Synthesis and Spectroscopic Studies of Pure and Rare Earth doped Sr_2CeO_4 Phosphors

The oxide based luminescent materials are popular due to the fact that they exhibit superior photoluminescence and cathodoluminescence properties which makes them useful as important components of color emission in plasma display panel (PDP), field emission display (FED), and lamps. Inorganic compounds doped with rare earth ions form an important class of phosphors, they possess a few interesting characteristics such as excellent high luminescence efficiency, chemical stability and flexible emission colors with different activators. Sr_2CeO_4 is an unusual luminescent inorganic oxide which can emit blue light while irradiated by UV light, cathode ray or X-ray. The blue emission from Sr_2CeO_4 was assigned to a charge transfer (CT) transition involving Ce^{4+} ion. Since it is an active center with 100% concentration, intensive studies on this phosphor have been focussed on its synthesis, structure, emission mechanism and its potential applications, such as employment in field emission displays. Since rare earth ions can be almost used to design unlimited new luminescent material because of its special 4f energy level transition and besides, Sr_2CeO_4 is a prominent host material for the incorporation of many trivalent luminescence centers such as Eu^{3+}, Dy^{3+}, Sm^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, etc., rare earth (RE) doped Sr_2CeO_4 continues to attract a lot of attention from researchers. Effective energy transfer from Ce^{4+} - O^{2-} charge transfer state (CTS) to these activation centers has been proposed to be responsible for their luminescence in Sr_2CeO_4.

It is clear from the previous reports that the preparatory technique and the precursors play an important part in the formation of Sr_2CeO_4 pure luminescent phase. Danielson et al., was the first to report an unusual luminescent inorganic oxide Sr_2CeO_4, which was identified by parallel screening techniques from within a combinatorial library (combinatorial chemistry). Since then, several preparatory routes have been developed for the synthesis of pure, single phase powders with controlled powder characteristics of Sr_2CeO_4 phosphor. Conventional solid state reaction technique usually requires high heating temperature for the preparation of Sr_2CeO_4. While, the synthesis of Sr_2CeO_4 via Poly ethylene glycol (PEG) sol-gel process, co-precipitation method, citrate–gel process, ultra spray pyrolysis and combustion reaction requires relatively lower temperature when compared to solid state reaction method. Other methods like microwave-hydrothermal and microwave solvothermal methods have also been adopted for the synthesis of Sr_2CeO_4. Although there are several techniques been tried out for the synthesis of fine Sr_2CeO_4 phosphor particles with good luminescence, research is still carried out to reduce the process complexity, controllability and cost. Therefore, in order to overcome some of these difficulties, new synthesis routes are being explored. Stoichiometry of the reacting metal ions plays an important role in the luminescence property of a phosphor. Hence, the stoichiometry was kept constant throughout the experiment and Sr_2CeO_4 was prepared by different routes to optimize a better route. Since the broad emission band of Sr_2CeO_4 is suitable for the doping of rare earth ions in pursuing new luminescent materials, rare earth (Sm^{3+}, Dy^{3+} and Eu^{3+}) ions were added to the blue phosphor to create white light emission from the Sr_2CeO_4 phosphor.

This thesis presents the synthesis and spectroscopic studies of pure and rare earth doped Sr_2CeO_4 phosphors. In this thesis, Sr_2CeO_4 was synthesized by solid state and sol-gel routes. Improved luminescence was seen as the preparatory condition was varied from solid state to sol-gel route. Sol-gel method is quite unique due to its low processing temperature and solution mixing, enabling the production of high purity and high homogeneity of end products. We also concentrated on synthesizing Sr_2CeO_4 with singly doped RE (Sm^{3+}, Dy^{3+} and Eu^{3+}) ions by sol-gel route to generate white luminescence. Structural characterization was carried out using techniques like Thermogravimetric analysis (TGA), X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), High Resolution Transmission Electron Microscopy (HRTEM) etc. to name a few. Optical characterization was done using absorption and emission spectroscopy. From the emission spectroscopy the phonon side band and colorimetric analysis were done for selected samples. X-ray photoelectron spectroscopic studies were carried out in order to examine the chemistry of the pure and rare earth doped phosphor. A genuine attempt is made here to investigate the nonlinear optical properties of pure and rare earth modified Sr_2CeO_4 phosphor prepared by the conventional method.

The thesis is divided into six chapters and the chapter wise summary of the same is given below.

Chapter 1 begins with a general introduction on phosphors and of Sr_2CeO_4 phosphor in particular is given. The structure of Sr_2CeO_4 is discussed in brief. Preparatory methods such as solid state reaction and sol-gel technique, their advantages and disadvantages are discussed. A short description on nanomaterials and its advantages is discussed. Spectroscopic properties of rare earth ions mainly samarium, dysprosium and europium are briefly described. The different characterization methods such as Transmission Electron Microscopy, X-ray Photo-electron Spectroscopy and Colorimetry are briefly touched upon. A brief account of phonon side band analysis and how it can be supplemented with Raman spectra of Sr_2CeO_4 materials are also incorporated. A brief discussion on the Z-scan technique for the study of nonlinear absorption in Sr_2CeO_4 samples is presented.

