

PREFACE

Optical spectroscopy refers to the range of interacting electromagnetic radiation lying within the so-called 'optical range' that includes the visible and some part of the ultraviolet and infrared spectral regions, i. e. 200–3000 nm range. The spectroscopy was originated centuries back but the discovery of laser has dramatically changed the definition of conventional spectroscopy and now lasers became an important tool to study the optical phenomena under the term 'laser spectroscopy'.

Since the last few decades, lanthanide (Ln) doped nano-materials have attracted great deal of attention due to their wide and promising applications in many diverse fields as solid state lasers, display devices, medical diagnostics, temperature sensors, etc. Rare earth (RE) ions consist of large number of sharp electronic energy levels spanning from infrared to X-ray region. RE ion (lanthanides) have been widely used as luminescent centers in optical materials that are frequently applied in fluorescent lamps, solid state lasers, optical amplifiers, optical data storage devices etc. The white light emitting diodes (LEDs), Nd:YAG laser, Er-doped fiber amplifiers etc. are some well-known examples of the versatility of trivalent REs as luminescent materials. The electronic transitions between the states within the $4f^n$ configuration of RE are generally parity forbidden and many levels have long lifetimes up to several milliseconds making it possible to observe the upconversion (anti-Stokes) emission phenomenon in trivalent ions. Recent research progress and future prospects indicate that upconversion characteristics of RE ion based luminescent materials remain interesting for a long time. Scientific challenges as well as societal needs in this research field would keep the involvement of chemists, physicists, biologists and material scientists. The RE doped nanomaterials have new potential uses as Biological assays, optical temperature sensing, security ink, finger print detection etc.

In order to study the optical dynamics of RE ions the lasers are best choice because of the monochromatic nature and high intensity. Lasers provide wavelength selective excitation of RE ions and power tunability advantages. Because of the high power density of lasers one can be able to observe the upconversion emission in RE ions. In the present work selective lasers have been used to get the up and down conversion emissions in certain RE doped materials.

In this thesis absorption and fluorescence techniques have been used for the upconversion and down conversion emission studies of some trivalent RE doped lanthanide phosphors. The other techniques were used for structural studies. The phosphors were prepared by conventional solid state ceramic route and facile auto-combustion processes.

The thesis has been divided into **six** chapters.

The first chapter contains general introduction and the importance of RE doped materials, basic properties of phosphors, and optical properties of some RE doped promising hosts such as fluoride, Titanate and molybdates in display and bimodal applications along with the theory used to explain them.

The second chapter contains the details of experimental techniques that were used for sample preparation and studying various structural & photophysical properties of RE doped phosphors. Brief description of the experimental techniques used is presented.

The third chapter aims to understand the upconversion emission in $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped $\text{Y}_2\text{Ti}_2\text{O}_7$ (EYYTO) phosphor. Highly-crystalline $\text{Y}_2\text{Ti}_2\text{O}_7: \text{Er}^{3+}/\text{Yb}^{3+}$ phosphor sample was synthesized through solid state ceramic route. X-ray diffraction (XRD) study confirms its pyrochlore cubic structure. The upconversion study with 976 nm excitation of sample showed upconversion emission bands in UV, blue, green and red regions with most intense band at 524-548 nm [$^2\text{H}_{11/2}$ ($^4\text{S}_{3/2}$) \rightarrow $^4\text{I}_{15/2}$]. Power dependence study of green [$^2\text{H}_{11/2}$ ($^4\text{S}_{3/2}$) \rightarrow $^4\text{I}_{15/2}$] and red bands 661 nm [$(^4\text{F}_{9/2})\rightarrow^4\text{I}_{15/2}$] confirmed the two photon absorption. Colloidal solution of EYYTO under 355 nm Nd-YAG laser excitation has been studied and its show diverse behavior to the powder one. Strong absorption at 1.45 μm [$^4\text{I}_{13/2}\rightarrow^4\text{I}_{15/2}$] has been observed which has been the well known line of Er^{3+} band used in optical telecommunication. Variation in CIE coordinates with laser input power has been observed which dictates its color tunability with laser diode power.

