LIST OF FIGURES AND TABLES

Captions

FIGURE No.

Chapter: 1				
Figure	1.1:	Schematic of the general luminescence mechanisms of phosphors: in localized centers (a and b) and semiconductors (c).	03	
Figure	1.2:	Periodic table of elements showing the position of lanthanides.	04	
Figure	1.3:	Partial 4f–4f energy-level diagram of Lanthanides.	06	
Figure	1.4:	Splitting of the Eu ³⁺ ion energy levels under various perturbations.	11	
Figure	1.5:	Schematic illustrating the crystal structure of pyrochlore $Y_2Ti_2O_7$.	15	
Figure	1.6:	Schematic illustrating the crystal structure of tetragonal CaMoO $_{4}$	17	
Figure	1.7:	General energy scheme related to the ESA	22	
Figure	1.8:	General energy schemes related to ETU processes: ET followed by ESA (A), successive energy transfer (B), cross-relaxation upconversion (C), cooperative sensitization (D), and cooperative phenomenon (E).	24	
Figure	1.9:	Energy scheme for the simplest photon avalanche process	25	
Figure	1.10:	(a) Resonant radiative energy-transfer process.	26	
Figure	1.10:	(b) Resonant nonradiative energy transfer.	26	
Figure	1.11:	Nonresonant energy-transfer process.	27	
Figure	1.12:	Ion-pair emission and absorption processes.	27	
Table	1.1:	Electronic configurations of atomic and trivalent ionic states of all the RE elements.	07	
Table	1.2:	Some of the important transitions of the RE ions and their applications.	08	
Table	1.3:	J splitting under various point symmetries.	11	
Table	1.4:	Selection rules for f-f transitions in rare-earth ions.	12	
Table	1.5:	Hypersensitive transitions observed in rare-earth ions.	12	

Table1.6:Energy of the maximum energetic phonons in different hosts.13

xviii

Page

Chapter: 2

Figure	2.1:	Schematics of Solid state reaction route.	34
Figure	2.2:	Schematic representation of facile auto-combustion technique.	35
Figure	2.3:	Mechanism of FESEM.	44
Figure	2.4:	Block diagram of FTIR spectrometer.	45
Figure	2.5:	Micro-Raman set-up (Renishaw, Model RM 1000) with Ar+-laser and heating cooling temperature cell THMS 600.	47
Figure	2.6:	Block diagram showing the principle of UV-VIS spectrometer.	48
Figure	2.7:	Experimental setup for recording steady state emission spectra.	49
Figure	2.8:	Experimental setup for lifetime measurements.	50
Table	2.1:	Specifications of the materials used.	33
		Chapter: 3	
Figure	3.1:	XRD patterns of $Y_2Ti_2O_7$ (YTO) and Er^{3+}/Yb^{3+} doped $Y_2Ti_2O_7$ (EYYTO) phosphor.	55
Figure	3.2:	Rietveld refinements for X-ray diffraction data of (a) $Y_2Ti_2O_7$ (YTO) and (b) 1 at.% Er ³⁺ and 2 at.% Yb ³⁺ doped $Y_2Ti_2O_7$ (EYYTO). Calculated positions of Brag reflections are shown by vertical tick marks (bottom) and top row shows the difference in observed and calculated diffraction peak intensity. Inset of (a) shows the expansion of typical Rietveld fitting to experimental data between 30.4 to 31.1°. Inset of (b) shows the polyhedral representation of $Y_2Ti_2O_7$.	56
Figure	3.3:	TEM images of (a) Er^{3+}/Yb^{3+} doped $Y_2Ti_2O_7$, (c) colloidal solution. Their corresponding SAED patterns are shown in (b) and (d), respectively.	58
Figure	3.4:	FTIR spectrum of Er^{3+}/Yb^{3+} doped $Y_2Ti_2O_7$ (EYYTO) phosphor.	59
Figure	3.5:	Raman spectra of (a) YTO and (b) EYYTO samples recorded at room temperature.	60
Figure	3.6:	Emission spectra of Er^{3+}/Yb^{3+} doped $Y_2Ti_2O_7$ phosphor under 976 nm excitation wavelengths at different pump power (up-conversion). Inset shows the expansion from 370-500 nm (bottom) and 775-900 nm (top). Digital photograph of the sample using green and red colour filters are shown in Inset.	61
Figure	3.7:	Energy level diagram of Er ³⁺ and Yb ³⁺ ions with proposed up- conversion mechanism under 976 nm laser excitation.	63

