Preface

The thesis entitled ‘Studies on Synthesis and Physicochemical Properties of some Rare-Earth (RE = Eu^{3+}, Tb^{3+} & Dy^{3+}) doped La_2O_3 & Y_2O_3 Nanoparticles and Electrodeposited ZnO from Nitrate Bath’ contains seven (7) chapters. The thesis is emphasized with the study on the synthesis and characterization of trivalent lanthanide ion (Ln^{3+} = Eu^{3+}, Tb^{3+} & Dy^{3+}) and Bi^{3+} doped rare earth (RE = La and Y) oxides for the production of multicolor luminescence and the possibilities of doping with luminescent ZnO nanoparticles in the form of thin films by electrodeposition. A brief introduction to lanthanides, nanoscience, and luminescence of trivalent lanthanide ions and electrodeposition of ZnO nanoparticles (a potential host material for rare earth doping) from nitrate bath is stressed in the Chapter 1. The luminescence of different lanthanide ions in a variety of hosts is discussed and focused on the doping of lanthanide ions in rare earth oxide nanoparticles. Different synthesis methods of luminescent nanoparticles and few of their properties along with their applications are discussed in detail.

Instrumentation and various characterization techniques used for characterizing the synthesized nanoparticles doped with lanthanide ions are discussed in Chapter 2. The brief working principles of variety of characterization techniques such as transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), photoluminescence spectroscopy (PL), Fourier transformed infra-red spectroscopy (FIR), thermo gravimetric analysis (TGA) and UV-Visible spectroscopy and cyclic voltammetry (CV) are discussed.

In Chapter 3, the observation of exceptional strong emission transitions \(^5D_j\) (j = 1 – 3) to \(^7F_j\) (j = 1 – 3) in Eu^{3+} ion doped La_2O_3 nanoparticles which can be used for multicolor emission is discussed. Synthesis of Eu^{3+} ion doped La_2O_2CO_3 and La_2O_3 nanoparticles through hydrothermal route with subsequent heat-treatment is discussed. It is found that La_2O_2CO_3 phase is highly stable at ambient atmosphere, although decomposes to La_2O_3 at or above 700 °C. Interestingly, 1 and 3 at.% Eu^{3+} doped samples heated at 900 °C under 278 nm excitation, show
exceptional strong emission transitions of $^5D_j$ ($j = 1 - 3$) to $^7F_j$ ($j = 1 - 3$) because of negligible cross-relaxation among $^5D_j$ ($j = 1 - 3$) levels and their integrated intensity is found to be more than that of $^5D_0$ to $^7F_j$ ($j = 1 - 3$). On increasing concentration of Eu$^{3+}$ up to 10 at.%, intensity from $^5D_1$ or $^5D_2$ levels decreases significantly, whereas intensity from $^5D_0$ level increases indicating relaxation of excited electrons from $^5D_{j=1,2}$ to $^5D_0$ level. Excitation at 394 nm show strong background emission intensity in 425 – 600 nm due to the different defect states/intermediate bands present within the band gap of the host. Many colors including blue, green, yellow, pink and red to white could be produced by changing concentration of Eu$^{3+}$, excitation wavelength and annealing temperature. Samples are dispersible and their films dispersed in PVA show efficient luminescence. Materials can be potential candidates for light emitting diodes (LEDs) and bio-labeling.

Synthesis and characterization of blue and green emitting Ce$^{3+}$ and Tb$^{3+}$ co-doped Y$_2$O$_3$ nanoparticles is reported in Chapter 4. Tb$^{3+}$ doped Y$_2$O$_3$ nanoparticles of 4-10 nm are synthesized from nitrate precursors by urea hydrolysis method in ethylene glycol medium at low temperature of 140 °C. Characteristic Tb$^{3+}$ ion green emission corresponding to $^5D_4 \rightarrow ^7F_j$ is observed to be very strong, which further increases with heat treatment temperature. Characteristic blue color emission of Ce$^{3+}$ ion transitions for $5d \rightarrow ^2F_{7/2}$ and $^2F_{5/2}$ (at 424 nm and 486.5 nm respectively) was found to be very strong in as-synthesized Ce$_{0.02}$Tb$_{0.06}$Y$_{1.92}$O$_3$ nanoparticles. However, its luminescence intensity decreases with increase in heating temperature or increase in the particle size/crystalinity, whereas a weak emission peak of Tb$^{3+}$ ion at 545 nm is observed. The polycrystalline nature of as-prepared sample is changed to highly crystalline state when heated at elevated temperature (1200 °C).

Chapter 5 is focused on synthesis and characterization of Y$_2$O$_3$ nanoparticles activated with rare earth ions (RE = Eu$^{3+}$, Dy$^{3+}$) and sensitized with Bi$^{3+}$ for red, yellow, blue and green emission. Eu$^{3+}$, Dy$^{3+}$ or Bi$^{3+}$ doped Y$_2$O$_3$ nanoparticles were synthesized by urea hydrolysis method in ethylene glycol medium at a low temperature of 140 °C.
Chapter 6 describes on electrodeposition of highly oriented three dimensional ZnO microarrays thin films over transparent conducting indium tin oxide (ITO) electrode. It can be mentioned that, ZnO is also a promising host for doping trivalent rare earth ions for use in thin film luminescent material. Un-doped ZnO is electrodeposited over indium tin oxide (ITO) glass substrate in an aqueous solution of 0.01 M Zn(NO$_3$)$_2$ at a low temperature of 80 °C, without any additives at a predetermined potential (-1.2 V) using Cyclic Voltammetry. The as-deposited ZnO thin film is characterized using XRD and AFM. The XRD pattern reveals the growth of ZnO along a preferred orientation of (002) plane. Particle size calculated from XRD data using Scherrer equation gives 40 nm. Highly oriented ZnO cluster along one direction can be observed from AFM image. Thus, a simple electrodeposition route could be employed to grow highly oriented ZnO thin film in an efficient way without any additives. The electrodeposited ZnO microarrays can also be used as a host for doping various trivalent lanthanide ions.

The overall summary and conclusion of the present thesis is discussed in Chapter 7. Possible future work which can be continued afterwards is also discussed in brief.