>
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<td>62</td>
<td>Sm$^{3+}$</td>
<td>Xe</td>
<td>$\uparrow$ $\uparrow$ $\uparrow$ $\uparrow$</td>
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<td>5</td>
<td>5/2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>63</td>
<td>Eu$^{3+}$</td>
<td>Xe</td>
<td>$\uparrow$ $\uparrow$ $\uparrow$ $\uparrow$ $\uparrow$ $\uparrow$</td>
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<td>0</td>
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<tr>
<td>64</td>
<td>Gd$^{3+}$</td>
<td>Xe</td>
<td>$\uparrow$ $\uparrow$ $\uparrow$ $\uparrow$ $\uparrow$ $\uparrow$ $\uparrow$</td>
<td>7/2</td>
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<td>7/2</td>
<td></td>
<td></td>
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<tr>
<td>65</td>
<td>Tb$^{3+}$</td>
<td>Xe</td>
<td>$\uparrow\downarrow$ $\uparrow$ $\uparrow$ $\uparrow$ $\uparrow$ $\uparrow$ $\uparrow$</td>
<td>3</td>
<td>3</td>
<td>6</td>
<td></td>
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<tr>
<td>66</td>
<td>Dy$^{3+}$</td>
<td>Xe</td>
<td>$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow$ $\uparrow$ $\uparrow$ $\uparrow$ $\uparrow$</td>
<td>5/2</td>
<td>5</td>
<td>15/2</td>
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<tr>
<td>67</td>
<td>Ho$^{3+}$</td>
<td>Xe</td>
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<td>6</td>
<td>8</td>
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<tr>
<td>68</td>
<td>Er$^{3+}$</td>
<td>Xe</td>
<td>$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow$ $\uparrow$ $\uparrow$</td>
<td>3/2</td>
<td>6</td>
<td>15/2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>69</td>
<td>Tm$^{3+}$</td>
<td>Xe</td>
<td>$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow$ $\uparrow$</td>
<td>1</td>
<td>5</td>
<td>6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>Yb$^{3+}$</td>
<td>Xe</td>
<td>$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$</td>
<td>1/2</td>
<td>3</td>
<td>7/2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>71</td>
<td>Lu$^{3+}$</td>
<td>Xe</td>
<td>$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
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</table>
The present thesis reports synthesis of Sr\(_2\)CeO\(_4\) phosphors doped with Dy, La, Eu, La(Eu), Eu(La), Dy(La) and Eu(Dy) of 0.01, 0.1, 0.2, 0.5 and 1.0% molar concentrations using conventional solid state reaction method. Strontium nitrate and Cerium oxide were used as starting materials. A stoichiometric mixture (2:1) of these starting powders was thoroughly homogenized using an agate mortar and pestle for 1 hour and then put into an alumina crucible. The homogenized mixture was heated in air from room temperature to 1200\(^\circ\)C with a heating rate of 5\(^\circ\)/minute for 3 hours. A systematic process of synthesis of Sr\(_2\)CeO\(_4\) through the solid state reaction technique was discussed in chapter-II. Total 36 samples were prepared and characterized using XRD, SEM, Particle size, FTIR and photoluminescence.

1.12 Organization of Thesis
The thesis consists of seven chapters. The following are the brief summary of the each chapter content.

Chapter one provides the General Characteristics of Luminescence, Rare earth ions and luminescence properties. Characteristic feature of Dy, La, and Eu Luminescence is also discussed.

Chapter two describes the synthèses of Sr\(_2\)CeO\(_4\) phosphores doped with Dy, La, Eu, Dy(La), Eu(Dy), La(Eu), Eu(La), Structure of Sr\(_2\)CeO\(_4\) and preparation of pure and rare earths doped Sr\(_2\)CeO\(_4\) phosphors.

Chapter three gives a summary of characterization techniques used in this study. This includes a brief description of these techniques.

Chapter four deals with the results and discussion of Sr\(_2\)CeO\(_4\) phosphors doped with Dy, La, Eu and their characterizations.

Chapter five deals with the results and discussion of Sr\(_2\)CeO\(_4\) phosphors co-doped with Dy(La), Eu(Dy), La(Eu), Eu(La) and their characterizations.

Chapter six deals with the results and discussion of Sr\(_2\)CeO\(_4\) phosphors synthesized using various fluxes.

Chapter seven is dedicated to the conclusions and future studies. The Sr\(_2\)CeO\(_4\) phosphor was prepared in the laboratory, shows excellent photoluminescence emission in the blue region which can be used as lamp phosphor.
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[16]. He, X.H., J. Rare Earth, 25(s), 50, (2007).