Figure	3.8:	Power dependence of (a) visible (524, 548 and 661 nm) and (b) UV, blue 380, 410 and 487 nm) bands.	64
Figure	3.9:	Variation of intensity of green $({}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2})$ to red $({}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2})$ band at different input laser powers of Er^{3+}/Yb^{3+} doped $Y_{2}Ti_{2}O_{7}$ (EYYTO) phosphor. Inset shows the possible transitions for green and red emissions.	65
Figure	3.10:	Variation in intensity with different input powers for (a) 524 and (b) 661 and (c) normalizing the emission intensity at 548 nm.	66
Figure	3.11:	(a) Absorption spectrum (b) Up-conversion spectrum of Er ³⁺ /Yb ³⁺ doped Y ₂ Ti ₂ O ₇ (EYYTO) colloidal nanoparticles.	67
Figure	3.12:	CIE chromaticity diagram at different laser input power showing the color tunabilty of Er^{3+}/Yb^{3+} doped $Y_2Ti_2O_7$ (EYYTO) phosphor.	68
Figure	3.13:	(a, b) show the variation of CIE coordinates with input laser power.	69
Figure	3.14:	Luminescence decay curve of Er^{3+}/Yb^{3+} doped $Y_2Ti_2O_7$ (EYYTO) phosphor ($\lambda_{em} = 548$ nm, $\lambda_{exc} = 976$ nm).	70
Table	3.1:	Parameters obtained after refinement of observed XRD data.	57
Table	3.2:	CIE coordinates with input laser power.	70
		Chapter: 4	
Figure	4.1:	(a), (b) and (c) XRD patterns of Gd ³⁺ (0, 2, 5, 7 and 10 at.%) co- doped CaMoO ₄ :Eu for ASP, 600 and 900 °C samples, respectively. Atomic percentage of Gd ³⁺ is given in figure itself. The symbol # represents the extra phase evolution.	77
Figure	4.2:	(a), (b), (c), (d) and (e) Rietveld plot of 0, 2, 5, 7 and 10 at.% Gd ³⁺ co-doped CaMoO ₄ :Eu samples annealed at 900 °C and (f) simplified polyhedral representation of Gd ³⁺ co-doped CaMoO ₄ :Eu having both [CaO ₈] and [MoO ₄] clusters.	78
Figure	4.3:	(a)- (e) Rietveld plots of Gd ³⁺ (0, 2, 5, 7 and 10 at.%) co-doped CaMoO ₄ :Eu annealed at 600 °C.	80
Figure	4.4:	FTIR spectra of ASP, 600 and 900 °C annealed samples of 5 at.% Gd ³⁺ co-doped CaMoO4:Eu.	83
Figure	4 5.	XPS spectrum of 5 at.% Gd^{3+} co-doped CaMoO ₄ :Eu annealed at	84
U	4.5:	900 °C showing constituent elements involved in compositions.	

Figure	4.7:	XPS spectra of Eu/Gd of (a) ASP and (b) 900 °C annealed, Gd ³⁺ (0,	86
		5 and 10 at.%) co-doped CaMoO4:Eu.	
Figure	4.8:	XPS spectra of O1s for (a) ASP and (b) 900 °C annealed, Gd ³⁺ (0, 5 and 10 at.%) co-doped CaMoO ₄ :Eu.	87
Figure	4.9:	Variation of relative peak intensity of peak2 to peak1 of O1s spectra of 0, 5 and 10 at.% Gd ³⁺ co-doped CaMoO ₄ :Eu for ASP and 900 °C annealed samples.	88
Figure	4.10:	TG-DTA curves of as-prepared precursor for CaMoO4:Eu in synthetic air.	88
Figure	4.11:	FE-SEM images of micro-spherical particles CaMoO ₄ :Eu for (a) as-prepared (b) 600 (c) annealed at 900 °C (d) particle size distribution for 600 °C and (e) for 900 °C annealed samples.	89- 90
Figure	4.12:	(a) TEM and (b) shows the elemental composition of a large area of ASP 5at.% Gd ³⁺ co-doped CaMoO ₄ :Eu nanophosphors, which is verified by the presence of Ca, Mo, Eu and Gd peaks. Cu peak comes from the Copper grid used for the electron microscopy analysis and (c), (d) and (e) HRTEM images for region (i), (ii), (iii) and (iv) of 5at.% Gd ³⁺ co-doped CaMoO ₄ :Eu at 900 °C. Scale bar is given under 20 nm.	91
Figure	4.13:	(<i>αhv</i>) ² <i>vs. hv</i> for ASP, 600 and 900 °C annealed samples of 5 at.% Gd ³⁺ co-doped CaMoO4:Eu in absorption spectra.	96
Figure	4.14:	Excitation spectra of Gd ³⁺ (0 and 10 at.%) co-doped CaMoO ₄ :Eu nanoparticles: (a) ASP, (b) 600 and (c) 900 °C annealed samples (monitoring emission at 613 nm).	97
Figure	4.15:	Luminescence spectra of $Gd^{3+}(0, 2, 5, 7 \text{ and } 10 \text{ at.}\%)$ co-doped CaMoO ₄ :Eu nanoparticles: (a) ASP (b) 600 (c) 900 °C (inset show the digital photographs of powder sample and polymer film under 266 nm laser excitation of 2 at.% Gd ³⁺ co-doped CaMoO ₄ :Eu.	99
Figure	4.16:	Typical fitting of magnetic and electronic dipole transitions of 5 at.% Gd ³⁺ co-doped CaMoO4:Eu heated at 600 °C.	100
Figure	4.17:	(a) Photoluminescence intensity variation of Gd^{3+} co-doped (0, 2, 5, 7 and 10 at.%) CaMoO ₄ :Eu of ASP, 600 and 900 °C annealed samples and (b) Asymmetric ratio A_{21} variation of Gd^{3+} co-doped (0, 2, 5, 7 and 10 at.%) concentration of CaMoO ₄ :Eu of ASP, 600 and 900 °C annealed samples.	101
Figure	4.18:	Schematic energy level diagram for transfer process between Gd ³⁺ /MoO ₄ ²⁻ and Eu ³⁺ ions in CaMoO ₄ .	103