The fourth chapter presents the structural and downshifting studies in Eu^{3+} activated CaMoO_4 phosphor via Gd^{3+} co-doping and is divided into **two parts**. In **Part I** of this chapter, Highly crystalline Gd^{3+} (0, 2, 5, 7 and 10 at.%) co-doped $\text{CaMoO}_4:\text{Eu}$ nanoparticles are synthesized *via* a facile auto-combustion route and its structural properties were studied. Influence of Gd^{3+} co-doping on structural properties of $\text{CaMoO}_4:\text{Eu}$ was studied in detail *via*

XRD, XPS, FTIR, FE-SEM and TEM studies. In order to get the higher crystallinity, the ASP sample was heated at 600 and 900 °C. The tetragonal scheelite phase with space group $I4_1/a$ and $Z = 4$ was found. Extra peaks in XRD patterns were found in the case of ASP and 600 °C and are not present in 900 °C. The FTIR spectrum showed bands at $\sim 815\text{ cm}^{-1}$ and 427 cm^{-1} , which are due to asymmetric stretching and bending vibrations of O–Mo–O of MoO_4^{2-} tetrahedra, respectively. From XPS study, Ca was found to be in the +2 oxidation state, while Mo, Eu and Gd were found to be in the +6, +3 and +3 oxidation states, respectively. The core binding energy peak at $\sim 141.1\text{ eV}$ corresponds to $\text{Eu}^{3+}(4d_{3/2})$. No peak at $\sim 127.1\text{ eV}$, corresponding to $\text{Eu}^{2+}(4d_{5/2})$, is observed. This supports the high probability of Eu^{3+} being present in the samples. The particle size increases with annealing.

In **Part 2** of this chapter, downshifting properties of Eu^{3+} activated CaMoO_4 via Gd^{3+} co-doping was studied. From PLE study, strong overlapping of Eu–O and $\text{Gd}^{3+}/\text{Mo–O}$ charge transfer bands was observed. Absorption/excitation intensity increases with Gd^{3+} indicating energy transfer from $\text{Gd}^{3+}/\text{Mo–O}$ to Eu^{3+} . Band gap decreases with annealing. In the photoluminescence study of Gd^{3+} co-doped $\text{CaMoO}_4:\text{Eu}$, the optimum PL intensity values are found at 2, 7 and 10 at% for ASP, 600 and 900 °C samples, respectively. Enhancement of luminescence was found with annealing due to the extent of the decrease of non-radiative rates arising from surface dangling bonds and –OH ions to the surface of the samples. The asymmetric ratios (A_{21}) of electric to magnetic dipole transitions are found to be in the range of $\sim 12\text{--}16$, which was relatively higher than those reported. The room temperature emission spectrum is dominated by the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition at 613 nm. Emission quantum yields up to 80% were obtained under excitation at 277 nm for ASP 10 at% Gd^{3+} co-doped $\text{CaMoO}_4:\text{Eu}$. From the photoluminescence decay studies on direct excitation at 395 nm and indirect excitation at 277 nm, energy transfer from Gd/Mo–O CT band to Eu^{3+} occurs. PL intensity variations have been studied in polar solvents; and found that these nanoparticles are dispersible and these dispersed particles can be incorporated in polyvinyl alcohol to make a film. The film shows the dark red emission after UV-radiation which can be useful in display devices. The quantum yields of as-prepared 2 and 10 at% Gd^{3+} co-doped $\text{CaMoO}_4:\text{Eu}^{3+}$ under 277nm (UV excitation) are 21 and 80%, respectively. The CIE co-ordinates for 5 at% Gd^{3+} co-doped with $\text{CaMoO}_4:\text{Eu}^{3+}$ for ASP, 600 and 900 °C were found to be (0.5334,

0.3711), (0.5331, 0.3708) and (0.6068, 0.3614), respectively. Through this study, high quality luminescent material was demonstrated by incorporating Gd^{3+} ion in Eu^{3+} activated $CaMoO_4$ matrix, which was of great importance in improving the luminescence efficiency of the red phosphor at a much lower cost.

The **fifth chapter** contains the upconversion studies on Li^+ co-doped $Y_2Ti_2O_7:Er^{3+}/Yb^{3+}$ phosphors were synthesized by a solid-state ceramic method. The structures of the phosphors were analyzed in detail by Rietveld XRD, XPS, FTIR, FE-SEM, Raman and PL measurements. The XRD study confirmed the pyrochlore phase with an fcc structure. The XPS study revealed the characteristic valence states and associated oxygen vacancies on the sample surface. Raman spectroscopy study reveals the surface defects associated with the sample and the structure corroborates with its pyrochlore type feature. Significantly enhanced green and red emissions were observed after introducing Li^+ ions, which may tailor the environment of surrounding Er^{3+} ions. With Li^+ ion inclusion, the decay profile of the green bands (548 nm) corroborates the prolonged decay time value as compared to the Li^+ -free sample.

Based on the fluorescence intensity (FIR) ratio technique, the phosphor was also studied for temperature sensing applications and showed good temperature sensitivity.

In the **last sixth chapter**, conclusions of overall studies have been summarized. Chapter also discusses further research plans on this topic.

