Summary

The properties of solids especially optical have been an area of scientific and technological interest for over three centuries. But in recent past for more than three decades great emphasis has been given to the display materials. Display devices are over a billion dollar industry and research and development to improve the output and efficiency of these devices is still going on. Scientists and academicians are working world over to improve the technology and to invent new display devices. The back bone of this industry is a small group of elements in the periodic table whose presence in minute quantity can effectively enhance the optical property of the material. These special groups of elements "Lanthanides" with Atomic number (Z) ranging from 57 to 71 are characterized by filling up of 4f shell. These elements along with yttrium and scandium from the periodic table are also known as "Rare Earths". They all have similar chemical property; the ions differ in the number of 'f' electrons in the 4f shell. This 4f orbital lies well inside the ion and is shielded from the surrounding by the filled $5s^2$ and $5p^6$ orbital. This shielding character of the 4f orbital is also responsible for the unique optical properties. Luminescence arising from these rare earth ions is widely used in color television, mobile phones, lamps (CFL), X-ray phosphor, scintillators to name a few. Technological as well as scientific development has led to understanding of many aspects of lanthanide luminescence.

For the last one and half decade the nanotechnology, with size limitation of less than 100nm, has been moving at a pace and gaining momentum, research in this field is becoming more and more active. Nanometer-sized phosphor powders exhibit spectroscopic properties that are different from their micrometer-sized counterparts. Generally, the observed luminescence in nanocrystalline materials has been explained using two arguments: (1) luminescence is dominated by quantum confinement effects and (2) luminescence is dominated by defect interactions and chemical species. In this regard the phosphor research has also awakened to the challenge and new and better materials with the size limitations are being pursued rigorously. A number of publications have appeared on the same and the effect on the size with the effect on the optical property has been a topic of great interest today. The goal of this research effort was to develop a

comprehensive understanding of the factors that affect the luminescence behavior and study the optical properties of synthesized (using sol-gel method) nanocrystal phosphors with crystallite sizes less than 100nm. Up till now the commercial phosphors are synthesized using solid state reaction which requires the raw materials to be ground using an high speed grinders/ball mills and fired at 1200-1600°C or more depending on the synthesis temperature for many hours with two or more intermediate grindings. Of late, much emphasis has been given to improve upon the synthesis technique so as to improve the optical properties of the phosphor without losing on the efficiency.

Sol-gel processing involves the production of a suspension of a solid in a liquid, followed by the removal of the liquid, and finally densification of the solid. It has the advantages of low processing temperatures, mixing at the molecular level to produce hybrid systems, fabrication of novel materials and moreover it is cost effective. In recent years the sol-gel process has become an attractive and intensive area of research, for the preparation of highly homogeneous glasses, ceramics, and composites. One merit of sol-gel chemistry is that it offers a convenient method to synthesize a material for hosting chemical reactions. Many different types of chemical species can be impregnated or 'doped' within the pores of a gel by adding them to the sol. The nature of gel synthesis allows researchers to investigate and control the pore size and to study the influence of pore size on the properties of the products. Usually inorganic metal salts or metal organic compounds such as metal alkoxide are used as precursors. Sol-gel method involves wet chemical synthesis of materials, so the composition of the materials can be tailored at molecular level. As a result, stoichiometrically homogeneous control of the doping is easily achieved. Sol-gel method is a very mild and flexible method to fabricate materials especially phosphors which have lately been synthesized extensively. For the last few decades sol-gel science has been of great interest for the crystallographers, much of the phosphor research is going on using this technique. It inspires us to further investigate and modify the method to exploit its maximum value in application. The better luminescent properties observed for sol-gel products when compared to solid state reaction have led to study and apply the synthesis method in the present work.

The chapter one gives a detailed introduction and overview of the research progress in the field of phosphors along with suitable references cited.

The second chapter describes the characterization techniques in details. Information regarding the calculation of the Commission Internationale de l'Eclairage (CIE) coordinates from the photoluminescence spectra are presented in this chapter along with references.

The third chapter deals with the synthesis of the Sr_2CeO_4 by solid state reaction, combustion and mainly by sol-gel technique. So, the synthesis, the reaction details, the raw materials used and the conditions for the synthesis have been discussed at length. A great deal of work has gone to make sure that the optimized condition for the sol-gel case resulted in the optically best suited material; moreover, the morphology (shape and size) of the material were found to be better for the sol-gel when compared with the other two. In combustion synthesis, the fuel was taken as citric acid and urea for all the cases and afterwards the fuel to oxidizer ratio for the urea was varied. Urea was found to be an efficient fuel for the combustion synthesis so it was used in the further studies. As the fuel to oxidizer ratio, plays an important role in the combustion synthesis, the ratio is varied (fuel lean and fuel rich) to achieve the highest luminescence output from this synthesis technique and it was found that when fuel to oxidizer ratio is 1 the sample is found to be with highest photoluminescence intensity. The comparison between all the synthesis techniques was done and sol-gel found to be the best among all the studied synthesis techniques here.

The fourth chapter has the details of the effect of doping of trivalent rare earth europium in the host matrix, and the energy transfer phenomenon. The synthesis techniques studied were both sol-gel and solid state reaction. Different concentrations of europium i.e. 0.5%, 1.0%, 1.5%, 2.0% and 4.0% (mole percent) were doped in the host Sr_2CeO_4. The photoluminescence intensity of all the samples was measured and an explanation for the mechanism of the energy transfer between the host and the dopant is explained. The comparison between the photoluminescence spectra of the phosphors synthesized by the sol-gel as well as solid state reaction technique are elaborated and it was found that there was difference in the photoluminescence emission spectra for both the techniques. The CIE coordinates of this phosphor were calculated by the equidistant wavelength method. It was found that the emission colour changes with the concentration of the europium doping and at 1.5mol%, the emission was white in colour. Excellent tenability of the host was found and it changed its emission colours with change in concentrations.

The fifth chapter describes the effect of doping trivalent rare earths mainly samarium, dysprosium and terbium in the host matrix. For the samarium, different concentrations of 0.03125%, 0.0125%, 0.1%, 0.5%, 1.0%, 1.5%, 2.0 % (mole percent) were taken. For the dysprosium and terbium doping in the host the concentrations studied were 0.5mol%, 1.0mol% and 1.5mol%. The samarium has also stabilized in the trivalent form so the spectra of both the samarium and it was found that the CIE colour coordinates of samarium were also in white region with less purity. Doping of trivalent rare earths (Dy^{3+}, Tb^{3+}) ions in the host lattice was also done to study the nature and type of emission. It was found that there was no substantial emission observed on doping the terbium. The dysprosium doping shows the emission from the charge transfer along with the dysprosium lines. The CIE coordinates of the $Sr_2CeO_4:Dy^{3+}$ was calculated and found to be x = 0.24 and y = 0.29 for 1.5mol% concentration.
The work presented in this thesis contains the synthesis of the host material with three different synthesis techniques and the summation of the positive features of the sol-gel synthesis sample. Luminescent characteristics of the synthesized samples are studied along with their phase and morphological studies. An attempt has been made to find out the applicability of the studied materials in the lamps etc. The basic requirements for the use of phosphors as lamp phosphor have been examined for the material under investigations.

From the above discussions and conclusions in the chapters prior to this, these are the following suggestions for the future work:

1. The synthesized phosphor should be studied in the devices like field emission display and compact fluorescent lamps.
2. The rare earth double dopants and non rare earths can be tried to get tunabilty in the colours.