Figure	4.19:	PL emission intensities spectra in different solvents viz. water, ethanol, methanol, DMSO and EG of ASP 2 at.% Gd ³⁺ co-doped CaMoO ₄ :Eu (inset show the digital photographs of dispersed solution in EG before and after irradiation under 266 nm Nd-YAG source excitation).	104
Figure	4.20:	Luminescence spectra of PVA thin film of as-prepared 2 at.% Gd ³⁺ co-doped CaMoO ₄ :Eu nanoparticles after incorporation of re-dispersed particles at 266 nm excitation.	105
Figure	4.21:	PL spectra of 2 at.% Gd^{3+} co-doped CaMoO ₄ :Eu for the quantum yield study.	106
Figure	4.22:	Lifetime decay spectra of ASP Gd ³⁺ (0, 5 and 10 at.%) co-doped CaMoO ₄ : Eu nanoparticles at (a) 277 and (b) 395 nm excitations.	107
Figure	4.23:	Lifetime decay spectra of 600 °C Gd ³⁺ (0, 5 and 10 at.%) co- doped CaMoO ₄ :Eu nanoparticles at (a) 277 and (b) 395 nm excitations.	108
Figure	4.24:	Lifetime decay spectra of 900 °C Gd ³⁺ (0, 5 and 10at.%) co- doped CaMoO ₄ :Eu ³⁺ nanoparticles at (a) 277 and (b) 395 nm excitations.	108
Figure	4.25:	(a) Mono- (b) diffusion equation fittings to luminescence decay curve (613 nm) of 600 °C annealed 5 at.% Gd ³⁺ co-doped CaMoO ₄ :Eu (λ_{exc} =277 nm). Fitting parameters are shown in figures itself. Inset of (a) shows the ln(<i>l</i>) vs t plot. and (c) bi-exponentail fitting to the decay curve of 5 at.% Gd ³⁺ co-doped CaMoO ₄ :Eu (λ_{exc} =395 nm).	111
Figure	4.26:	Typical Bi-exponential fittings with residuals to the luminescence decay curve (613 nm) of 10 at.% Gd ³⁺ co-doped CaMoO ₄ :Eu annealed at 900 °C (λ_{exc} = 395 nm). Bottom portion of figure show the residual vs. Independent Variable	112
Figure	4.27:	(a) Bi- (b) mono-exponential curve fits to luminescence decay curve (613 nm) of 0 at. % Gd ³⁺ co-doped CaMoO ₄ :Eu annealed at 900 °C (λ_{exc} = 395 nm).	112
Table	4.1:	Calculated values of <i>a, c, V</i> and <i>D</i> for Gd ³⁺ (0, 2, 5, 7 and 10 at %) co-doped CaMoO ₄ :Eu at 600 °C and 900 °C.	81
Table	4.2:	Peak positions of the magnetic dipole transition ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ and electric dipole transition ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ and their respective FWHM of ASP, 600 and 900 °C heated samples of Gd ³⁺ (Gd ³⁺ = 0, 2, 5, 7 and 10 at.%) co-doped CaMoO ₄ :Eu. λ_{exc} = 266 nm.	102