Chapter 2 discusses the synthesis and structural characterization of Sr_2CeO_4 prepared by different techniques. In the introductory part a brief review of the Sr_2CeO_4 phosphor is given. Sr_2CeO_4 blue phosphor was synthesized by different techniques to improve the luminescence properties. The samples were characterized by TG/DTA, X-Ray diffraction, Fourier transform infra red spectroscopy, Scanning electron microscopy, Transmission electron microscopy, UV-Vis spectroscopy and Photoluminescence spectroscopy. The X-ray diffraction confirms the structure of the system to be orthorhombic. The optical band gap of Sr_2CeO_4 was calculated from the absorption spectrum. The fluorescence spectra reveal that the intensity of emission increases when the preparatory technique is varied from solid state reaction to sol-gel.

Chapter 3 is concerned with the colorimetric studies of pure and rare earth doped Sr_2CeO_4. Pure and Rare earth (Eu^{3+}, Sm^{3+}, Dy^{3+}) doped Sr_2CeO_4 phosphors synthesized using sol-gel technique show Red Green Blue (RGB) emissions. The photoluminescence of the samples were taken. The emission spectra of the samples were converted into the CIE 1931 color coordinate system. The color coordinates corresponding to the prominent emissions were determined. The stability of the phosphors to excitation wavelength variations and the purity of the colour were also measured. In particular, Sr_2CeO_4: 2% Eu^{3+} phosphor when excited at 278 nm, shows white light emission, which has CIE color coordinates x = 0.35, y = 0.34. White light emission obtained from Sr_2CeO_4:2% Eu, sample shows purity of 94 % for blue, 100 % for green color and 100 % for red color. The correlated color temperature calculated is found to be 4770 K for Sr_2CeO_4:2% Eu when excited at 278 nm is close to the standard horizon light.

Chapter 4 describes the structural and phonon side band analysis of Eu^{3+} doped Sr_2CeO_4. Eu^{3+} doped Sr_2CeO_4 ceramics have been synthesized by sol-gel route using citric acid and ethylene glycol. Transmission Electron Microscopy (TEM) reveals that Sr_2CeO_4:5% Eu^{3+} consists of coarse particles that are irregular in shape and are of size in the range 200 – 400 nm. At higher magnification, these particles were seen to be agglomerates of nanocrystallites in the size range 4 – 6 nm. The local structure of rare earth ion in Sr_2CeO_4 ceramics was investigated using Eu^{3+} as a probe. The emission spectra of Eu^{3+} doped Sr_2CeO_4 show several inhomogeneously broadened bands due to f-f transitions. The phonon side band (PSB) spectrum associated with the excitation transition $^7F_0 \rightarrow {^5D_2}$ is used to analyse the local asymmetry of the rare earth ions in Sr_2CeO_4 ceramics. Micro Raman spectroscopic studies of the sample are used to supplement the phonon side band results. The PSB and the fluorescence studies on the other hand helped us to probe the local structural evolution and its dependence on observed spectral intensities. Branching ratios were calculated for all the transitions of Sr_2CeO_4:5% $Eu^{3+}$and the highest value corresponds to the strongest peak at 613 nm. Asymmetric ratio is also found to be highest for Sr_2CeO_4:5% Eu^{3+}.

Chapter 5 presents the X-ray Photoelectron spectroscopic studies of pure and Eu^{3+} doped Sr_2CeO_4 and Z-scan study of pure and Sm^{3+} modified Sr_2CeO_4. X-ray photoelectron spectroscopic studies were carried out in order to examine the chemistry of pure and Eu^{3+} doped Sr_2CeO_4 phosphor. XPS spectra of the samples elucidated that Ce atoms on the surface are in the +4 oxidation state, though the existence of other states (+3) cannot be excluded. A depth profiling of Eu^{3+} doped Sr_2CeO_4 with ion sputtering showed an increased Ce concentration in the subsurface region (internal part of grains) having 30 nm depth with respect to surface concentration of Ce. The peak values of Sr $3d_{5/2}$ from the surface of all samples were centered at about 132.9 eV. An open aperture z-scan technique was employed to investigate the nonlinear optical properties of Sr_2CeO_4 and Sm^{3+} modified phosphor prepared by the conventional method. The z-scan data was analysed to extract the nonlinear parameters namely nonlinear absorption coefficient.

Chapter 6 describes the conclusion and future work. This chapter sums up the salient features of the work described in this thesis and the scope for potential developments in this field.

The research work presented in the thesis has either been published in or communicated to reputed international journals, conference proceedings and presented in various national/international seminars.

Papers published in International Journals

1. *A New Synthetic pathway of Sr_2CeO_4 phosphor and its characterization*,
   R. Seema and K. Nandakumar,
   Journal of Luminescence, 131 (2011) 2181-2184.

2. *An open aperture z-scan study of Sr_2CeO_4 blue phosphor*,
   R. Seema, C. S. Suchand Sandeep, Reji Philip and K. Nandakumar,
   Journal of Alloys and Compounds, 509 (2011) 8573-8576.

3. *X-ray Photoelectron spectroscopic studies of pure and Eu^{3+} doped Sr_2CeO_4,*
   R. Seema, Janez Kovac, Uros Cvelbar, K. Nandakumar, Solid State Communications (communicated).

4. *Colour tuning capability of Eu^{3+} doped Sr_2CeO_4 phosphors,*
   R. Seema, Nuja S. John, K. Nandakumar, Material Letters (communicated).

5. *Structural and Phonon side Band analysis of Eu^{3+} doped Sr_2CeO_4*
   R. Seema, K. Nandakumar, Journal of Solid State Chemistry (communicated).