Table	4.3:	Parameters obtained after fitting [I = $I_1 \exp(-t/\tau_1-Dt^{0.5})-I_2\exp(-t/\tau_2) + I_b$] equation to the decay data of as-prepared, 600 and 900 °C samples at 277 nm excitation	109
Table	4.4:	Parameters obtained after bi-exponential fit to the decay data of as-prepared, 600 and 900 °C samples at 395 nm excitations.	110
Table	4.5:	Parameters obtained after mono-exponential fit to the decay data of as-prepared, 600 and 900 °C samples at 395 nm excitations.	113
Table	4.6:	Radiative rate constants of Gd ³⁺ co-doped CaMoO ₄ :Eu samples after mono-exponential curve fit to the luminescence decay curve under 395 excitation.	114
Table	4.7:	Variation of CIE co-ordinates of ASP, 600 and 900 °C annealed Gd ³⁺ (0, 2, 5, 7 and 10 at.%) co-doped CaMoO ₄ :Eu samples.	115
		Chapter: 5	
Figure	5.1:	XRD pattern of (a) Er^{3+}/Yb^{3+} doped $Y_2Ti_2O_7$ and Li ⁺ (2, 5, 7, 10 and 15 at.%) co-doped $Y_2Ti_2O_7$ (b) Shifting of (222) peak with Li ⁺ ion concentration and (c) Change in peak position and FWHM of (222) peak in 20.	121- 122
Figure	5.2:	Observed, calculated, and difference X-ray diffraction patterns of Li ⁺ (0 at.%)co-doped Er ³⁺ /Yb ³⁺ :Y ₂ Ti ₂ O ₇	124
Figure	5.3:	(a) Survey Scan of 2 at.% Li ⁺ co-doped Y ₂ Ti ₂ O ₇ :Er ³⁺ /Yb ³⁺ (b) XPS spectra of Yb(4d), (c) XPS spectra of Er(4d) and (d) XPS spectra of Li1s.	126
Figure	5.4:	XPS spectra of (a) Y (3d) (b) Ti (2p) and (c) O (1s) of Li ⁺ co- doped $Y_2Ti_2O_7:Er^{3+}/Yb^{3+}$ (at% of Li ⁺ ion is shown in figure itself) and (d) ratio of deconvoluted relative peak positions with respect to Li ⁺ ion concentration.	127
Figure	5.5:	Measured FT-IR transmission spectra of $Y_2Ti_2O_7$:Yb ³⁺ /Er ³⁺ /Li ⁺ co-doped phosphors: (a) 0 at.%, (b) 2 at.%, (c) 5 at.%%, (d) 7 at.%, (e) 10 at.% and (f) 15 at.% Li ⁺ ion.	129
Figure	5.6:	Raman spectra of Li+(0, 2, 5, 7, 10 and 15 at.%) co-doped EYYTO.	130
Figure	5.7:	FE- SEM micrographs of Li ⁺ co-doped $Y_2Ti_2O_7$: Er^{3+}/Yb^{3+} (a) Li ⁺ free (b) 2 at.%(c) 5 at.% (d)7 at.% (e) 10 at.% and (f) 15 at.% Li ⁺ .	132

Figure	5.8:	(a) Emission spectra of Li ⁺ (0, 2, 5, 7, 10, and 15 at%) co- dopedY ₂ Ti ₂ O ₇ :Er ³⁺ /Yb ³⁺ phosphor under 976 nm excitation. Insets (i) and (ii) show the expansion in 380–500 nm and 750– 900 nm. The digital photographs of EYYTO:2Li ⁺ were recorded using a Nikon Coolpix P500 digital camera using a suitable colour filters and (b) shows the integral intensity of green and red emissions as a function of the concentration of Li ⁺ ions.	133
Figure	5.9:	Power dependence of green and red bands (524, 548 and 661 nm)	136
Figure	5.10:	Power dependence of UV and blue bands (380, 410 and 487 nm).	136
Figure	5.11:	Schematic partial energy level diagram and energy transfer processes involved in the up-conversion process.	137
Figure	5.12:	Upconversion-based temperature sensing behaviour of 2 at.% Li ⁺ co-doped $Y_2Ti_2O_7$:Er ³⁺ /Yb ³⁺ phosphor, (a) green UC emission spectra measured at 298 and 673K, (b) monolog plot of the FIR (using 524 and548 nm emission)as a function of the inverse absolute temperature, (c) the FIR relative to the temperature and (d) sensor sensitivity as a function of the temperature.	138
Figure	5.13:	(a) Variation in the Up-conversion intensity at different pump power densities and (b) Variation in FIR at different pump power densities at room temperature.	141
Figure	5.14:	CIE diagram for Li ⁺ (0 and 2 at.%) co-doped Y ₂ Ti ₂ O ₇ :Er ³⁺ /Yb ³⁺ .	142
Figure	5.15:	Decay curve showing EYYTO:2Li of 548 nm (⁴S _{3/2} →⁴I _{15/2}) band under 976 nm excitation.	143
Table	5.1:	Atomic Coordinates, Isotropic Thermal Parameters, and Occupancy Obtained from Rietveld Refinement.	124
Table	5.2:	Selected Bond Distances Obtained from Rietveld Refinement.	125